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Great Lakes Science Advisory Board
Report to the International Joint Commission

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1983 Annual Report

**Report of the
Aquatic Ecosystem Objectives Committee**

Preface

This report to the Science Advisory Board was prepared by the Aquatic Ecosystem Objectives Committee (AEOC). Though the Board has reviewed and approved this report for publication, some of the specific conclusions and recommendations may not be supported by the Board.

1983 Annual Report

Report of the Aquatic Ecosystem Objectives Committee

November 1983
Windsor, Ontario

Preface

This report to the Science Advisory Board was prepared by the Aquatic Ecosystem Objectives Committee (AEOC). Though the Board has reviewed and approved this report for publication, some of the specific conclusions and recommendations may not be supported by the Board.

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Recommendations

The Aquatic Ecosystem Objectives Committee (AEOC) makes the following recommendations to the Science Advisory Board (SAB) for consideration and forwarding to the International Joint Commission (IJC) and the Parties of the Great Lakes Water Quality Agreement (GLWQA).

1. REVISED OBJECTIVES

Microbiology (Chapter 2.1)

EXISTING OBJECTIVE

Waters used for body contact recreation activities should be substantially free from bacteria, fungi or viruses that may produce enteric disorders or eye, ear, nose, throat and skin infections or other human diseases and infections.

Microbiological Indicators (Chapter 2.1.1)

RECOMMENDATION

For the protection of human recreational users of nearshore waters from increased gastrointestinal (GI) illnesses,* the enterococcus (mE) geometric mean level should not exceed 11/100 mL; similarly the Escherichia coli (mTEC) geometric mean level should not exceed 23/100 mL. Mean levels should be monitored by analyzing a minimum of five samples from one location collected over a four-week period.

NOTE: The values specified above are the lowest statistically significant, detectable indicator levels associated with the onset of GI swimming-associated illnesses; as well, the "no-effect" levels cannot be measured. It is recommended that regulatory agencies, in achieving these objectives, should develop standards which may be based on GI illness rates per 100,000 persons (y) using the following relationships with levels of the organisms (x₁) (see also Fig. 1):

For Enterococcus per 100 mL (x₁) the regression equation is:

$$y = -213.2 + 613.8 \log x_1.$$

* Illness is considered synonymous with symptoms such as fever, vomiting, diarrhea and stomach cramps, and is not meant to suggest the classically reportable symptoms such as those expressed in typhoid fever, etc.

For E. coli per 100 mL (x_2) the regression equation is:

$$y = -150.5 + 423.5 \log x_2$$

Pseudomonas aeruginosa (Chapter 2.1.2)

RECOMMENDATION

For the protection of human recreational users of nearshore waters from ear infections, no more than twenty-five percent (25%) of the analyses should have levels of Pseudomonas aeruginosa (mPA method) greater than 10 P. aeruginosa per 100 mL.

NOTE: Under these conditions, the mean or median level of P. aeruginosa WTTT usually be < 1 per 100 mL.

Diazinon (Chapter 2.2)

EXISTING OBJECTIVE

The concentration of diazinon in an unfiltered water sample should not exceed 0.08 microgram per litre for the protection of aquatic life.

RECOMMENDED OBJECTIVE

For the protection of aquatic life, the maximum waterborne concentration of diazinon shall not exceed 0.003 $\mu\text{g/L}$, except that it may range up to 0.1 $\mu\text{g/L}$ once every 30 or more days for periods not to exceed 2 days.

2. NEW OBJECTIVE

Polynuclear Aromatic Hydrocarbons (chapter 2.3)

RECOMMENDATION

For the protection of aquatic life, the levels of benzo(a)pyrene in the sediments or in organisms serving as a food source for fish should not exceed 1.0 $\mu\text{g/g}$; levels of BaP in water should be less than 0.01 $\mu\text{g/L}$.

NOTE: Other 3-5 ring PAH have been observed in the Great Lakes ecosystem and some of these are carcinogenic and are strong inducers of mixed function oxidase enzymes; they may be of equal or greater concern.

3. OTHER

The SAB/IJC are recommended to formally accept the offer of the Great Lakes Fishery Commission (GLFC) to jointly fund the Task Force on Indicators of Environmental Quality and to jointly publish with the GLFC their report entitled "A proposed approach for the application of biological indicators to the determination of ecosystem quality in the Great Lakes basin."

I. Introduction

During the period of the 1972 Great Lakes Water Quality Agreement, two Committees (Water Quality Objectives Subcommittee -- WQOS and Scientific Basis for Water Quality Criteria -- SBWQC) were responsible for formulating new or modifying existing water quality objectives. Their collective efforts resulted in Annex 1 of the 1978 Great Lakes Water Quality Agreement. Since the signing of that Agreement, it has been the responsibility of the Aquatic Ecosystem Objectives Committee (AEOC) to ensure that Annex 1 is kept current. In 1980, AEOC recommended to the Science Advisory Board the adoption of two new objectives (pentachlorophenol and polychlorinated dibenzodioxins), the revision of two existing objectives (lead and microbiology) and the adoption of four objectives previously proposed by WQOS/SBWQC (silver, chlorine, temperature and nutrients). In 1981, AEOC's recommendations included the revision of the selenium objective, the confirmation of the mirex objective and the development of a mechanism to define Limited Use Zones. The Science Advisory Board has concurred with these objectives and the International Joint Commission has recommended them to the Parties, with caveats for chlorine and temperature. In 1982, the AEOC re-confirmed the silver objective, reviewed a new contaminant (polychlorinated styrenes) and re-examined an old one (asbestos). The AEOC also described a number of research activities required for the development of Objectives.

In the past year, the AEOC developed a review document on the occurrence, behaviour and effects of polynuclear aromatic hydrocarbons (PAH) in the Great Lakes. A series of symposia on this group of chemicals already existed under the management of the Battelle Laboratories at Columbus, Ohio. The AEOC, with funds provided by the SAB, supported a special session at the seventh such symposium - October 26-28, 1982. A number of the participants at this session were invited, in advance, to review the draft document and to discuss it with the AEOC at a special meeting after the symposium. The AEOC has been extremely pleased with the response of these individuals and is of the opinion that the sub-chapter on PAH appearing in this report is greatly enhanced as a consequence of this peer review process. The AEOC plans to avail itself of such opportunities whenever they present themselves and additionally, hopes to be able to gather appropriate experts in a similar forum for other objectives.

The framework¹ for developing objectives was developed by WQOS/SBWQC and is restated here for the sake of clarity. It is understood that the terms, water quality and ecosystem quality, are equivalent for the purposes of the AEOC.

1. In developing specific water quality objectives, the philosophy of protecting the most sensitive use is employed.

¹ International Joint Commission. New and Revised Great Lakes Water Quality Objectives, Volume II. Washington, D.C. and Ottawa, October 1977. pp. 3-7.

2. The objectives serve as a minimum target wherever water quality objectives currently are not being met.
3. For jurisdictionally-designated areas which have outstanding natural resource value and existing water quality better than the objectives, the existing water quality should be maintained or enhanced.
4. Specific water quality objectives are to be met at the periphery of mixing zones. This assumes that water quality conditions better than the objectives will result beyond the mixing zones. The objectives should be implemented in concert with limitations on the extent of mixing zones or zones of influence and localized areas as designated by the regulatory agencies.
5. In recommending objectives to protect raw drinking water supplies, it has been assumed that a minimum level of treatment is provided before distribution to the public for consumption.
6. Adoption of objectives does not preclude the need for further study of the effects of pollutants on the aquatic environment.
7. Since infinite combinations of water quality characteristics may occur, the objectives often are unable to take into account antagonistic, synergistic and additive effects because of lack of data.
8. Since new data may lead to modified recommendations, the objectives are subject to continual review.
9. No adequate scientific data base can exist for establishing scientifically justifiable numerical objectives for "unspecified non-persistent toxic substances and complex wastes". Therefore, criteria for developing an operationally defined objective for local situations have been recommended.

The AEOC endorses this framework with the caveat that objectives do not consider socio-economic factors. The Committee agrees with previous recommendations (Water Quality Board 1980)² that socio-economic impact assessment is the responsibility of the jurisdictions and should be done at the time of setting of regulations or standards. Objectives should not be construed as regulations or standards but should be considered as goals to be achieved and as a minimum basis for developing regulations or standards by the jurisdictions.

In the course of their development, the objectives have been subject to iterative reviews within the Committee and by scientists with relevant expertise. The Committee, however, welcomes any comments or additional scientific evidence relevant to any of the objectives and consistent with the above philosophy.

² Alternatives for Managing Chlorine Residuals: A Social and Economic Assessment. Final Report of the Chlorine Objectives Task Force to the Great Lakes Water Quality Board. Windsor, Ontario, April 1980.

2. Objectives

2.1 MICROBIOLOGY

EXISTING OBJECTIVE

Waters used for body contact recreation activities should be substantially free from bacteria, fungi, or viruses that may produce enteric disorders or eye, ear, nose, throat and skin infections or other human diseases and infections.

RATIONALE: MICROBIOLOGICAL RECREATIONAL WATER QUALITY OBJECTIVES

Bathing water objectives based on fecal coliforms have attempted to provide a means for reducing sewage microorganisms in recreational waters to low levels. The quantities and types of sewage bacteria in bathing waters exhibit only general relationships to illness in swimmers. Swimming related illnesses are known to be eye, ear, nose, skin and gastrointestinal in nature. Microorganisms that can cause these illnesses can be present in sewage polluted recreational waters, but are not always in sufficient numbers to cause infections. The uncertainties about the quantities of organisms and their pathogenicity have led to the addition of safety factors to regulations making them more stringent. These safety factors, intended to correct for theoretical and technological anomalies, can result in overprotection by regulations which can be costly to maintain.

Therefore, the establishment of precise relationships between indicator and specific bathing related illness is desirable for use in regulatory criteria. It is also important that the specific illness indicator reflect the probable source of disease organisms. Therefore, recommendations have been developed for bather protection, specifically from gastroenteritis illness based on human enteric indicator microorganisms and for protection specifically against ear infections, based on the opportunistic pathogen most commonly associated with ear infections, Pseudomonas aeruginosa. Recent epidemiological work has provided firm cause/effect data for these recommendations. As further data become available to support the cause/effect relationships for the other defined bathing acquired illnesses mentioned earlier, specific recommendations will be made. Ideally they will deal with the specific pathogens involved and will also consider viruses.

2.1.1 MICROBIOLOGICAL INDICATORS

RECOMMENDATION

For the protection of human recreational users of nearshore waters from increased gastrointestinal (GI) illnesses,* the enterococcus (mE) geometric mean level should not exceed 11/100 mL; similarly the *Escherichia coli* (mTEC) geometric mean level should not exceed 23/100 mL. Mean levels should be monitored by analyzing a minimum of five samples from one location collected over a four-week period.

NOTE: The values specified above are the lowest statistically significant, detectable indicator levels associated with the onset of GI swimming-associated illnesses; as well, the "no-effect" levels cannot be measured. It is recommended that regulatory agencies, in achieving these objectives, should develop standards which may be based on GI illness rates per 100,000 persons (y) using the following relationships with levels of the organisms (x₁) (see also Fig. 1):

For Enterococcus per 100 mL (x₁) the regression equation is:

$$y = -213.2 + 613.8 \log x_1.$$

For *E. coli* per 100 mL (x₂) the regression equation is:

$$y = -150.5 + 423.5 \log x_2$$

RATIONALE

Introduction

Pathogenic microorganisms in water are difficult to monitor due to problems with sample collection, analytical techniques and because they occur only sporadically in polluted water. Historically, surrogates have been used to indicate fecal pollution and the microbiological quality of the water. Total coliforms (TC) have been the traditional indicator for over 70 years, but since some coliforms are natural inhabitants of water and soil, the TC group is now infrequently used. (Table 1 by Dufour (1982) shows that only 23.3% of 56 U.S. jurisdictions presently use TC). The fecal component of the total coliforms are those coliforms that are present in the feces of warm-blooded animals and the fecal coliforms (FC) test determines that fraction. The presence of FC does not unequivocally establish the presence of disease-producing bacteria. Statistical analysis, however, can show that if the FC count reaches a certain level, there is a high probability of the concurrent presence of some types of human pathogens. The presence of FC usually indicates the presence of human or animal feces.

* Illness is considered synonymous with symptoms such as fever, vomiting, diarrhea and stomach cramps, and is not meant to suggest the classically reportable symptoms such as those expressed in typhoid fever, etc.

whenever such results are reported. While both enterococci and E. coli values are suggested to be used in regulating water quality, either may be used individually.

Sampling

The data used to derive the relationships which form the basis of the recommendation, were obtained by sampling throughout the period of use with the bathers present. The ambient water quality, embracing any pollution inputs and the discharges from bathers, is an important consideration. The IJC "Roundtable on the Surveillance and Monitoring Requirements for Assessing Human Health Hazards posed by Contaminants in the Great Lakes Basin Ecosystem" (IJC, 1982) also suggests that: "The conditions under which samples are collected should be recorded, with such details as the estimated bather load at the time, so that appropriate interpretation of the results can be made." The "Roundtable" also recommended that routine samples be taken at a depth of 15 to 30 cm below the surface, and where water is about 1.5 meters deep. A specific representative site (or sites) at a beach should be chosen and five samples from that site in each four-week period should be tested. Results from these samplings will adequately represent the water quality for that period, as well as be a reasonable minimum number of samples that most agencies can collect. However, a Saturday and a Sunday sample collected at the time of the peak of the bathing load would give the ideal bather use, water quality information. Nevertheless, Bennett (1969) showed that five samples over four weeks adequately defined the four-week period's water quality. Results from five samples also provide a reasonable data base from which to calculate a valid, representative, geometric mean.

Whereas former criteria incorporated an arbitrary factor for current experiences such as weather, rain, sewage plant malfunctions, laboratory variations (which erred on the side of safety) the relationships on which the recommendations were based are more exact and have already built in these and other important considerations. So, additional percentile values to allow for these factors are not required.

Microorganisms in Recreational Waters

Recreational use of water in the form of body-contact recreation is normally perceived as swimming, wading, or the inadvertent contact with water by boaters, hunters, or fishermen. There are virtually no studies with respect to the last group and relatively few epidemiological studies on bathing. Cabelli (1977) defined swimming as "significant exposure of the upper-body orifices to the water".

Early work on this subject is by Smith, et al., (1951) on the Ohio River and by Smith and Woolsey (1952) on the Ohio River and Long Island beaches. Streeter (1951) compared the bacteriological standards of various jurisdictions for the Ohio River Valley Water Sanitation Commission (ORSANCO) and recommended that the monthly arithmetic average (MPN) for total coliforms not exceed 1000 per 100 mL, nor should total coliforms in 20% of the samples for any given month exceed 2400 per 100 mL.

