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### Report of the Aquatic Ecosystem Objectives Committee 1981

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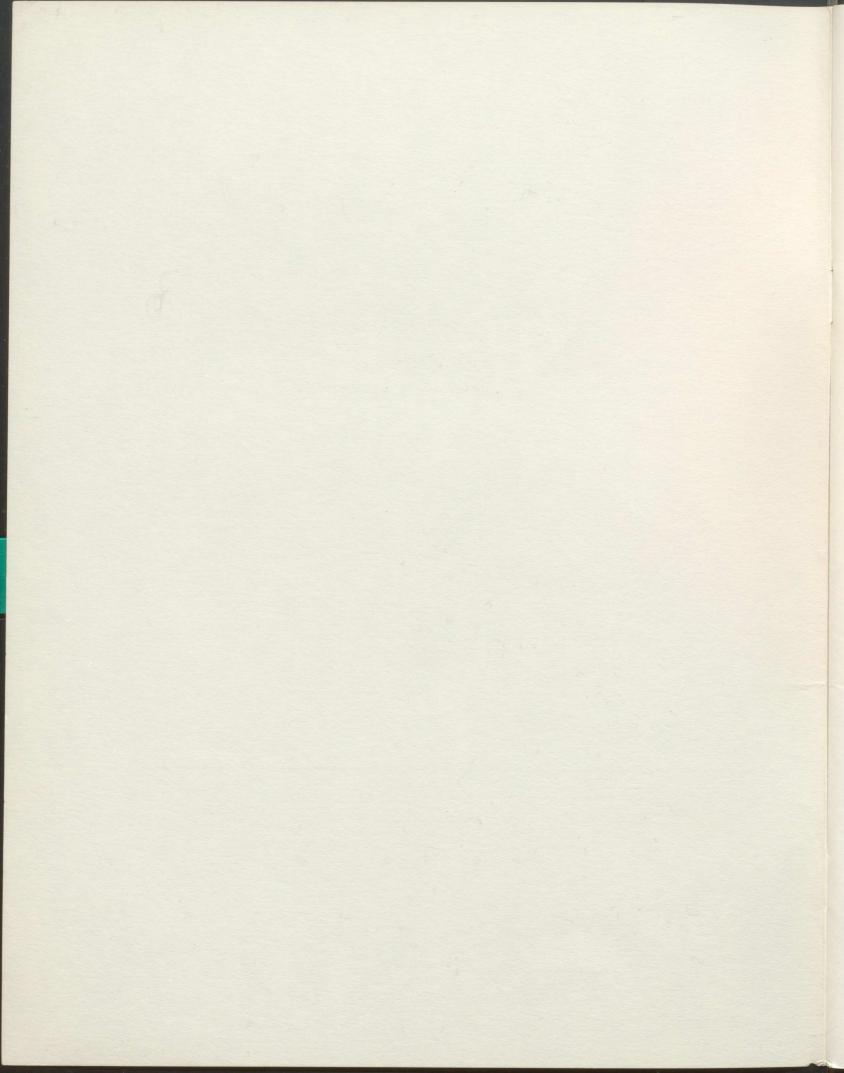
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Report to the

Great Lakes Science Advisory Board

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Report of the Aquatic Ecosystem Objectives Committee (1981)



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Great Lakes Science Advisory Board

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November 1981

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## Preface

This report to the Science Advisory Board was prepared by the Aquatic Ecosytem 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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# Summary of Recommendations

### A) REVISED OBJECTIVE

It is recommended that the following changes be adopted to replace the existing objective in Annex 1, paragraph 2 of the 1978 Great Lakes Water Quality Agreement:

### Selenium

Concentrations of total selenium in unfiltered water samples should not exceed 1  $\mu$ g/L to protect aquatic life. Concentrations in sediments should not exceed 5  $\mu$ g/g dry weight to protect aquatic life. Concentrations in aquatic biota should not exceed 3  $\mu$ g/g wet weight to protect predatory fish and mammals.

### B) RE-EXAMINED OBJECTIVE

Through updating of the relevant scientific literature, the Committee reaffirms the following objective:

### Mirex

For the protection of aquatic organisms and fish-consuming birds and animals, mirex and its degradation products should be substantially absent from water and aquatic organisms. Substantially absent here means less than detection levels as determined by the best scientific methodology available.

Note: The best detection levels for mirex (1977), as determined by a survey of laboratories in the Great Lakes region, are 0.005  $\mu$ g/L for water and 0.005  $\mu$ g/g for biological tissues.