Stevenson (1953) attempted to correlate illness from swimming with water quality at Lake Michigan beaches, the Ohio River and Long Island. He found a significant increase in incidence of illness among swimmers when the total coliform count equalled or exceeded 2300 per 100 mL.

The ORSANCO Water Users Committee (1971) estimated a relationship of approximately 1:5 of fecal to total coliforms in the Ohio River and determined that fecal coliforms were somewhat more accurate bacteriological indicators of fecal contamination from warm-blooded animals and humans.

McCabe (1980) combined the effect level of 2300 total coliforms per 100 mL of Stevenson with the fecal:total coliform ratio from the report of the Committee on Water Quality Criteria to the Federal Water Pollution Control Administration in 1968 to obtain 400 FC/100 mL and by applying a safety factor of approximately two, arrived at a maximum recommended level of 200 fecal coliforms per 100 mL for recreational water. Although this level of fecal coliforms has since been widely used in the United States, it has become apparent that its derivation and extrapolation from a total coliform index is a serious weakness.

The geometric mean of 200 FC per 100 mL was accepted by the United States Environmental Protection Agency (EPA) as the no-effect level in 1968 and this was derived from 40 FC per 100 mL which was taken to be the detectable health effect level. The EPA "Red Book" (US-EPA, 1976) states: "Based on a minimum of five samples taken over a 30-day period, the fecal coliform bacterial level should not exceed a log mean of 200 per 100 mL, nor should more than 10 percent of the total samples taken during any 30-day period exceed 400 per 100 mL". It does not justify the 10% but uses this value to allow for "variations in environmental conditions". Although many jurisdictions have adopted this approach, it has no statistical basis.

Most jurisdictions (Dutka, 1973) had discarded the use of the total coliform parameter (Table 1) as an indication of surface water pollution for the reasons mentioned earlier. Obviously part of the difficulties of associating it with bather illness rates was that there was probably little reason to expect such correlation. Cabelli (1981) has shown that in both marine and fresh waters there is very poor, if any, correlation between TC and bather illness. The level of 200 FC/100 mL criteria has no determined validity of its own but relies entirely on extrapolations from dubious TC/illness associations. Furthermore, Cabelli, et al., (1979) and Dufour (1982) have shown very poor correlation between illness and FC, further weakening its credibility as the primary bathing water quality indicator. It is apparent that these parameters are not the best indicators of bather illness.

Recently, Cabelli (1978, 1975) conducted a three-phase, major epidemiological study at New York City bathing beaches. The first phase was conducted in 1972 and 1973; the second phase, in 1974; and the last, in 1975. This study of the bathers at Coney Island and Rockaways ocean beaches, New York City, suggested that a significant difference in illness rates existed between the marginally polluted Coney Island Beach and the relatively unpolluted Rockaways Beach. Illness was defined as highly-credible symptoms (Table 4 in Dufour, 1982) (multiple or unmistakably recognized symptoms) reported by bathers during a follow-up interview and the differences were

between swimmers and non-swimmers at the respective beaches. Illness and symptoms are used synonymously here since the studies considered fever, vomiting, diarrhea, cramps, stomach pains, or a combination of these, as markers. The classical, seriously debilitating diseases, such as typhoid fever, or the mandatory reportable diseases, while possibly implicated at subclinical levels, are not intended in the use of the word illness. Cabelli, et al., (1979) extended the data base and derived additional support for their illness/indicator relationships from the study at the "highly-polluted" Mediterranean beach of Alexandria, Egypt. Cabelli (4) also suggested that enterococci (*Streptococcus faecalis* and *Streptococcus faecium*) may be superior indicators of bathing beach quality. In these studies, *E. coli* and illness rates also correlated well. Additional work by Cabelli (1981) and by Cabelli, et al., (1979) was done in the brackish waters of Lake Pontchartrain during 1977 and 1978. The type of illness observed at these beaches was, to a large extent, "gastroenteritis of unknown etiology", which has more recently been ascribed to infection by Norwalk agents or rotavirus. The conclusion of all of this work is that enterococci and *E. coli* are more reliable bathing water quality indicators than the currently used fecal coliform (Cabelli, 1981).

Cabelli's studies dealt with marine waters and as Dufour (1982) has pointed out, results on marine beaches are different from freshwater beaches. In 1979-80, freshwater epidemiological work done on Lake Erie near Erie, Pennsylvania and on Keystone Lake at Tulsa, Oklahoma, was reported by Dufour (1982). Again, enterococci and *E. coli* showed better correlation with swimming associated illness at freshwater beaches than did fecal coliform: correlation coefficients were 0.65, 0.51 and 0.23; respectively. He concluded that the health effect/water quality relationship is substantially different for fresh waters than for marine waters for the same rate of highly credible GI symptoms and again confirmed the use of enterococci as a better indicator. Figure 1 shows the relationship for enterococci and *E. coli* mean densities and gastrointestinal symptom rates at freshwater bathing beaches. Figure 2 shows a much poorer correlation for FC than do enterococci or *E. coli*. Dufour does not recommend specific guidelines, but instead presents use-effect graphs. These show the rates of highly credible GI symptoms per 100,000 persons compared to mean indicator densities. A number of data points were used to develop the relationship shown on Figure 1, but the lowest highly statistically significant effect levels for enterococci and *E. coli* were observed at densities of 11/100 mL and 23 *E. coli*/100 mL for freshwater beaches. It is therefore from these levels that objectives were developed.

Previously, bathing water quality was regulated by the limiting the presence of fecal material which could potentially carry human disease organisms rather than by controlling the actual illnesses contracted by the bathers swimming in water of varying quality. That approach, because of the imponderables of levels and diversity of pathogens, population at risk, socio-economic groups, etc., necessitated regulatory agencies to add margins of safety in the objectives developed. The recommendations here are based on true indicator/illness rate relationships which permit agencies to determine the regulation that best suits their areas of jurisdiction. The indicator levels recommended would help to regulate water quality so that there would be no increase in gastrointestinal illnesses while bathing and would be in accord with a non-degradation policy. It is recognized however, that agencies must have the latitude to develop less stringent regulations which, while exposing users to greater risks, may not affect a significantly larger population.

The illnesses contracted by swimmers in marginally clean waters are often short-lived, rarely critical, not generally reported in health statistics and consequently, the extent of the affected population is most often unknown. To determine these illnesses accurately, epidemiological studies of large numbers of bathers would be needed at each beach to determine the population affected. Through the use of the data presented, the illness rate can be readily calculated and regulations can be promulgated, allowing consideration of local circumstances.

The regression lines in Figure 1 and the corresponding equations for enterococci and *E. coli* associated with illness rates, can be used to more rationally regulate bathing water quality. Jurisdictions can use this information to forecast the expected gastrointestinal rate of illness in bathers over background by measuring the indicator microorganism levels and projecting them on the graph in Figure 1. By determining the level of indicators at a location (e.g. the mid-point of a beach) at one time (e.g. on a weekend), the expected illness rate of users at that location at that time can be calculated. Similarly, the average monthly illness rate at a location on a beach can be predicted by relating monthly geometric means of enterococci and/or *E. coli* using this graph. Should the regulating agency become aware that the illness rate as measured by the rising level of indicators is increasing, it can determine the cause and source of pollution in the usual manner, calculate the cost of remedial measures and decide whether or not the additional illness rate is significant enough to proceed with remedial action. The agency can then elect to employ a regulation using this illness relationship along with the cost benefit calculation. This information permits the development of regulations that are relevant to the gastrointestinal illness associated directly with swimming and because they are based on sound associations, should not force jurisdictions to add costly margins of safety.

For the purpose of calculating the levels of indicators, the regression equations can be rearranged in the following manner. The enterococcus equation for x_1 (level of organism, $x_1/100$ ml) will then be:

$$x_1 = 10(0.00163 y + 0.347);$$

similarly, the *E. coli* equation will be:

$$x_2 = 10(0.00236 y + 0.355).$$

where y is the illness rate per 100,000 persons. The enterococcus relation was developed for a range of organism levels of 4 x_1 500 while that for *E. coli* was over 2 x_2 3000.

Summary

The recommended indicator organisms are enterococci, at an objective maximum for the geometric mean of 11/10 mL and *E. coli* at 23/100 mL. At levels higher than these, some risk will be present, the extent of which the jurisdictions may determine from the information in Figure 1 and the corresponding regression equations.

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FIGURE 1

SWIMMING ASSOCIATED RATE FOR HIGHLY CREDIBLE
G.I. SYMPTOMS PER 100000 PERSONS

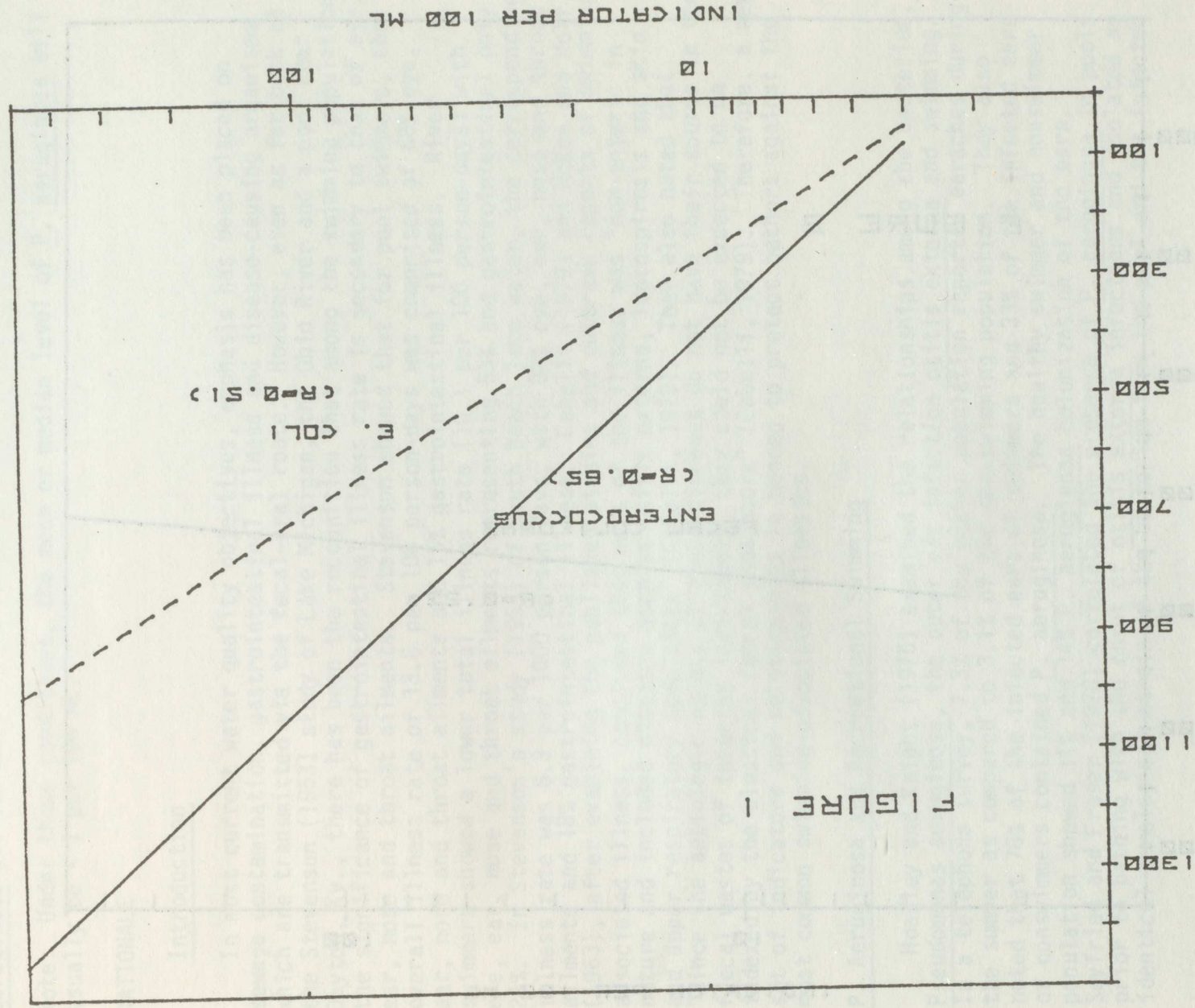
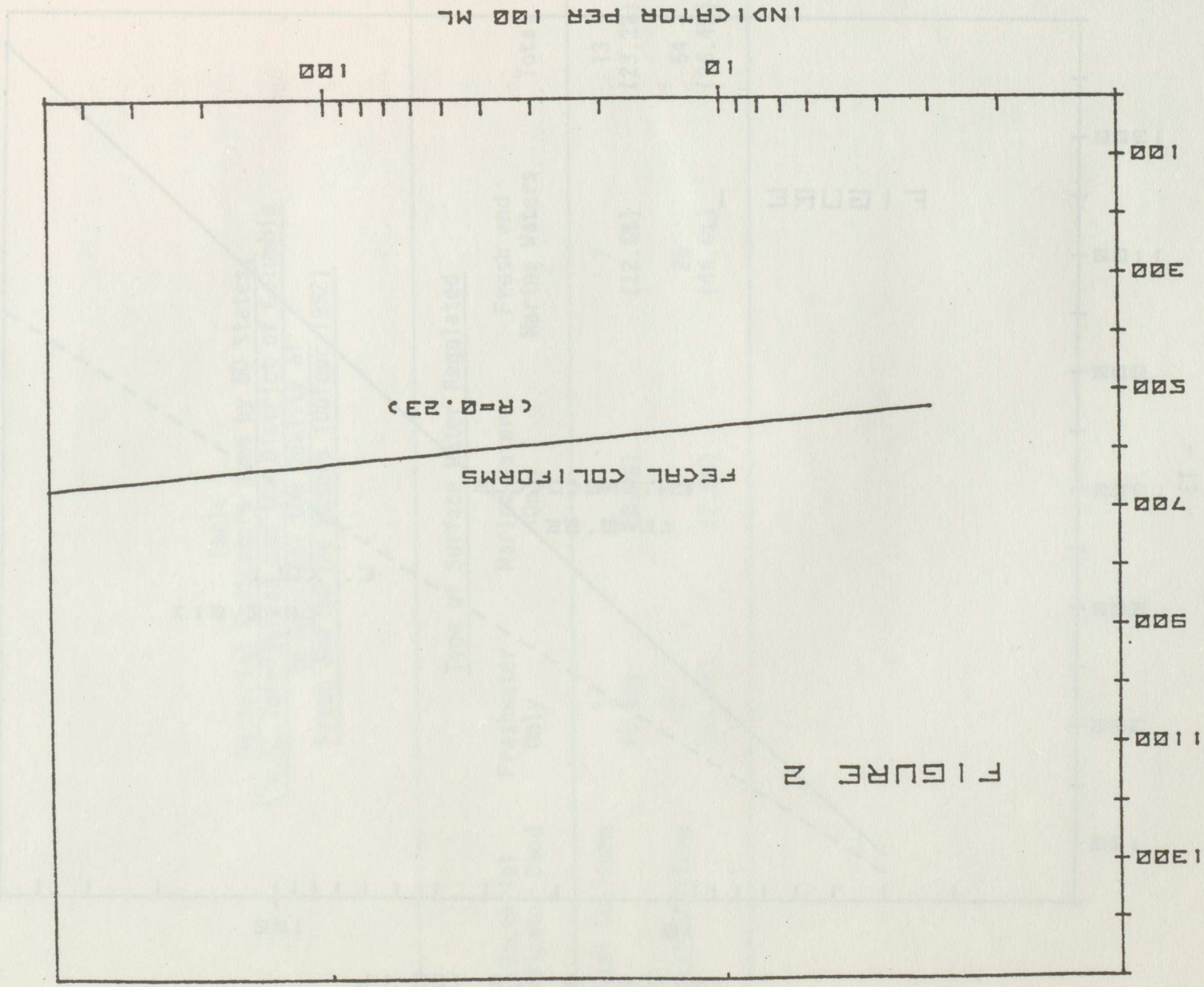


FIGURE 1

FIGURE 2

SWIMMING ASSOCIATED RATE FOR HIGHLY CREDIBLE
G.I. SYMPTOMS PER 100000 PERSONS



2.1.2 PSEUDOMONAS AERUGINOSA

RECOMMENDATION

For the protection of human recreational users of nearshore waters from ear infections, no more than twenty-five percent (25%) of the analyses should have levels of Pseudomonas aeruginosa (mPA method) greater than 10 P. aeruginosa per 100 mL.