### C) LIMITED USE ZONES

The Committee recommends that development of a comprehensive Limited Use Zone mechanism be undertaken in fulfilment of the requirements of Annex II of the Great Lakes Water Quality Agreement. In support of this position, the Committee further recommends the identification of all areas of outstanding natural resource and/or biological sensitivity as well as the location and nature of all industrial and municipal discharges to the Great Lakes.

### Sentematry of Recommendations

#### SALASS OF THE ALE OF T

It is recommended that the following changes be adopted to replace the existing objective, in Annex 1, paragraph.? of the 1978 Great Lakes Water Dowifity Agreements

#### Selentum

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### I. Introduction

During the period of the 1972 Great Lakes Water Quality Agreement, two Committees (Water Ouality Objectives Subcommittee -- WOOS and Scientific Basis for Water Quality Criteria -- SBWOC) 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 the adoption of two new objectives, two revised objectives and four previously proposed objectives.

The framework<sup>1</sup> for developing objectives was developed by WQOS/SBWQC and is reprinted here for the sake of clarity.

- 1. In developing specific water quality objectives the philosophy of protecting the most sensitive use is employed;
- 2. Adoption of objectives does not preclude the need for studying the aquatic environment and effects of conditions on related organisms and uses. Since infinite combinations of water quality characteristics may occur, the objectives do not take into account antagonistic, synergistic and additive effects;
- 3. Since new data may lead to modified recommendations the objectives are subject to continual review.
- 4. No adequate scientific data base exists for establishing scientifically justifiable numerical objectives for certain unspecified non-persistent toxic substances and complex wastes. Therefore, criteria for developing an objective for local situations have been recommended.
- 5. Biological effect levels are recognized as well as the concentrations of a substance or level of physical effects.
  - 6. The objectives serve as a minimum target wherever water quality objectives currently are not being met.
  - 7. 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.
- 8. 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.
  - 9. 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.

AEOC endorses this framework with the additional view that objectives do not consider socio-economic factors because the Committee agrees with previous recommendations (Water Quality Board 1980)<sup>2</sup> that socio-economic impact assessment is the responsibility of the jurisdictions. Objectives should not be construed as regulations or standards. Objectives should be considered as a goal 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 scientific colleagues with relevant expertise. The Committee, however, welcomes any comments or additional scientific evidence which are relevant to any of the objectives and which are consistent with the above philosophy.

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

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

### 2. Objectives

SELENIUM

### EXISTING OBJECTIVE

The concentration of total selenium in an unfiltered water sample should not exceed 10  $\mu$ g/L to protect raw water for public water supplies.

### RECOMMENDED OBJECTIVES

Concentrations of total selenium in an unfiltered water sample should not exceed 1  $\mu$ g/L to protect aquatic life. Concentrations in sediments should not exceed 5  $\mu$ g/g dry weight to protect aquatic life. Concentrations in aquatic biota should not exceed 3  $\mu$ g/g wet weight to protect predatory fish and mammals.

### SUMMARY

### WATER

Canadian and U.S. Health agencies consider human health to be protected when waterborne selenium concentrations are 10  $\mu$ g/L or less. This concentration is also intended to protect aquatic biota from the toxic effects of selenium. However, the field studies reviewed in this document indicate that waterborne selenium concentrations of 5-10  $\mu$ g/L were associated with sediment and food chain contamination that caused acute lethality to predatory fish. Waterborne selenium has been shown to contribute to food chain contamination through direct uptake by both plankton and sediments (and hence benthos) but the threshold waterborne selenium concentration contributing to lethal food chain contamination has not been determined. Therefore, in order to be protective, it is the considered opinion of the AEOC that waterborne selenium concentrations should not exceed 1  $\mu$ g/L until further research can identify such a threshold.

### SEDIMENTS

Great Lakes sediment concentrations of selenium are normally less than  $1 \mu g/g$  but, in a reservoir, concentrations greater than  $20 \mu g/g$  in surficial sediments were associated with apparent food chain accumulation of selenium and mortality of predatory fish. No effects were observed in control areas with a sediment concentration of 1-5  $\mu g/g$ . The threshold sediment concentration associated with fish mortality has not been established. Therefore, the AEOC recommends that selenium in sediments should not exceed 5  $\mu g/g$  dry weight for the protection of aquatic life.