Note: Under these conditions, the mean or median level of P. aeruginosa will usually be < 1 per 100 mL.

RATIONALE

Introduction

In most current water quality objectives, emphasis has been placed on sewage contamination, gastrointestinal illness and disease-causing organisms which are transmitted via the fecal-oral route. However, even as far back as the Stevenson (1953) study of Lake Michigan, the Ohio River and a pool near Dayton, Ky., there has been the recognition that among the swimming population the significance of gastrointestinal illness rate is secondary to that of eye, ear, nose and throat ailments. Stevenson showed that for pool swimmers, the overall illness rate of 13.8 per 100 person-days was comprised of 68% eye, ear, nose and throat ailments and 15% gastrointestinal illness. River swimmers showed a lower total illness rate (10.1 per 100 person-days) with eye, ear, nose and throat ailments representing 53% and gastrointestinal only 24%. In Stevenson's study (1953) of South Beach lake water, the corresponding illness rate was 8.3 per 1000 person-days, with 82% eye, ear, nose and throat ailments and 18% gastrointestinal illness. Cabelli (1979) and McKee and Wolf (1963), after examining the published studies and outbreak reports of swimming associated illness, concluded that most of the illness was "non-enteric in nature and included diseases such as otitis externa, leptospirosis and skin and upper respiratory complaints" (Cabelli, 1979). They also noted that "since the aetiologic agents of these diseases do not have their source in the faecal wastes of infected individuals, they could not be expected to be indexed by the classical faecal indicators" (Cabelli, 1979). Therefore, a new set of indicators and relationships is needed to protect bathers against the most common swimming-associated illnesses.

P. Aeruginosa and Recreational Swimming

Hoadley and Knight (1975) examined the relationships among the bacterium, Pseudomonas aeruginosa, the outer ear infection otitis externa and swimming. In a telephone survey, 7.3% of the bather population reported earaches during the summer as compared to 3.1% of the non-swimming population. They also noted that 78% of the infected ears of swimmers and 33% of the infected ears of nonswimmers contained P. aeruginosa. The healthy swimmer and nonswimmer population showed 11% and 14% P. aeruginosa colonization of the ears. Seyfried and Fraser (1978) correlated the presence of P. aeruginosa in pools prior to bathing with the onset of otitis externa infections and isolated an identical serological strain of the bacterium from the pool and the infected

ear of a bather. Weingarten (1977) also reported an outbreak of otitis externa caused by P. aeruginosa while Burger (1983) showed an increased otitis externa case rate among swimmers using a beach where P. aeruginosa was present in high concentration. P. aeruginosa was also isolated from the ears of swimmers more frequently after swimming than before. Calderon and Mood (1982) reported that there was a significantly higher proportion of swimmers in their otitis externa cases than in their control population. They also were able to isolate P. aeruginosa from 50% of the infected ears in their study but from none of the controls.

Dutka (1973), Hoadley (1977a, b) and others have considered P. aeruginosa to be "a ubiquitous bacterial species easily isolated from surface waters and soil". However, Dutka (1979) later revised this opinion when he found that P. aeruginosa was virtually absent in the central parts of the Canadian Great Lakes and Hudson Bay waters. Hoadley (1977b) also suggested that "the species probably does not normally inhabit northern temperature surface waters unless recently affected by human activity or the activities of domestic animals". Based on studies conducted on the Great Lakes (IJC, 1976, 1977; OME, 1981) and many inland lakes in Ontario (Burger, 1983), P. aeruginosa is absent from Ontario surface waters except where influenced by human activity and may be reported more frequently in warmer southern United States surface water because of growth in the warmer water (Hoadley, 1977b).

Drake (1966) suggested that P. aeruginosa levels from 1 to 10 per 100 mL could be expected in rivers with low but definite levels of contamination. P. aeruginosa levels less than 100 per 100 mL can be demonstrated in water adjacent to human activity (Hoadley, 1977a) and in excess of 100 organisms per 100 mL in waters receiving surface drainage from urban areas or waters recently contaminated with sewage. In raw domestic sewage, concentrations of 10^5 to 10^6 P. aeruginosa per 100 mL are common. Slightly in excess of 10% of healthy adults in the United States are intestinal carriers of P. aeruginosa although Cabelli (1979) suggested that Pseudomonas aeruginosa is "infrequently isolated from normal human faeces". In pool waters, Seyfried and Fraser (1978) found P. aeruginosa levels to be low, but shifts from 0 per 100 mL to as high as 348 per 100 mL were common. Calderon and Mood (1982) reported a median P. aeruginosa level of 0 per 100 mL with a range up to 37.8 per 100 mL. In all of these studies, the levels of P. aeruginosa in natural bathing waters were low, 0 to 100 per 100 mL.

Fecal or sewage contamination is one possible source for the Pseudomonas aeruginosa present in bathing water; however, the bathers themselves are also a source of the organism (Hanes and Fossa, 1971; Cabelli, 1977). This means that in areas with minimal water exchange, the levels of Pseudomonas aeruginosa may be related to the bather load. Burger (1983) noted that P. aeruginosa levels varied diurnally and seasonally in a pattern similar to the number of bathers.

When dealing with the Pseudomonas aeruginosa and the diseases, otitis externa and skin rash, the situation is quite different from that of the coliform group of indicators and gastrointestinal illness. P. aeruginosa is not an indicator by virtue of its relationship to a disease-causing organism but is itself the pathogen or disease-causing organism. Jones (1965) claimed that P. aeruginosa was the major etiological agent in otitis externa. Hoadley

(1977a), in reviewing the literature on otitis externa, produced the same kind of evidence. Therefore, the presence of Pseudomonas aeruginosa in a recreational water and the exposure of bathers to an occasional high level of the disease organism in the water or even to a single organism, poses a health hazard to the bather (Burger, 1983). This means that the averaging out of extremely high values for comparison with a water quality objective based on an arithmetic or geometric mean ignores the health hazard to the individual bather who swims when the levels are high. This concept suggests that a hazard exists not only when average levels are high but also when very high levels are present in the bathing area for infrequent, short, periods.

Sampling

The data used to derive the relationships which form the basis of the recommendation were obtained by sampling throughout the period of use with the bathers present. The ambient water quality, embracing any pollution inputs and the discharges from bathers, is an important consideration. The IJC (1982) also suggests that "the conditions under which samples are collected should be recorded, with such details as the estimated bather load at the time, so that appropriate interpretation of the results can be made". This "Roundtable" review also recommended that routine samples be taken at a depth of 15 to 30 cm below the surface, where the water is about 1.5 meters deep. For P. aeruginosa, it is important to adhere closely to this suggestion since the surface of the water is most usually in contact with ears. A specific representative site (or sites) at a beach should be chosen and five samples from that site in each four-week period should be tested. Results from these samplings will adequately represent the water quality for that period, as well as be a reasonable minimum number of samples that most agencies can collect. However, a Saturday and a Sunday sample collected at the time of the peak of the bathing load would give the ideal bather use water quality information. Nevertheless, Bennett (1969) showed that five samples over four weeks adequately defined the four-week period's water quality. Results from five samples also provide a reasonable data base from which to calculate a valid representative geometric mean and its twenty-five/seventy-five percentile values.

Effect Levels

The concentration of P. aeruginosa in water at which ear infections start to be reported is very low (Hoadley and Knight, 1975; Seyfried and Fraser, 1978; Weingarten, 1977; Burger, 1983; Calderon and Mood, 1982). Burger (1983) found that 12 bathers out of 100 experienced ear infections when the 75 percentile P. aeruginosa levels were in the range 10 to 100 per 100 mL. When the 75 percentile levels were 2 or less Pseudomonas per 100 mL, a background ear infection rate of 8 per 100 bathers was observed. Median P. aeruginosa levels were < 1 per 100 mL in both these cases. Calderon and Mood (1982), however, were unable to develop a statistically significant relationship between P. aeruginosa levels and the incidence of otitis externa, but their study did show differences between the levels for their cases and controls.

The Ontario bathing use objective (OME, 1979) states that: "because the occurrence of disease-causing organisms is being measured directly, a

potential health hazard exists when pathogenic organisms (e.g. Pseudomonas aeruginosa, Salmonella typhi and Polio virus), can be enumerated and frequently isolated from the water". For Pseudomonas aeruginosa, the above discussion supports this recommendation. But the evidence also suggests that the 75% percentile Pseudomonas aeruginosa level of 10 organisms per 100 mL can be substituted for the generalized statement "enumerated and frequently isolated". This means that seventy-five percent (75%) of the sample analyses must show less than 10 organisms per 100 mL or conversely that a maximum of 25% of the analyses may have levels greater than 10 per 100 mL. Therefore, the levels of Pseudomonas aeruginosa should not be greater than 10 P. aeruginosa per 100 mL in more than twenty-five (Cabelli, 1977) percent of the analyses to protect bathers from ear infections.

Whereas former criteria incorporated an arbitrary factor for current experiences such as weather, rain, sewage plant malfunctions and laboratory variations, which erred on the side of safety, the relationships on which the recommendations were based are more exact and have already built in these and other important considerations. Additional percentile values to allow for these factors are thus not required.

Summary

The objective recommended here has taken into account the opportunistic pathogenic nature of the organism, Pseudomonas aeruginosa, the existing levels of the organism in Great Lakes waters and the findings of many medical and environmental studies. The mPA method (Levin and Cabelli, 1972) is recommended for specificity and simplicity. The objective allows some numbers of the organism to be present without undue concern but protects the bather from frequent high levels of the organism. As stated by Hoadley (1977a), "The value of P. aeruginosa as an indicator of potential health hazards associated with water must be judged solely on the basis of the potential hazard associated with its own presence. There is no reason to suggest that P. aeruginosa might be a good indicator of the possible presence of other pathogens ... conventional indicators of fecal contamination are of little general value to indicate the possible presence of P. aeruginosa".

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2.2 DIAZINON

EXISTING OBJECTIVE

The concentration of diazinon in an unfiltered water sample should not exceed 0.08 microgram per litre for the protection of aquatic life.

RECOMMENDED OBJECTIVE

For the protection of aquatic life, the maximum waterborne concentration of diazinon shall not exceed 0.003 µg/L, except that it may range up to 0.1 µg/L once every 30 or more days for periods not to exceed 2 days.

RATIONALE

Exposure to Diazinon

Diazinon is the common and most frequently used trade name for the insecticide 0,0-diethyl-0-(2-isopropyl-4-methyl-6-pyrimidyl) phosphorothioate. It is used in or on soil for control of wireworms, nematodes, grubs, cutworms and maggots; on the flesh and leaves of forage, field crops, fruits and vegetables; as a seed protectant; and for control of cockroaches and other household pests (Berg, 1981). It is applied in the form of wettable powders, emulsified mixtures, dusts, coated granules and ultra-light volume sprays. For non-agricultural purposes, it is incorporated into polyethylene micro-capsules from which it is slowly released to prolong the time for exposure. Its use on field crops such as corn (e.g. for rootworms) and in orchards would seem to be the largest source of diazinon in the Great Lakes Basin. According to the manufacturer, its use on field crops is diminishing, but increasing on vegetable and flower gardens and for household pest treatment (Dr. William Campbell, Ciba Geigy Corp., personal communication).

The measured water solubility of technical grade diazinon (87.1% purity) is about 40 mg/L (Jarvinen and Tanner, 1982; Martin, 1971). Its half-life at 20° C in distilled water is 31, 185, 136 and 6 days at a pH of 5.0, 7.4, 9.0, and 10.4; respectively (Gomaa, et al., 1969). Diazoxon, the more toxic oxidation metabolite of diazinon, is also most stable under neutral conditions, but is hydrolyzed several times more rapidly than the parent compound (ibid.). The laboratory-determined half-life for encapsulated diazinon in Lake Superior water is greater than 230 days, compared to 30 days for the straight technical grade (Jarvinen and Tanner, 1982).

While diazinon appears moderately persistent from laboratory hydrolysis experiments, there is substantial evidence that it can be degraded biologically under field conditions (Paris and Lewis, 1973). For example, Sethunathan and Pathak (1972) found that diazinon could be completely broken down in 3 to 5 days when incubated in water from rice paddies that had received at least three previous pesticide applications. Very little was degraded in previously untreated water over a 12-day incubation period. Aerobic conditions accelerated and the presence of suspended soil particles inhibited the breakdown process. Specific soil micro-organisms have been identified which degrade diazinon (Gunner and Zuckerman, 1968).

In a study in which diazinon was metered continuously into an outdoor experimental stream for three months, the half-life was found to be about half as long (20 days) in 5 gal., unsterilized water samples exposed to sunlight as in shaded samples (Parkhurst, et al., 1981). Thus, a large number of site-specific conditions, including the treatment history of an area where the pesticide is used, will significantly influence its effectiveness as well as its potential for causing adverse effects.

Another consideration in evaluating exposure to diazinon, is that all of several types and ages of formulations were found by Meier, et al., (1979) to contain about 0.5% sulfotepp. This manufacturing impurity has been demonstrated to be up to 75 times more toxic to fish than diazinon or its degradation products. It is slightly less toxic than diazinon to birds, however (Dr. Richard Honeycutt, Ciba Geigy Corporation personal communication). Sulfotepp has been found to resist hydrolysis; each of four diazinon formulations retaining substantial toxicity after essentially complete destruction of the diazinon (Meier, et al., 1979). Recent discussions (September 1982) with Dr. William Campbell indicate that Ciba Geigy Corporation, the manufacturer, currently has an internal specification for controlling sulfotepp concentrations at 0.2% or less of the technical grade product, but that it is usually present at about 0.1%.

Diazinon has been found in three watersheds tributary to Lakes Huron and Erie. Concentrations ranged from non-quantifiable ($< 0.01 \mu\text{g/L}$) to $140 \mu\text{g/L}$ between May 1975 and April 1977 (Frank, et al., 1978). In the sandy soil of Hillman Creek watershed (Braun and Frank, 1980), mean diazinon concentrations of 0.006 and $0.001 \mu\text{g/L}$ in the water during the 1975-6 and 1976-7 seasons gave rise to fish levels of $0.017 \mu\text{g/g}$ (black crappie), $0.018 \mu\text{g/g}$ (brown bullhead) and $0.092 \mu\text{g/g}$ (gizzard shad). There are no known records of diazinon being discovered in water or in other samples from the open waters of the Great Lakes, nor would it be expected there.

Toxicity of diazinon

Exposure of the green alga Scenedesmus quadricaudata to 100 and 1000 $\mu\text{g/L}$ of diazinon for 10 days produced no effects on cell number, photosynthesis, or biomass (Stadnyk, et al., 1971). Additional fish and invertebrate laboratory mortality data are presented in Table 1. The data are arranged in the order of their toxicity values from least to greatest as an aid to evaluating relative sensitivity. However, exposure times are highly variable.

Table 1
Fish and invertebrate median mortality values ($\mu\text{g/L}$ diazinon)

	24 hr	48 hr	96 hr	Other LC ₅₀ Data	References
<u>Pimephales promelas</u> (fathead minnow)			7800 6900		Allison and Hermanut, 1977 Jarvinen and Tanner, 1982
<u>Salmo clarki</u> (cutthroat trout)			1700		Johnson and Finley, 1980
<u>Salvelinus namaycush</u> (lake trout)			602		Johnson and Finley, 1980
<u>Salvelinus fontinalis</u> (brook trout)			770		Allison and Hermanut, 1977
<u>Helisoma trivolis</u> (snail)				168 hr. LC ₅₀ -528	Morgan, 1977
<u>Gammarus lacustris</u> (amphipod)	800	500	200		Sanders, 1969
<u>Salmo gairdneri</u> (rainbow trout)	380	170	90		Cope, 1964
<u>Physa gyrina</u> (snail)			48		Morgan, 1977
<u>Paraleptophlebia pallipes</u> (mayfly)	243	134	44	168 hr. LC ₅₀ 32	Morgan, 1977
<u>Pteronarcys californica</u> (stonefly)	155	60	25		Sanders and Cope, 1966
<u>Baetis intermedius</u> (mayfly)	358	55	24		Morgan, 1977
<u>Lepomis macrochirus</u> (bluegill sunfish)	52	30	22 168		Cope, 1964 Johnson and Finley, 1980
<u>Asellus communis</u> (isopod)			21		Morgan, 1977
<u>Acroneuria ruralis</u> (stonefly)		294	16		Morgan, 1977

Table 1
Fish and invertebrate median mortality values (μg diazinon/L) (cont'd)

	24 hr	48 hr	96 hr	Other LC ₅₀ Data	References
<u>Orconectes propinquus</u> (crayfish)	2,846	537		168 hr. LC ₅₀ -15	Morgan, 1977
<u>Crangonyx sp.</u> (amphipod)			14		MERS, 1980 (unpublished)
<u>Pteronarcys dorsata</u> (stonefly)				30-day LC ₅₀ -4.6	NAS/NAE, 1973
<u>Daphnia magna</u> (cladoceran)				50-hr. LC ₅₀ -4.3	Sanders and Cope, 1966
<u>Hydropsyche bettoni</u> (caddisfly)				30-day LC ₅₀ -3.54	NAS/NAE, 1973
<u>Ophiogomphus rupinsulensis</u> (dragonfly)				30-day LC ₅₀ -2.2	NAS/NAE, 1973
<u>Simocephalus serrulatus</u> (cladoceran)		1.8 (60° F) 1.4 (70° F)			Sanders and Cope, 1966
<u>Acroneuria lycorias</u> (stonefly)			1.7	30-day LC ₅₀ -1.25	NAS/NAE, 1973
<u>Ephemereilla subvaria</u> (mayfly)				30-day LC ₅₀ -1.05	NAS/NAE, 1973
<u>Daphnia pulex</u> (cladoceran)		0.9 0.8			Sanders and Cope, 1966 Johnson and Finley, 1980
<u>Gammarus pseudolimnaeus</u> (amphipod)	49	3	2	168-hr. LC ₅₀ -0.5	Morgan, 1977
<u>Gammarus fasciatus</u> (amphipod)			0.2		Johnson and Finley, 1980
<u>Chironomus tentans</u> (midge)	0.4	0.1	0.03	168-hr. LC ₅₀ -0.03	Morgan, 1977

It is clear from Table 1 that fish are generally less sensitive to acute diazinon exposure than invertebrates. Sensitivity among invertebrates is highly variable, with no taxonomic group restricted to one extreme or the other. Short-term exposure to concentrations up to 1 $\mu\text{g/L}$ appears likely to significantly affect some of the smaller crustaceans (amphipods and cladocerans). The limited data available indicate that a single midge species would be susceptible to acute exposure to concentrations under 0.1 $\mu\text{g/L}$.

Available laboratory chronic toxicity data, also listed in order of increasing toxicity in Table 2, indicate that exposures of longer duration (several weeks to several months) will affect fish at about 1 $\mu\text{g/L}$ and at least one insect species (Chironomus tentans) at 0.0006 $\mu\text{g/L}$. It is our opinion, however, that the 0.003 $\mu\text{g/L}$ concentration, causing a 33% delay in development rate to emergence in C. tentans, is the lowest ecologically significant effect level available for diazinon.

Morgan (1977) applied diazinon to a small natural stream in 12 successive doses of 3 $\mu\text{g/L}$ from July through September. Each application lasted three hours and was repeated every three days. He concluded that Diptera (including midges), Ephemeroptera (mayflies) and Trichoptera (caddisflies) were more responsive than other groups during the 5-week exposure period, but that "the overall effect was minor" compared to the control.

A recent study (Arthur, et al., manuscript) involving a continuous dosing of diazinon into outdoor experimental streams presents data that seem to contradict Morgan's (1977) field observations. The experimental streams were naturally colonized while being continuously supplied with upper Mississippi River water (above Minneapolis, MN) at a rate of 2.2 m^3/sec . Two parallel streams were dosed for 12 weeks at concentrations increasing in 2 or 3 steps from approximately 0.3 to 5 and from 3 to 22 $\mu\text{g/l}$. A third reference channel remained untreated. In this study, chironomid midge numbers were not significantly reduced although the response of individual species in this and other taxonomic groups was not closely followed. A delay in midge development like that reported by Morgan (*ibid.*) was suggested in the stream study but at higher concentrations. Similarly, isopods were unaffected at concentrations exceeding the 96-hour LC_{50} for a species studied by Morgan (*ibid.*) and Hyalella amphipods were rapidly eliminated at concentrations well below the 96-hour LC_{50} Morgan reported for a species of this genus. These puzzling inconsistencies may be explainable on the basis of substantial differences in individual species sensitivities, differences in immediate exposure conditions, differences in degree of resolution of results between lab. and field studies, or something entirely different. While effects on some groups (amphipods, mayflies, caddisflies, damselflies) were observed at the lowest concentration tested (0.3 $\mu\text{g/l}$), there were no consistent differences between streams in either total macro-invertebrate abundance or species diversity at concentrations up to 30 $\mu\text{g/l}$.

The significance of these test results is determined by consideration of questions for which there are no definitive answers. The question arises, for example, about the adequacy of these data for making evaluations of the hazards of diazinon to all natural aquatic ecosystems. The data would seem to suggest that other midge species could be expected to have substantially different sensitivities than Chironomus tentans (as among other taxonomic

Table 2.
Fish and Invertebrate chronic effects (laboratory)

<u>Description</u>	<u>Reference</u>
<u>Jordanella floridae</u> (flag fish) Time to embryo progeny hatch decreased 8 to 18% at 14 to 240 $\mu\text{g/L}$ (highest concentration tested); growth of adult males after 160 days and embryo progeny hatch reduced at 88 $\mu\text{g/L}$, not at 54 $\mu\text{g/L}$.	Allison, 1977
<u>Pimephales promelas</u> (fathead minnow) Reduced hatching and increased incidence of scoliosis at 32.2 $\mu\text{g/L}$ during a full life cycle chronic test; no no-effect concentration obtained, although 3.2 $\mu\text{g/L}$ appeared close.	Allison and Hermanutz, 1977
<u>Salvelinus fontinalis</u> (brook trout) Reduced progeny growth at 0.55 $\mu\text{g/L}$ (lowest concentration tested) after 17-week exposure during a 10-month partial life-cycle chronic test; no no-effect concentration tested.	Allison and Hermanutz, 1977
<u>Daphnia magna</u> (cladoceran) Reproduction significantly reduced at 0.3 $\mu\text{g/L}$ during 21-day life-cycle exposure; no significant effect at 0.15 $\mu\text{g/L}$.	NAS/NAE, 1973
<u>Chironomus tentans</u> (midge) Egg development delayed significantly and time to emergence (82 days) increased 13 and 33% at 0.0006 and 0.003 $\mu\text{g/L}$; no no-effect concentration tested.	Morgan, 1977

groups), but the others could turn out to be more sensitive as well as less sensitive. And finally, perhaps, what would be the significance to an aquatic ecosystem of losing just one, or even all, midge species? A moderate approach might assume that some midge species are at least an order of magnitude less sensitive than *C. tentans*^{*}, that the occasional (probably temporary) loss of one or more midge or other species will have a minor impact on the system involved, that no other structural or functional ecosystem characteristics will be importantly effected and that most ecosystems exposures to diazinon will be on the order of hours or days, rather than weeks or months. Based on this analysis, a diazinon concentration of 0.1 µg/L (the 48-hour LC₅₀ for midges) might be considered an acceptable objective. More conservatively, 0.003 µg/L would be considered a maximum continuous value and even more conservatively, accepting the many factors of uncertainty, a concentration of 0.0001 µg/L or less would be deemed necessary to ensure total protection of aquatic ecosystems.

Another dimension of diazinon toxicity to fish is related to its acetyl-cholinesterase (ACHE) enzyme inhibition mode of action. Weiss (1961) demonstrated that inhibition occurs rapidly over an exposure period of a few hours and that while the reaction is reversible, complete recovery of ACHE activity takes 30 days or more for some species. Such a recovery period is required by bluegills, a member of the centrarchid family especially vulnerable to acute diazinon exposure and to organophosphate poisoning generally (Weiss, 1959). It has also been demonstrated (Weiss, 1958) that previously exposed fish with reduced ACHE activity levels are more susceptible to subsequent exposure than are unexposed fish. Therefore, short-term toxicity test results probably only apply in the case of single exposures. Lower objective values to protect fish should be specified if multiple exposures are expected to occur within 30 days of one another. Whether or not similar considerations apply to invertebrates is unknown.

While frogs seem to be very resistant to organophosphate poisoning (LD₅₀ > 2000 mg diazinon/kg, Tucker and Crabtree, 1970), concern has been expressed that they could accumulate sufficient residues to affect organisms ingesting them for food. Tadpoles exposed to 1 mg/L parathion and 5 mg/L fenthion by Hall and Kolbe (1980) accumulated 60 times the water concentrations and were lethal to mallard ducks when fed in a single meal. Mallards (and other birds) exhibit about the same sensitivity to diazinon as to fenthion and parathion with single-dose LD₅₀'s of 3.54, 5.94, and 2.13 mg/kg respectively (Tucker and Crabtree, 1970). It seems unlikely, however, that diazinon would be present long enough in nature at sufficient concentrations to result in accumulation of toxic levels in frogs. Fish are probably sensitive enough to be directly affected before accumulating levels that are lethal to another organism eating them.

* Mulla and Khasawinah (1969) found a 10 to 15 times range in sensitivity among four chironomid midge species exposed to each of the organophosphate pesticides parathion, dursban and abate.

Several instances have been reported of birds, mostly waterfowl, being poisoned from ingestion of crops or vegetation treated with diazinon for pest control (Stone, 1979; Hill and Fleming, 1982). These mortalities apparently resulted from approved, but either unwise or unfortunate application of the pesticide. The label directions warn that birds feeding on treated areas may be killed. Diazinon treatment of field crops and applications to golf courses during spring and autumn bird migrations have been especially hazardous. Obviously, the use of diazinon and certain other organophosphate and carbamate pesticides (e.g., parathion, fenthion, dursban, carbofuran, phorate) should be avoided where birds might ingest the residues.

Hazards to man resulting from aquatic contamination are thought to be slight. Diazinon is rapidly metabolized in mammals to less toxic products, does not accumulate in tissues and has produced no teratogenic or embryotoxic effects (Vettorazzi, 1976; Lewis and Tatken, 1980). Based on chronic no-effect levels of 0.1 to 0.02 mg/kg body weight per day for several mammals, an adult daily intake for man of 0.002 mg/kg body weight was established by the U.N.'s World Health Organization/Food and Agriculture Organization. Diazinon does not accumulate to any appreciable degree in fish (Miller, et al., 1966; Allison and Hermanutz, 1977). Exposure of fish to 1 $\mu\text{g/L}$ for several days (a concentration well above those required to protect aquatic organisms) would result in tissue residues of about 0.1 mg/kg. This level, if ingested by man as part of a 100 g meal of fish, would be well below the 0.002 mg/kg body weight acceptable daily intake.

Based on these data, a two-level objective is recommended for diazinon. Mean levels should not exceed 0.003 $\mu\text{g/L}$, but may range up to 0.1 $\mu\text{g/L}$ every 30 or more days for periods not to exceed 2 days.

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2.3 POLYNUCLEAR AROMATIC HYDROCARBONS

RECOMMENDATION

For the protection of aquatic life, the levels of benzo(a)pyrene in the sediments or in organisms serving as a food source for fish should not exceed 1.0 µg/g; levels of benzo(a)pyrene in water should be less than 0.01 µg/L.

NOTE: Other 3-5 ring polynuclear aromatic hydrocarbons have been observed in the Great Lakes ecosystem and some of these are carcinogenic and are strong inducers of mixed function oxidase enzymes; they may be of equal or greater concern.

RATIONALE

Sources

Polynuclear Aromatic Hydrocarbons (PAH) are organic compounds composed of two or more fused rings. The most commonly studied PAH found in the environment include benzo(a)pyrene (BaP), anthracene, benzo(a)anthracene, fluoranthene, indeno(1,2,3-cd)pyrene, phenanthrene, perylene and pyrene. Many other PAH have been recognized. PAH are of concern in aquatic environments not only because they are ubiquitous contaminants but also because many, particularly BaP, are well documented carcinogens. PAH may be formed during any incomplete combustion of organic matter. Important industrial sources of PAH include coal gasification and liquifaction processes, combustion of fossil fuels (gasoline, kerosene, coal, natural gas, diesel fuel), waste incineration, as well as production of coke, carbon black, coal tar pitch, asphalt and petroleum cracking (Hangebrauck, *et al.*, 1967). Other sources of PAH which may be important in terms of human exposure are foods which have absorbed PAH, cigarette smoking, agricultural burning and the use of items such as internal combustion engines.

Waste effluents of certain industrial processes, for example electrolytic reduction of magnesium and ferro-alloy smelting, provide a direct route of entry for PAH to aquatic ecosystems (Bjorseth, *et al.*, 1979; Lunde and Bjorseth, 1977). PAH also gain entry to aquatic ecosystems through several other routes, including precipitation and fallout from the atmosphere, runoff from asphalt covered surfaces (e.g. roads) and oil spills.

Fossil fuels such as crude or bunker oil contain PAH and may be spilled accidentally into aquatic environments, including the Great Lakes. High molecular weight PAH fractions of several crude oils have been shown to resist weathering (Hallett, *et al.*, 1983; Law, 1980) and PAH in bunker oil have been found to concentrate after weathering in the St. Lawrence River (Palm and Alexander, 1978).

PAH are also produced during forest fires and volcanic eruptions. One species of bacteria (*Platymonas* sp.) was reported to synthesize 1.15 µg/L of BaP during four months of culturing in normal medium (Erhardt, 1972); However, this result is controversial. Few environments are free of PAH and it has been suggested that BaP may have been accumulated rather than synthesized.

Source data are shown in Table 1. Estimates of BaP emission in Ontario indicate that a large proportion was from coke production although the contributions from wood and open burning were not available (Statistics Canada, 1978; Ontario Ministry of Natural Resources, 1977). The reduction in U. S. BaP emissions through the 1960s reflected both a shift from the use of wood or coal to oil or gas for home heat and an improvement in emission control techniques. Increases in fossil fuel combustion and a reversion back to wood for home heating probably underly the more recent increase in BaP emissions. These increased emissions also reflect the increase in the production of iron and steel in the Great Lakes.

Chemistry

Formation

The chemistry of PAH formation is a complex function of many parameters, but the general mechanism is quite well understood. At usual combustion temperatures (500-800°C) aliphatic carbon-carbon and carbon-hydrogen bonds break easily. The free-radicals formed during pyrolysis recombine to produce PAH which accumulate as pyrosynthesis proceeds. Aromatic ring systems are stable at these temperatures in the chemically reducing atmospheres found at the centre of flames (Badger, et al., 1960, 1964, 1968).

Table 1
Estimated PAH Emissions

	BaP			Total PAH
	U.S. late 1960's ¹	U.S. mid 1970's ²	Ontario mid 1970's ³	U.S. mid 1970's ⁴
Total (Mt/yr)	1107	290	18	14600
	----- Percent -----			
Heat & Power:				
Coal	39.	9.3	0.1	1.3
Oil	0.2	0.9	0.3	0.1
Gas	0.2	0.3	0.3	0.1
Wood	3.6	25.	--	53.
Open Burning	41.	18	--	17.
Coke Production	1.8	38	52.	4.3
Forest Fires	12.6	3.8	46.	10.1
Mobile Sources	2.0	4.5	1.8	16.

1 NAS (1972)

2 Faoro and Manning (1981)

3 OME (1979)

4 Peters, et al., (1981)

Physical State of Atmospheric PAH

Based on the relatively high boiling and melting points of PAH, their generally low vapour pressures at ambient temperature and their sorption properties, atmospheric PAH are almost exclusively adsorbed on airborne particulates (for example fly ash) (Commins, 1962; Thomas, *et al.*, 1968). However, 3 to 5 ringed PAH may occur in the vapour phase, depending on temperature (Yamasaki, *et al.*, 1982).

The size of the PAH-bearing particles inhaled by humans may be the key factor in determining health risk. Small particles are able to penetrate deep into the alveoli of the lung, while larger aerosols gain only limited entry to the respiratory tract. A Canadian study showed that 70-90% of PAH collected in Toronto were adsorbed to particles with an aerodynamic diameter less than 5 μm (Pierce and Katz, 1975). Other BaP-containing aerosols had average mass median diameters of 0.65 μm (Albaglia, *et al.*, 1974).

More recently, a new type of particulate has been identified, making up about 1% of fly ash. This carbonaceous material is like a honeycomb in shape and is relatively large compared to other particulates. This type of particle accounts for more than 25% of the total surface area of fly ash and has twice the affinity for PAH as do other fractions of fly ash. It is estimated that about 70% of total PAH are adsorbed on this material (Natusch, 1983). Adsorption on this type of carbonaceous material renders PAH less susceptible to photodegradation, thus permitting relatively long atmospheric residence times. On the other hand, the large size of these particles restricts their access to the lungs.

Physical State of PAH in Aquatic Ecosystems

PAH have a very low solubility in water and are thought to exist primarily adsorbed to organic particles. The solubility of benzo(a)pyrene in water is 0.004 mg/L at 27°C. Certain synthetic detergents and natural products such as humic acids may aid in the solubilization of PAH. PAH are also sorbed to humic and fulvic acids with approximately the same partition coefficients as for organic particulates (Landrum and Giesy, 1981; Gjessing and Bergland, 1981; Landrum, *et al.*, 1982). Small molecules such as toluene, benzene, hexane and cyclohexane may form aggregates or complexes with PAH (Landrum, *in press*). This phenomenon may be important under spill conditions or where small molecules are present at relatively high levels (> 1 mg/L), as these complexes increase the apparent water solubility of PAH.

Transport and Transformation of PAH

Transport in Air

Particle size is the major factor affecting the transport behaviour of PAH-containing particulates. Particle sizes generally range in diameter from 0.01 μm to 10 μm with the bulk of PAH being associated with particles having a diameter less than 5 μm .

The larger particles are selectively removed from air by gravitational settling or impaction; in turbulent air, they are selectively deposited on rough surfaces (Winchester, 1980). A consideration of Stoke's law indicates

that in rising air, particles smaller than 2 μm in diameter would remain suspended (Winchester, 1980). Particle shape and density are also important to the transport behaviour of particulate-associated PAH.

Dispersion of PAH in the atmosphere occurs by diffusion, convection and advection, all of which depend upon meteorological conditions. Such dispersion has the effect of diluting emissions close to the source and accounts for the appearance of PAH at locations distant from the source. At least 20 PAH have been shown to be transported over long distances (Winchester, 1980). Additionally, atmospheric residence times of various PAH were estimated, taking into account photocatalytic transformation. These varied from a few minutes to 500 hours. On this basis, it was predicted that PAH may travel from a few to several thousand kilometers (Blau and Gusten, 1983).

Transport in Water

As in air, transport of PAH occurs by diffusion, convection and advection. Sedimentation is probably the most important route for clearance of PAH from lakes and depends largely on particle size as in the atmosphere, although it may be reduced by interaction with humic materials and smaller organic molecules. These interactions should facilitate distribution and prolong the residence time of PAH in the water column.

Atmospheric Transformation

In the atmospheric environment, the fate of PAH is influenced largely by its photochemical behaviour. PAH containing three or more rings are able to absorb solar radiation at wavelengths above 300 nm. The excited PAH react with O_2 to produce highly reactive intermediates (singlet oxygen molecules) resulting in the rapid oxidation and degradation of PAH (NAS, 1972; Radding, *et al.*, 1976; Geacintov, 1973; Katz, *et al.*, 1978; Tosine, 1978).

PAH adsorbed to surfaces and in aerosols may be photo-oxidized rapidly but, depending on the affinity of the photooxidation products for the particulate, underlying layers of PAH may be protected from further exposure to solar radiation (NAS, 1972). PAH found in weathered oils may persist for considerable periods, probably due to the physical matrix (Hallett, *et al.*, 1983).

Aquatic Transformation

Differences in photolysis rates are due primarily to differences in the absorption spectra of PAH. Volatilization also plays a key role in environmental persistence in this compartment. Volatilization rates decrease by factors of 3 to 10 with each additional benzene ring. With the exception of naphthalene, the rates of photolysis of dissolved PAH are higher than the rates of volatilization (Table 2). Such photolysis is believed to cause the breakdown of the molecule, which would effectively minimize its toxicity. In the aquatic environment where sorption to humics and association with algae occur, photolysis may be enhanced (Zepp, *et al.*, 1981; Zadelis and Simmons, *in press*; Warshausky, *et al.*, *in press*), thereby reducing the concentration of parent compounds in the upper portion of the water column. Sorbed PAH, on the other hand, may become less susceptible to photolytic processes due to shading and particle settling below the photic zone.

Oligochaetes mix the top few centimeters of sediment. This process redistributes organic contaminants such as PCBs (White and Klar 1982) and brings them to the surface. If PAH behave in a similar manner, the exposure of benthic organisms may be increased.

For higher trophic levels, exposure to PAH will occur via both water and diet. Since *P. hoyi* ultimately constitutes a major dietary component for some fishes in the Great Lakes at some stages in their lives and because of the relatively high concentrations of PAH in *P. hoyi*, these organisms are responsible for a large proportion of PAH exposure for some fishes.

Fish biotransform PAH well and it is unlikely that PAH will accumulate in their tissues unless there are high PAH concentrations in the water. In fact, low levels of PAH are generally found in fishes except in cases of high local contamination, e.g. the Black River, Ohio (Baumann, et al., 1982). The absence of parent PAH does not necessarily indicate lack of exposure but rather may reflect biotransformation. Further, since the dihydrodiol metabolites are carcinogenic derivatives of PAH, high levels of these in fish may pose problems for piscivores. The levels of both parent compounds and metabolites are therefore important in the assessment of exposure hazard and possible food chain transport of PAH.

The metabolism of naphthalene and anthracene in various tissues of coho salmon (*Oncorhynchus kisutch*) has been demonstrated (Roubal, et al., 1977). Up to 46% of anthracene in fish flesh was found in a metabolized form 144 hours after injection. Lu, et al., (1977) showed that the bioaccumulation factor for BaP in mosquito fish (*Gambusia affinis*) after three days' exposure was less than 1, whereas for snails the corresponding value was 2177. The monooxygenase activity, as measured by BaP metabolism, is undetectable in marine bivalves (Vandermeulen and Penrose, 1978) whereas rainbow trout (*Salmo gairdneri*) readily metabolize BaP (Egaas and Varanasi, 1982). Relative monooxygenase activities for fish are roughly one order of magnitude below those of amphibians, birds and mammals, including primates (Walker, 1978). Therefore, despite the fact that PAH have high Kow's, they do not bioaccumulate to the same extent as DDT and HCB as originally predicted by Lu, et al., (1977).

These limited data support the theory that parent PAH will bioaccumulate in the lower levels of aquatic food chains but not in fishes, birds and mammals. It is not expected, therefore, that high levels of parent PAH will be found in fish and birds monitored in the Great Lakes. However, metabolites of PAH may bioaccumulate at higher trophic levels and a lack of parent PAH in tissues may not fully describe the hazard to these organisms.

PAH in the Great Lakes Ecosystem

Some 27 PAH were identified in surface sediments taken from locations in each of Lakes Ontario, Erie and Huron (Strosher and Hodgson, 1973; IJC, 1976). Perylene, pyrene, benzopyrenes, benzoperylenes, fluoranthenes, benzofluoranthenes and chrysene were among those commonly present at higher than average PAH concentrations. Total concentrations of PAH reached a maximum in the surface sediments of 14 $\mu\text{g/g}$ for Lake Ontario, 54 $\mu\text{g/g}$ for Lake Erie and 1.2 $\mu\text{g/g}$ for Lake Huron. A representative list of the PAH found at

different sediment depths is shown in Table 4 for an open Lake Ontario site. Few PAH were detectable in open lake waters. Methyl naphthalenes, biphenyl and methyl anthracenes were the only PAH detectable at concentrations from 0.003 µg/L to 0.6 µg/L (Strosher and Hodgson, 1975).

Table 4
PAH in Lake Ontario Sediment (43° 39' N, 78° 12' W)
(Strosher and Hodgson, 1973; IJC, 1976)

(µg/g Dry Sediment)

Aromatic	0-5 cm	10-15 cm	20-25 cm	30-35 cm	55-60 cm	70-75 cm
Biphenyl	0.014	0.007	0.009	0.004	0.004	0.004
Tetrahydropyrene	0.056	0.029	¹ -	-	-	-
Fluoranthene	0.281	0.058	-	-	-	-
Pyrene	0.056	0.029	-	-	-	-
1,2-Benzanthracene						
Chrysene	0.025	0.088	0.052	-	-	-
Triphenylene						
Dimethyl Chrysene	0.112	-	-	-	-	0.018
2,3-Benzofluoranthene	0.450	0.029	0.017	0.017	0.020	0.009
Methyl Benzofluoranthene	0.056	-	-	-	-	-
Benzpyrenes	0.337	-	0.017	0.034	0.010	0.009
Perylene	0.056	0.029	0.017	0.034	0.30	0.046
Methyl Benzpyrene	0.056	-	-	-	-	-
Methyl Perylene	0.112	-	-	-	0.010	0.027
20-Methyl Cholanthrene	0.337	-	-	-	-	0.018
Benzperylene	0.225	-	-	-	-	-
Coronene	0.562	-	-	-	-	-
Total Aromatics	2.935	0.269	0.112	0.089	0.084	0.131

¹ less than detectable

Similar types and concentrations of PAH were found in western Lake Erie and Lake Huron sediments (Eadie, et al., 1982b). PAH were also detected in oligochaetes and midges. A survey of Great Lakes sediment concentrations suggests that the lower lakes sediments are more contaminated than those of Lake Superior (Table 5).

Table 5
PAH in Great Lakes Surficial Sediments ($\mu\text{g/g dry}$)¹

Compound	Lake				
	Superior	Michigan	Huron	Erie	Ontario
Phenanthrene	0.034	0.533 + 0.382	0.272	0.346 + 0.092	0.0585
Fluoranthene	0.088	0.754 $\bar{\pm}$ 0.444	0.487	0.569 $\bar{\pm}$ 0.442	0.615 + 0.394
Pyrene	0.053	0.607 $\bar{\pm}$ 0.399	0.356	0.391 $\bar{\pm}$ 0.091	0.647 $\bar{\pm}$ 0.594
BaP	0.028	0.480 $\bar{\pm}$ 0.146	0.294	0.255 + 0.152	
n	1	7	1	3	5
				<u>Range of Data</u>	
Phenanthrene		0.006-1.268		.018-.431	0.040- 0.205
Fluoranthene		0.009-1.664		.065-.285	0.210-1.000
Pyrene		0.008-1.430		.057-.287	0.056-1.182
BaP		0.004- 0.944		.056-.173	0.076- .306

¹ data from Gschwend and Hites (1981); Eadie (in press); Eadie, et al. (1982b); IJC (1977); Eadie, et al. (in press).

Sewage waters and industrial effluents can be heavily contaminated by PAH, and PAH are also commonly found in drinking water and surface waters throughout the world. IARC (1973) reported BaP concentrations in drinking water up to 0.0234 $\mu\text{g/L}$ and in surface waters, sewage effluent and industrial discharges at levels up to 0.114, 34.5 and 1.84 $\mu\text{g/L}$, respectively.

Plant effluents discharging into Hamilton Harbour on Lake Ontario have contained a range of PAH concentrations from 0.02-66 $\mu\text{g/L}$, with benzo(a)pyrene concentrations ranging from 0.03-30 $\mu\text{g/L}$ (Smillie, et al., 1978). The most recent survey of representative PAH in open Great Lakes water is described in Table 6 and shows mean concentrations of six PAH ranging from 0.006-0.024 $\mu\text{g/L}$. These values are higher than for most aquatic ecosystems, except for those heavily impacted by urban or industrial sources.

Carp (a bottom feeder) and pike (a predator) collected from Hamilton Harbour and the Detroit River contained low levels of PAH (Table 7). Four of these, perylene, benzo(k)fluoranthene, benzo(a)pyrene and coronene, were found at quantifiable levels; those in Hamilton Harbour being higher. A number of others, including some methylated PAH, were detected but not at levels sufficient to permit their quantification.

Table 6
PAH in Great Lakes Water Systems ($\mu\text{g/L}$)¹

(n = 6)

	Phenanthracene	Anthracene	Fluoranthene	Pyrene	Chrysene	Benzo(a)pyrene
Mean	0.024	0.006	0.015	0.014	0.014	0.012
S	0.025	0.006	0.009	0.006	0.010	0.008

¹ Eadie, et al., in press

Table 7
Polynuclear Aromatic Hydrocarbons in Fish
 (Hallett, et al., 1978)

($\mu\text{g}/\text{kg}$ fresh weight fillets)

PAH	Hamilton Harbour		Detroit River	
	Carp ¹	Pike ²	Carp	Pike
Perylene	0.074 \pm .058	0.042 \pm .025	0.008 \pm 0.14	0.030 \pm .020
Benzo(k)fluoranthene	0.023 \pm .022	0.017 \pm .014	0.003 \pm .006	0.015 \pm .010
Benzo(a)pyrene	0.138 \pm .074	0.069 \pm .044	0.012 \pm .019	0.046 \pm .041
Coronene	0.243 \pm .130	.0162 \pm .070	0.038 \pm .045	0.074 \pm .085
Naphthalene	+ ³	+		+
-1-methyl	+	+		+
-2-methyl	+	+		+
-dimethyl		+		+
-1-phenyl	+	+		+
Anthracene	+	+		+
-1-methyl	+	+		+
-2-methyl	+	+		+
-9-methyl				+
Phenanthrene	+	+		+
-1-methyl	+	+		+
-2-methyl	+	+		+
Biphenyl	+	+		+
Acenaphthene		+		+
Fluorene		+		+
Fluoranthene	+	+		+
Pyrene	+	+		+
1,2-Benzofluorene		+		+
2,3-Benzofluorene		+		+
Chrysene	+	+		+
Dibenz(a,h)anthracene	+	+		+

¹ Cyprinus carpio

² Esox lucius

³ + = detected

Similarly, herring gulls (*Larus argentatus*) from Lake Ontario at or near Kingston, Ontario, (Table 8) contained levels of PAH slightly lower than those found in the fish (Hallett, et al., 1977). The herring gull is primarily piscivorous and can metabolize PAH. Therefore, the gull, like fishes, demonstrates little bioaccumulation of PAH.

Toxicology and Metabolism

PAH are lipid soluble, hydrophobic compounds that are metabolized by animals to more polar compounds to facilitate excretion (Sims and Grover, 1974). These polar compounds may induce tumours. In addition, mutagenicity and teratogenicity have been reported. Such toxic effects have been studied most frequently in mammals and a summary is shown in Table 10. The balance of this review discusses the processes of metabolism in mammals, the occurrence of PAH metabolism in fishes and the association of tumour prevalence in fish populations with pollution by environmental PAH.

Metabolism

The enzymes responsible for metabolic conversions are collectively known as aryl hydrocarbon hydroxylases (AHH), cytochromes P450 and P448, or mixed function oxidase (MFO). AHH has been found in bacteria, algae, higher plants, invertebrates, fishes, reptiles, birds and mammals (Marquardt, 1977). Ironically, this enzyme system also results in conversion of many procarcinogenic PAH to their ultimate carcinogenic epoxide or dihydrodiol forms. The epoxides may be further metabolized in one of several ways: the epoxide may non-enzymatically isomerize to yield phenols; it may combine with glutathione; or alternatively, the enzyme epoxide hydrolase may convert the epoxide to a transdihydrodiol. Dihydrodiols and phenols then form glucuronides and sulfates, (Gilboin and Tso, 1978) which may be excreted.

The carcinogenic and mutagenic activity of PAH is probably due to the interaction of electron deficient reactive metabolites such as epoxides and dihydrodiol-epoxides with critical nucleophilic biomacromolecules, such as DNA (Miller and Miller, 1976). Epoxide hydrolase activity may be crucial in determining the sensitivity of a particular species to PAH-induced carcinogenesis or mutagenesis; species which are able to metabolize the epoxides or dihydrodiols rapidly are relatively insensitive, since there is less chance of interaction between the epoxide and key biomolecules (Oesch, et al., 1977). Alternatively, sensitive cells may produce reactive metabolites faster or have reduced capacity to conjugate carcinogenic intermediates.

Table 8
 Polynuclear Aromatic Hydrocarbons in
 Great Lakes Herring Gull Lipid
 (Hallett, et al., 1977)

COMPOUNDS	CONCENTRATION $\mu\text{g}/\text{kg}$		MASS SPECTRAL CONFIRMATION
	PIGEON ISLAND	KINGSTON	
Naphthalene	0.050	0.054	+ ¹
2-methyl Naphthalene	0.036	0.005	+
1-methyl Naphthalene	0.043	0.009	+
Biphenyl	0.151	0.017	+
Acenaphthene	0.038	0.007	+
4-methyl Biphenyl	0.061	0.010	+
Fluorene	0.044	0.003	+
Anthracene	0.152	0.024	+
Phenanthrene	nd ²	0.002	+
1-phenyl Naphthalene	0.008	0.008	
2-methyl Phenanthrene	0.021	0.007	+
1-methyl Phenanthrene	0.010	0.015	+
9-methyl Anthracene	0.011	0.025	+
3,6-dimethyl Phenanthrene	nd	0.012	+
Fluoranthene	0.082	0.017	+
Pyrene	0.076	0.015	+
1-aza Pyrene	a ³	a	
9-acetylanthracene	a	a	
1,2-benzofluorene	a	a	+
2,3-benzofluorene	a	a	+
1-methyl Pyrene	a	a	+
2-acetyl Phenanthrene	a	a	
1,1-binaphthyl	a	a	
Chrysene	0.053	a	+
Benzo(e)pyrene	0.026	0.021	+
Benzo(a)pyrene	0.038	0.030	+
Perylene	0.053	0.026	
9-dichloromethylene Fluorene	b ⁴	b	+b
Dimethyl Biphenyl	b	b	+b

1 + = confirmed presence

2 nd = Not detected

3 a = PCB interference

4 b = Standards of compounds unavailable. Compounds identified by mass spectra

PAH which include a "bay region" in their structure and an unsubstituted carbon in the position *peri* to the terminal benzene ring, are usually carcinogenic (Jerina, *et al.*, 1977; Yang, *et al.*, 1983). This structure is shown for BaP, in Figure 2. Other PAH with similar structures are often carcinogenic as well.

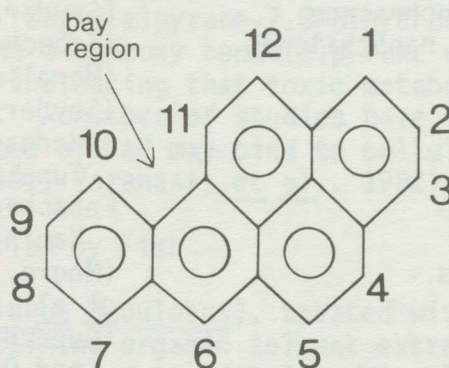


Figure 2. "Bay region" structure in BaP

Since all PAH studied are metabolized in a similar manner, BaP will serve to illustrate the production of an ultimate carcinogen from a "bay region" PAH. BaP is first converted, via AHH and epoxide hydrase, to benzo(a)pyrene-7,8-dihydrodiol. Further epoxidation produces the carcinogen, benzo(a)pyrene-7,8-dihydrodiol-9,10-epoxide, which is detoxified by conversion to a tetrahydrotetrol and eliminated via the metabolic pathways discussed above. Alkylated PAH are usually metabolized by hydroxylation of the alkyl side chain; however, "bay region" metabolites of alkyl-PAH have been identified as well (Yang, *et al.*, 1983).

Induction of MFO Systems

AHH is an inducible enzyme system which has been examined in detail by Nebert, *et al.*, (1981). Many substrates, highly variable in size and shape, induce activity of this system (Table 9).

Table 9
Great Lakes Chemicals Which
Induce Unique Forms of AHH

TOXIC CHEMICALS	REFERENCE
Benzo(a)pyrene	(Conney, <u>et al.</u> , 1957)
3-methyl cholanthrene	(Nebert and Gelboin, 1968)
Benzo(a)anthracene	(Nebert and Gelboin, 1968)
7,12-dimethyl benzo(a)anthracene	(Snyder, <u>et al.</u> , 1966)
methylated benzenes and naphthalenes	(Fabacher and Hodgson, 1977)
pp'-DDT	(Morello, 1965)
Benzene	(Snyder, <u>et al.</u> , 1966; Fabacher and Hodgson, 1977; Morello, 1965; Tunek and Oesch, 1979)
Mirex	Fabacher and Hodgson, 1976; Kaminsky, <u>et al.</u> , 1978)
Polybrominated biphenyls	(Moore, <u>et al.</u> , 1978; Robertson, <u>et al.</u> , 1980)
TCDD	(Guenther, <u>et al.</u> , 1979; Mikol and Decloitre, 1979; Parkinson, <u>et al.</u> , 1980a,b; Ahotupa and Aitio, 1980)
Lindane	(Mikol and Decloitre, 1979; Parkinson, <u>et al.</u> , 1980 a,b; Ahotupa and Aitio, 1980)
Polychlorinated biphenyls	(Parkinson, <u>et al.</u> , 1980a,b)
Halogenated naphthalenes and terphenyls	(Ahotupa and Aitio, 1980)

AHH inducers have been classified into two major types: those inducing cytochrome P₄₄₈ and those that induce cytochrome P₄₅₀ (Conney, 1982). Some chemicals do not induce all enzymes in the MFO system; other chemicals may even suppress some enzymes. The production of active metabolites (e.g. "bay region" dihydrodiol epoxides) may exceed the organism's ability to eliminate these compounds allowing a buildup of carcinogens. Conversely, substances like butylated hydroxyanisole (BHA) are anticarcinogenic because they inhibit or alter the regioselectivity of AHH. BHA also induces a wide variety of detoxifying enzymes.

Induction of the enzyme system commences with the passive transfer of the inducer (e.g. BaP) across the cell membrane and the highly specific binding to a gene receptor. Following apparent transfer of the inducer-receptor complex to the nucleus, the response includes the activation of numerous structural genes. The induction of metabolic enzymes from these structural genes then leads to the formation of reactive intermediates of PAH and/or detoxified products for elimination (Nebert, et al., 1981).

MFO Induction in Fish

It was shown earlier that fish efficiently metabolize PAH. Rainbow trout and coho salmon possess an inducible form of cytochrome P₄₄₈. This form was not induced by mirex, kepone, p,p'-DDT, or by p,p'-DDE - all considered to be P₄₅₀ inducers (Vodicnik, et al., 1981; Willis, et al., 1978). The P₄₄₈-type inducers, 3-methylcholanthrene and PCB (Arochlor 1254), strongly induced some components of the MFO system of trout. Thus, fish are capable of metabolizing significant quantities of 4 and 5 ringed PAH under natural conditions, which allows for their elimination and their lack of accumulation.

Benzo(a)pyrene is extensively metabolized in adult and juvenile English sole (Parophrys vetulus). Benzo(a)pyrene-7,8-dihydrodiol, benzo(a)pyrene-9,10-dihydrodiol and 1- and 3-hydroxy benzo(a)pyrene were found in bile, liver, muscle and gonads, indicating that toxic metabolites were formed (Varanasi and Gmur, 1981). A number of studies have further shown that certain reactive metabolites of BaP may bind to cellular macro-molecules in fish (Varanasi, et al., 1981, Varanasi, et al., 1982).

Consequence of PAH Metabolism by Fish

Brown bullheads (Ictalurus nebulosus), treated with repeated skin applications of a PAH-containing organic solvent extract obtained from heavily polluted river sediment, developed progressive skin alterations including epidermal hyperplasia and papillomas (Black, 1983). Brown bullheads from eastern Lake Erie and the upper Niagara River, where sediments and water contain elevated levels of PAH, were observed to possess epidermal neoplasms; including one observation of a highly invasive carcinoma. The anatomic location of the lesions near the mouth suggests that contaminants encountered during feeding may have been a factor (Black, 1982).

Sonstegard (1977) surveyed 50,000 Great Lakes fish between 1973 and 1976. Gonadal tumors in carp, goldfish (Carassius auratus) and hybrids of these species were observed as well as papillomas in white suckers (Catostomus commersoni). There was significant tumor frequency clustering for white suckers in the industrialized western region of Lake Ontario. All white suckers in this region had neoplasms exclusively associated with the lips. The upper lip, which has direct contact with bottom sediments, was most affected.

Toxicology

PAH are of concern toxicologically due to their ability to induce carcinogenic responses in mammals. In addition, mutagenicity and teratogenicity have been reported. A summary of toxic effects in mammals for PAH commonly found in water is shown in Table 10. Further, PAH and specifically anthracene, are acutely toxic to fish at low levels (circa 12µg/L) in the presence of sunlight (Bowling, et al., 1983). A statistically significant, dose-related increase in the incidence of stomach tumors (papillomas and carcinomas) was shown to occur in mice fed with 1-250 µg/L BaP in their diet (Neal and Rigdon, 1967). Tumors are also found in fishes, although the precise dose level producing this effect is unknown.

Table 10
The toxicity¹ to mammals of PAH commonly found in water
 (Christiansen, 1976)

(mg/kg)

<u>Compound</u>	<u>Animal</u>	<u>Carcinogenicity</u>	<u>Neoplastic</u>	<u>Mutagenicity</u>	<u>Teratogenicity</u>	<u>Lethality²</u>	<u>Relative Carcinogenicity³</u>
Anthracene	rat	18000	3300	- ⁴	-	-	?
Benzo(a)anthracene	mouse	2-240	-	-	-	-	+
Benzo(f)fluoranthene	mouse	40-72	-	-	-	-	-
Benzo(j)fluoranthene	mouse	288	-	-	-	-	-
Benzo(k)fluoranthene	mouse	72	2640	-	-	-	0
Benzo(a)pyrene	rat	5-55	0.25-4563	-	-	-	-
	mouse	0.002-7	-	750	240	50-500	-
	monkey	2	-	-	-	-	-
	rabbit	17	-	-	-	-	-
	hamster	21-432	-	-	-	-	-
Benzo(e)pyrene	mouse	516	140-160	-	-	-	-
Benzo(ghi)perylene	-	-	-	-	-	-	0
Chrysene	mouse	200	99	-	-	-	+
Dibenzo(ah)anthracene	rat	0.5	-	-	-	-	+
	mouse	0.76-360	0.006-80	-	-	10	-
	guinea pig	-	30	-	-	-	-
Fluoranthene	rabbit	-	-	-	-	2000-3000	0
Indeno(1,2,3cd)pyrene	mouse	72	-	-	-	-	+
Phenanthrene	mouse	-	71	-	-	700	?
Perylene	-	-	-	-	-	-	0
Pyrene	mouse	-	10000	-	-	-	0
Fluorene	mouse	-	-	-	-	-	+

1. These data are derived from a variety of exposure routes (oral, dermal, subcutaneous, intravenous, intraperitoneal, intramuscular, intracranial, intratracheal) over a broad range of exposure times (days to weeks).
2. Lethality may refer to lethal doses (LD50s) or to lowest lethal doses.
3. Relative activity on mouse epidermis - '0' = inactive; '+' = active; from Wynder and Hoffman (1962).
4. '-' = no data

PAH are mainly noted for the carcinogenicity of neoplasticity in mammals (Table 10). Benzo(a)pyrene was discovered to be carcinogenic many years ago and has been extensively studied using a variety of exposure routes. However, only a few tests have used oral dosages. These tests show positive tumorigenicity at dietary levels ranging from 5 to 10 mg/kg in rats (W. Gibel, 1964, in IARC) and hamsters (W. Dontenwill and U. Mohr, 1962, (Z. Krebsforsch, 65, p. 56 in IARC). BaP has been shown to induce tumors in mice in a dose-response related manner of dietary levels of 40 to 250 mg/kg (Rigdon and Neal found in the World Health Organization Drinking Water document). It is important to note that the concept of threshold levels for carcinogenicity or tumorigenicity has not been established. Single doses of benzo(a)pyrene at levels below the above dietary levels have been shown to induce tumors (W.H. Peirce, Nature, 189, p. 164, 1961).

Current Regulatory Standards

Air Quality

Occupational standards are usually expressed as Threshold Limit Values (TLV) and refer to concentrations of substances to which repeated exposure can occur without adverse effects. A TLV of 0.2 ng/m^3 for coaltar pitch volatiles (benzene soluble fraction), aimed at minimizing exposure to anthracene, BaP, phenanthrene, acridine, chrysene and pyrene, was adopted as the U.S. federal standard under the Occupational Safety and Health Act of 1970; the Ontario Ministry of Labour has adopted a similar standard.

A coke oven emission standard (benzene soluble fraction) with a TLV of 0.15 ng/m^3 over 8 hours was also promulgated by the U.S. Occupational Safety and Health Administration. It has recently been recommended that this be lowered to 0.1 ng/m^3 as a cyclohexane soluble fraction.

The bulk of atmospheric PAH are associated with airborne particulate matter. Current ambient air quality criteria for suspended particulates in Ontario are $60 \text{ } \mu\text{g/m}^3$ as an annual geometric mean, or $120 \text{ } \mu\text{g/m}^3$ averaged over 24 hours. The corresponding U.S. figures established National Primary Ambient Air Quality Standards of 75 and $260 \text{ } \mu\text{g/m}^3$, respectively, while the desirable secondary standards are 60 and $150 \text{ } \mu\text{g/m}^3$ for annual and daily measurements, respectively. Ontario regulations limit particulate emissions at $100 \text{ } \mu\text{g/m}^3$ (measured as a half-hour average concentration at the point of impingement).

Drinking Water

The World Health Organization (WHO) has recommended a maximum of $0.2 \mu\text{g/L}$ of PAH in drinking water expressed as a sum of six indicator PAH - fluoranthene; benzo(b)fluoranthene; benzo(k)fluoranthene; BaP; benzo(ghi)perylene; and indeno(1,2,3cd)pyrene. Recently, the World Health Organization (WHO) has proposed a limit of $0.01 \mu\text{g/L}$ for BaP in drinking water.

The U.S. Environmental Protection Agency has set no specific limit for PAH in drinking water. However, the agency opted to require the best available technology, namely treatment with granular activated carbon, to minimize exposure to potentially harmful chemicals including PAH. Such a procedure was

deemed necessary "as a reasonable insurance policy to protect against what the agency perceives to be a carcinogenic hazard of low levels of organic chemicals in drinking waters" (Costle, 1978). Two thirds of PAH concentration can be eliminated in modern treatment plants through conventional treatment (Borneff, 1974). Mutagenic activity of drinking water, as demonstrated by Salmonella typhimurium strains TA98 and TA100, was eliminated after virgin granular activated carbon treatment (Meier, et al., 1982).

SUMMARY AND RECOMMENDATIONS

The exposure to PAH of organisms in the Great Lakes ecosystem is extensive. The PAH most commonly reported in sediments and water are not the methylated series associated with petroleum hydrocarbons but are mainly the unsubstituted ones arising from combustion processes. PAH accumulation may occur in organisms at trophic levels below fishes but the presence and significance of their metabolites in all levels are only poorly known. By analogy with mammalian systems, however, such compounds, whether parent PAH or metabolites, are deemed to be a concern. As a consequence, anthropogenic inputs are considered to be undesirable.

BaP is only one of the many PAH found in the Great Lakes Basin ecosystem, but the Aquatic Ecosystem Objectives Committee feels that limitations on BaP will also, de facto, limit the others. It is also the PAH for which the most scientifically defensible data base exists.

BaP has been shown to induce tumors in mammals in a dose-response related manner at dietary levels of 40-250 mg/kg. These data were used as the basis of a risk assessment for human exposure via drinking water and resulted in the proposed WHO guideline of 0.01 $\mu\text{g/L}$. Mixtures of PAH, including BaP, have also been found to cause tumors in fishes although the precise levels for them are not so well established for mammals. Sediment and benthic organisms which serve as food sources for many fishes are known to have similar levels of PAH including BaP. Additionally, since fishes are continuously exposed to water levels (as compared to the intermittent exposure of humans via drinking water), it is felt that at least comparable protection would be necessary to protect fishes against direct accumulation.

Therefore, the AEOC recommends a level of 0.01 $\mu\text{g/L}$ of BaP as a maximum concentration in water for the protection of fish and other aquatic organisms from carcinogenic or tumorigenic effects.

Benzo(a)pyrene has been shown to elicit tumorigenic response at mg/kg levels in the diet. The AEOC is recommending a maximum level of 1 mg/kg of BaP in sediment in order to limit the concentrations that would be accumulated in benthic invertebrates. This objective should then protect fish and other organisms from potential tumorigenic and carcinogenic effects caused by the consumption of PAH-contaminated benthos.

Objective

For the protection of aquatic life, the levels of benzo(a)pyrene in the sediments or in organisms serving as a food source for fish should not exceed 1.0 $\mu\text{g/g}$; levels of BaP in water should be less than 0.01 $\mu\text{g/L}$.

NOTE: Other 3-5 ring PAH have been observed in the Great Lakes ecosystem and some of these are carcinogenic and are strong inducers of MFO enzymes. They may be of equal or greater concern.

Research and Monitoring

1. Evidence presented in the scientific rationale of this objective demonstrates that PAH do not bioaccumulate in fish and herring gulls of the Great Lakes ecosystem. However, PAH are bioaccumulated by species at lower trophic levels including freshwater clams, snails, midges and Pontoporeia hoyi. Monitoring for PAH using biological indicator species should therefore concentrate on lower trophic levels. Direct monitoring for PAH in water and sediment should be carried out, particularly where sediments have previously been observed to contain high levels. Such monitoring should not be restricted to those PAH forms in present or proposed regulations, but should also include others which have been found in the Great Lakes ecosystem.
2. Benthic organisms have been shown to extensively bioaccumulate PAH from sediments. The effects of these accumulations on benthos should be investigated in terms of ecosystem health.
3. The importance of the sediment as a source of contaminants, particularly as they affect fish, should be investigated. Tumor prevalence and MFO activity in fish should be monitored in concert with monitoring activities for concentrations in sediments and biota.
4. An analytical intercomparison exercise for all agencies involved in monitoring environmental PAH is needed for an accurate comparison of results.
5. Since it is known that higher organisms such as fish and mammals effectively metabolize PAH and since some such metabolites are known to be carcinogens, metabolites as well as parent compounds should be studied. These studies should address the occurrence, toxicity and biotransformations of these compounds and the results considered for future monitoring studies.

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3. Report on Task Force on Indicators of Ecosystem

Development

The Aquatic Ecosystem Objectives Committee (AEOC) has, as one of its terms of reference, to "develop aquatic ecosystem objectives."

Since its inception in 1979, the Committee has wrestled with the problem of how to describe a true ecosystem objective for the Great Lakes - especially for the oligotrophic parts of the system. In 1982, the AEOC requested approval from the Science Advisory Board (SAB) for the formation of a task force to examine, in particular, the feasibility of using lake trout as a measure of ecosystem health.

The Task Force on Indicators of Ecosystem Quality (TFIEQ) was officially approved by the SAB in August, 1982 and an organizational and orientational meeting was held in Windsor during that month. Subsequent meetings were held at Bancroft, Ontario, (November 1982) Madison, Wisconsin, (February 1983) and Shackleton Point, N.Y., (May 1983) for the purpose of concept development of the lake trout as an indicator of ecosystem quality, the consideration of other candidate indicator organisms, or for manuscript preparation; respectively. A meeting of part of the task force to establish an outline for the manuscript was held at Winnipeg, Manitoba, in January 1983 and a final review of a draft manuscript took place at Milwaukee, Wisconsin in late August, 1983.

Following the Bancroft meeting in November 1982, the Great Lakes Fishery Commission (GLFC) offered to support the Task Force jointly with the International Joint Commission (IJC). The TFIEQ and the AEOC are grateful for this offer of support.

Terms of Reference

The terms of reference of the proposed TFIEQ were to:

- appraise, evaluate and critique the feasibility of using an indicator (integrator) organism as a suitable surrogate for depicting a "healthy" Great Lakes;
- if feasible, produce an objective with supporting rationale applicable for inclusion into the 1978 Great Lakes Water Quality Agreement and in accordance with the Terms of Reference for the AEOC;
- identify and recommend appropriate system variables for future monitoring based on these concepts; and
- explore and develop, if appropriate, other ecosystem approaches with potential application to the Great Lakes Basin.

The TFIEQ interpreted and the AEOC agreed, that its charge is described under three general areas of concern: (1) to address the policy adopted by

the IJC for an "ecosystem approach"; (2) to develop the concept of an indicator-integrator organism using the lake trout as an example; and (3) to further the concept of an "ecosystem objective" through use of the lake trout and other complementary indicator organisms.

The Task Force has exceeded the above Terms of Reference by providing in addition, a methodology by which this conceptual approach may be transferred into management decision-making and ultimately, into action along the lines of rehabilitation or measures to mitigate stresses.

Related Activities

A number of activities of other groups are under way which are relevant to the work of the TFIEQ. Those with which the Task Force is particularly involved are:

- (1) Salmonid Watch - the Salmonid Watch has been active for more than a year now and is intended to itemize areas of global environmental concern utilizing various salmonid species as indicators. The chairman and several members of the TFIEQ are associated with this initiative. The Salmonid Watch is sponsored by the International Union for the Conservation of Nature.
- (2) The Associate Committee on Scientific Criteria for Environmental Quality (National Research Council Canada) has commissioned a report on the strengths of approaches being used to assess impacts within aquatic ecosystems. The chairman and one member of TFIEQ are participating in this initiative.
- (3) Conference on Lake Trout Research - This conference, sponsored by the GLFC, dealt with strategies for rehabilitation in the Great Lakes and was designed specifically to identify research needs for the lake trout, establish optimum experimental design and to recommend resource allocation. The chairman of the TFIEQ has participated in all pre-conference activities, including the Habitat Group at the conference held at Goderich, August 1983.
- (4) Health of Aquatic Communities Task Force (HACTF) (SAB) - This group has similar goals to the TFIEQ in that it seeks information on ways to measure stresses on aquatic ecosystems. The chairpersons of both the TFIEQ and the HACTF participate as members in AEOC meetings.

Report Status

The Task Force has produced the first draft of a document entitled "A Proposed Approach for the Application of Biological Indicators for the Determination of Ecosystem Quality in the Great Lakes Basin". The general consensus of the TFIEQ and AEOC is that the manuscript should initially be reviewed internally, although scientists external to TFIEQ and AEOC with appropriate expertise have been encouraged to provide contributions. At least three have complied and made significant contributions to date.

The introduction to the documents establishes the terms of reference of the Task Force relative to the responsibilities of the IJC and the GLFC, as documented in the 1978 Water Quality Agreement and the ratification of the Convention on Great Lakes Fisheries of 1955, which created the GLFC.

A discussion of ecosystem attributes outlines new approaches that may be taken to assess the status of the Great Lakes ecosystem and will complement existing methods. One such approach is through the use of indicator-integrator organisms. A search for an aposite organism of general utility was finalized by the establishment of a set of criteria that would describe the "near-perfect" organism for this purpose. Of the many species considered, the lake trout came closest to satisfying all of the criteria. The Task Force thereby proceeded to develop the concept of indicator-integrator organisms utilizing the lake trout as an exemplary organism for oligotrophic systems. The amphipod Pontoporeia hoyi is proposed as a suitable organism to complement the lake trout in oligotrophic systems, while the walleye is deemed a most appropriate organism for mesotrophic systems; the Forster's tern is recommended for use as an indicator for wetlands surrounding the Great Lakes.

An ecosystem objective for oligotrophic systems based only on the lake trout is described as the attainment and maintenance of an environment of sufficient scope and quality to ensure the perpetuation of a moderately stable cold-water community of organisms. Within this stable community, naturally reproducing, genetically diverse stocks of lake trout will be the terminal predators and the primary controlling compartment. Implicit within the objective is the understanding that optimal harvests of lake trout and other cold-water community components may be taken by various user groups without disrupting the steady-state unduly, and that the harvest intended for human consumption shall be safe and palatable.

The remainder of the Task Force document provides accounts of historic conditions of environment and biota providing a metric by which to judge current conditions using indicator species. The principal impacts on lake trout are described under four general headings including: exploitation, sea lamprey, contaminants and other culturally induced effects such as eutrophication, acid loading, habitat alterations and introductions of exotic species.

A practical example to the use of the indicator species approach is provided by a dichotomous key of stress symptoms which will allow the ecosystem manager to identify the likely source of a stress using symptoms elicited by lake trout following one or more cultural interventions. While this key as currently constituted, does not represent exhaustive treatment of all stress possibilities, the accumulation of appropriate data over time will ensure more complete coverage.

The dichotomous key at present, however, will be useful in assisting the ecosystem manager to consider all likely sources of ecosystem impacts as determined through careful consideration of the status of lake trout stocks. A menu-driven computerized version of the dichotomous key provides both a sequential and a systematized approach to the problem of identifying the general level of ecosystem "health".

Future initiatives of the Task Force should address rates of response to degradation or rehabilitation; the use of other indicators for the assessment of different environments; a closer examination of other biological indicator approaches; the indicator approach as it relates to rehabilitation success.

It is suggested that the report should be published jointly by the GLFC and the IJC. This would acknowledge, in part, the invaluable assistance which the GLFC has provided to the TFIEQ. In this connection, it is recommended that the SAB recommend that the IJC formally accept the GLFC's offer of joint sponsorship of the TFIEQ.

4. Future Directions

TOXAPHENE AND LINDANE

An objective currently exists for lindane but reports of its occurrence in the Great Lakes system need re-examination. Recent information indicating toxaphene presence in upper lakes fishes and interference in some PCB determinations raises concerns about the levels and possible impact of this pesticide. A review for each of these substances is in preparation.

AMMONIA

The existing objective for ammonia does not take into account the impact of alkalinity on toxic effects to aquatic biota. A re-examination of the data base is in process.

TERMS OF REFERENCE FOR THE
AQUATIC ECOSYSTEM OBJECTIVES COMMITTEE OF THE
SCIENCE ADVISORY BOARD

The Aquatic Ecosystem Objectives Committee (AEOC) of the Science Advisory Board will:

1. Develop specific ecosystem objectives. Where feasible, these should be in the form of use effect curves, for various uses, and always including the most sensitive use.
2. Regularly review objectives and recommend amendment or introduction, based upon all available criteria.
3. Establish task forces to develop position papers on which to base the development of new or altered objectives.
4. Set general goals for when the objectives will be reviewed and define some minimum scientific information at which an objective can be derived.
5. Develop an approach for the selection and ordering of parameters to be addressed.
6. Identify gaps in the scientific information needed to develop objectives and recommend the means to fill the gaps.

Appendix

TERMS OF REFERENCE

COMMITTEE MEMBERSHIP

ACKNOWLEDGEMENTS

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2. Regularly review objectives and recommend amendment or introduction, based upon all available criteria.
3. Establish task forces to develop position papers on which to base the development of new or altered objectives.
4. Set general guidelines under which the objectives will be developed and define some minimum levels of scientific information at which an objective can be defined.
5. Develop an approach for the selection and ordering of parameters to be addressed.
6. Identify gaps in the knowledge needed to develop objectives and recommend the research required to fill the gaps.

MEMBERSHIP

The AEOC will consist of eight members: two aquatic toxicologists, three water quality specialists (one each from the provincial, state, and one of the federal governments), a limnologist, an aquatic chemist, and a human health aspects expert.

SUBMISSION OF PROPOSED OBJECTIVES

"Since the Science Advisory Board has the responsibility for advising on policy implications of proposed objectives on an ad hoc basis, the Commission plans to advise the Science Advisory Board to take the initiative in the study of new or revised water quality objectives, in consultation with the Water Quality Board as required, and to forward reports simultaneously to the Commission and the Water Quality Board. Thus, the study of objectives will not be dependent on actions of the Water Quality Board, but there will be an opportunity for the Board to advise the Commission on the practicability of the objectives under consideration or on the need for additional study from the Water Quality Board perspective." (Excerpt from a letter dated May 13, 1980, from the International Joint Commission to the Secretary of the Water Quality Board).

REVISED AND APPROVED BY THE
SCIENCE ADVISORY BOARD
SEPTEMBER 3, 1980

MEMBERSHIP
AQUATIC ECOSYSTEM OBJECTIVES COMMITTEE

Mr. G.P. Brezner
Manager of Technical Services
ORSANCO
414 Walnut Street
Cincinnati, Ohio 45202
(513) 421-1151

Mr. G. Craig
Limnology and Toxicology Section
Ontario Ministry of the Environment
P.O. Box 213
Rexdale, Ontario M9W 5L1
(416) 248-3011

Mr. J. Eaton
Environmental Research Lab - Duluth
U.S. Environmental Protection Agency
6201 Congdon Boulevard
Duluth, Minnesota 55804
(218) 727-6692 (FTS) 783-9557

Dr. D.J. Hallett
Scientific Advisor
Regional Director General's Office
Department of Environment, Ontario Region
55 St. Clair Avenue East, 7th Floor
Toronto, Ontario M4T 1M2
(416) 966-6406

Dr. P.V. Hodson
Great Lakes Fisheries Research Branch
Department of Fisheries and Oceans
Canada Centre for Inland Waters
P.O. Box 5050
Burlington, Ontario L7R 4A6
(416) 637-4559

Dr. E.V.D.K. Perrin
Dept. of Laboratory Medicine
Children's Hospital of Michigan
Wayne State University
Detroit, Michigan 48201
(313) 494-5502
Mailing Address
23618 Dundee
Huntington Woods, Michigan 48070

Dr. A. Robertson
Director, National Marine Pollution
Program Office
NOAA/NMPP0, Room 610, N/MPP
Rockwell Building
11400 Rockville Pike
Rockville, Maryland 20852
(301) 443-8823 (FTS) 443-8823

Mr. R.A. Ryder
Fish and Wildlife Research Branch
Ontario Ministry of Natural Resources
P.O. Box 2089
Thunder Bay, Ontario P7B 5E7
(807) 683-6232/31

Dr. W.M.J. Strachan (Chairman)
National Water Research Institute
Department of Environment
Canada Centre for Inland Waters
P.O. Box 5050
Burlington, Ontario L7R 4A6
(416) 637-4222

SAB Liaison Members

Dr. M. Evans (from June 1983)
Great Lakes Research Division
Institute of Science & Tech. Bldg.
University of Michigan
2200 Bonisteel Boulevard
Ann Arbor, Michigan 48109
(313) 763-6540

Secretariat Responsibilities

Dr. A.E.P. Watson
Research Scientist
International Joint Commission
Great Lakes Regional Office
100 Ouellette Avenue, 8th Floor
Windsor, Ontario N9A 6T3
(519) 256-7821 - Windsor
(313) 226-2170 - Detroit

Dr. D.C. McNaught (until April 1983)
Minnesota Sea Grant Program
University of Minnesota
1988 Fitch Avenue
St. Paul, Minnesota 55108
(612) 373-1708

TASK FORCE ON INDICATORS OF ECOSYSTEM QUALITY
OF THE COMMITTEE ON AQUATIC ECOSYSTEM OBJECTIVES

Mr. Richard A. Ryder (Chairman)
Ministry of Natural Resources
Fish and Wildlife Research Branch
P.O. Box 2089
Thunder Bay, Ontario P7B 5E7
(807) 683-6232/31

Dr. Joseph H. Leach
Research Scientist
L. Erie Fisheries Branch Station
Fish & Wildlife Research Branch
Ministry of Natural Resources
R.R. #2
Wheatley, Ontario NOP 2P0
(519) 825-4171

Dr. Henry A. Regier
Institute for Environmental Studies
University of Toronto
Toronto, Ontario M5S 1A4
(416) 978-7338

Dr. Steve Kerr
Bedford Institute of Oceanography
Marine Ecology Laboratory
Dartmouth, Nova Scotia B2Y 4A2
(902) 426-3792

Dr. John Magnuson
Laboratory of Limnology
University of Wisconsin
Madison, Wisconsin 53706
(608) 262-3304

Dr. Ray Oglesby
N.Y. State College of
Agriculture and Life Sciences
Dept. of Natural Resources
Cornell University
Ithaca, New York 14853
(607) 256-2298

Dr. Andrew Robertson (member AEOC)
Director
Nat'l. Marine Pollution Prog. Office
NOAA/NMPPPO, NMPP Room 610
Rockwell Building
11400 Rockville Pike
Rockville, Maryland 20852
(301) 443-8823
FTS 443-8823

Resource Persons

Dr. Stan Smith
924 Northwood Street
Ann Arbor, Michigan 48103
(313) 761-1912

Dr. Mike Henderson
Fisheries Research Section
Ontario Ministry of Natural
Resources
P.O. Box 50
Maple, Ontario LOJ 1E0
(416) 832-2761, ext. 251

Dr. H.J. Harris
Dept. of Environmental Sciences
Room 105 - Sea Grant College
University of Wisconsin-Green Bay
Green Bay, Wisconsin 54302
(414) 465-2796

Dr. R. Horrall
Marine Studies Center
Meteorological and Space Studies
Center
1225 West Dayton Street, Room 1205
University of Wisconsin-Madison
Madison, Wisconsin 53706
(608) 263-3261

Secretariat Responsibilities

Dr. Clayton J. Edwards
Biologist
International Joint Commission
Great Lakes Regional Office
100 Ouellette Avenue, 8th Floor
Windsor, Ontario N9A 6T3
(519) 256-7821 - Windsor
(313) 226-2170 - Detroit

ACKNOWLEDGEMENTS

The members of the AEOC gratefully acknowledge the efforts of those individuals and their agencies who prepared or reviewed material associated with the following objectives:

POLYNUCLEAR AROMATIC HYDROCARBONS

Dr. Richard Addison
Bedford Institute of Oceanography
Marine Ecology Laboratory
Department of Fisheries & Oceans Canada
Dartmouth, Nova Scotia

Dr. John J. Black
Roswell Park Memorial Institute
New York State Department of Health
666 Elm Street
Buffalo, New York

Dr. D.A. Eastmond
Brigham Young University
Department of Zoology
669 WIDB
Provo, Utah

Dr. Ronald A. Hites
School of Public and Environmental
Affairs, Indiana University
400 E. Seventh Street
Bloomington, Indiana

Dr. E.J. LaVoie
Naylor Dana Institute for
Disease Prevention
American Health Foundation
Dana Road
Valhalla, New York

Dr. Usha Varanasi
Northwest and Alaska Fisheries Center
Environmental Conservation Division
NMFS - NOAA
2725 Montlake Boulevard East
Seattle, Washington

Dr. Paul Baumann
Museum of Zoology
1812 N. High Street
Columbus, Ohio

Dr. Brian J. Eadie
Great Lakes Environmental Research
Laboratory - NOAA
2300 Washtenaw Avenue
Ann Arbor, Michigan

Dr. P.P. Fu
National Center for Toxicological
Research
Food and Drug Administration
Jefferson, Arkansas

Dr. Peter F. Landrum
Great Lakes Environmental Research
Lab, NOAA
2300 Washtenaw Avenue
Ann Arbor, Michigan

Dr. G.R. Sirota
Department of Fisheries & Oceans
Canada
Fisheries Research Branch
P.O. Box 550
Halifax, Nova Scotia

Dr. Demetrios Zadelis
Environmental Chemistry Section
School of Public Health
109 Observatory #2530
Ann Arbor, Michigan

MICROBIOLOGICAL INDICATORS

L.T. Vlassoff
Ontario Ministry of the Environment
P.O. Box 213
Rexdale, Ontario

B.J. Dutka
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario

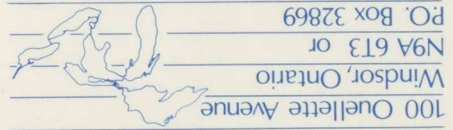
G.W. Fuhs
Environmental Health Institute
N.Y. State Department of Health
Albany, New York

A.P. Dufour
U.S. Environmental Protection Agency
Health Effects Research Laboratory
Cincinnati, Ohio

A.H. Vajdic
Ontario Ministry of the Environment
P.O. Box 213
Rexdale, Ontario

INTERNATIONAL JOINT COMMISSION

GREAT LAKES REGIONAL OFFICE



100 Ouellette Avenue

Windsor, Ontario

N9A 6T3 or

P.O. Box 32869

Detroit, Michigan 48232-2869