### AQUATIC BIOTA

Selenium appears to be an important nutrient for fish, with deficiency symptoms appearing at dietary concentrations less than 0.1  $\mu$ g/g and a suggestion of deficiencies (less than maximum activity of a selenium requiring

enzyme) at concentrations up to  $0.35 \ \mu g/g$ . Dietary toxicity to mammals and fish however, starts at dietary concentrations of 4-5  $\mu g/g$ , so there is very little difference between an adequate and a toxic diet. Mortality of fish in the field was associated with consumption of benthos containing 20-70  $\mu g$  Se/g dry weight, or 4-14  $\mu g$  Se/g wet weight based on an estimated 80% moisture content. Therefore, to protect predatory mammals and fish from the toxic effects of dietary selenium, aquatic biota should not contain more than 3  $\mu g$  Se/g wet weight.

### INTRODUCTION

The current water quality objective for selenium is: <u>Concentrations of</u> total selenium in an unfiltered water sample should not exceed 10 micrograms per litre to protect raw water for public water supplies.

Note: The effect of high dietary selenium concentrations on fish-eating birds and wildlife is unknown. Based on the response of laboratory mammals, concentrations of selenium approaching  $3 \mu g/g$ , wet weight, in whole fish should be regarded with concern.

The above objective was based on a literature review (IJC 1977) showing:

- 1) the sources of selenium;
- 2) typical levels in the Great Lakes ecosystem;
- 3) the nutritive requirements and toxic levels for mammals;
- 4) toxic levels for plants;
- 5) acute toxicity to aquatic biota; and
- 6) evidence of biotransformation and transfer up aquatic food chains.

The objective was restricted to water and was based on human health, primarily because data on the significance of residues in other compartments of the aquatic ecosystem and on selenium chronic toxicity to aquatic biota were not available. Since that rationale was written (1975-1976), a variety of studies have been published that provide a better picture of selenium as a nutrient and as a toxicant. This rationale will cover laboratory and field studies, relate toxic concentrations of selenium to observed levels in the environment, but will not repeat the information covered in 1976.

### ACUTE TOXICITY

The acute lethality of selenium to invertebrates has been shown for daphnids and <u>Hyalella azteca</u>. The 96 h LC50's for <u>Daphnia magna</u> in hard water (329 mg/L as  $CaCO_3$ ) and <u>Daphnia pulex</u> in soft water (standard test medium) were 0.43 and 0.50 mg/L respectively (Halter <u>et. al.</u>, 1980; Schultz <u>et al.</u>, 1980). Lethality to <u>D</u>. <u>pulex</u> was a function of age with 96 h LC50's being 0.126 mg/L for fed juveniles and 0.50 mg/L for fed adults. Feeding reduced toxicity since the 96 h LC50 for unfed D. pulex was 0.07 mg/L (Schultz et al., 1980). The 96 h LC50 for an amphipod <u>Hyalella azteca</u> was 0.34 mg/L while the 336 h (14d) LC50 was 0.07 mg/L (Halter et al., 1980).

Recent studies of the acute lethality of waterborne selenium to fish confirms previous reports of LC50's between 5 and 50 mg/L. Rainbow trout (Salmo gairdneri) appear relatively sensitive with 96 h LC50's between 8 and J3 mg/L and 9 and 16 day LC50's of 6.5 and 5.0 mg/L respectively (Hodson <u>et</u> al., 1980; Goettl <u>et al.</u>, 1976). Fish tested in soft water (30-36 mg/L as CaCO<sub>3</sub>) (Goettl <u>et al.</u>, 1976) were less sensitive to a 96 h exposure than were fish in hard water (135 mg/L as CaCO<sub>3</sub>) (Hodson <u>et al.</u>, 1980), perhaps due to other water quality factors (e.g., pH) or simply to experimental error. Carp (<u>Cyprinus carpio</u>) were much less sensitive (96 h LC50 = 35 mg/L) when tested in static bioassays (Sato <u>et al.</u>, 1980). The most sensitive species tested, fathead minnow (<u>Pimephales promelas</u>), had 96 and 336 h LC50's of 1.0 and 0.6 mg/L respectively in a very hard water (329 mg/L as CaCO<sub>3</sub>) (Halter <u>et al.</u>, 1980).

Injected sodium selenite was lethal to channel catfish (<u>Ictalurus</u> <u>punctatus</u>) within 48 hours at a dose of 3 mg Se/kg (Ellis <u>et al.</u>, 1937). At lower concentrations, toxicity was not evident for 4-10 days after which there was mortality due to liver, spleen and kidney damage associated with an apparent loss of osmoregulation (edema) and abnormal erythropoiesis. These effects were caused by a single dose of 0.9 mg Se/kg or daily injections of 0.04 mg/kg (total Se dose = 0.2 mg/kg).

Exposure to selenium has also been shown to reduce the acute toxicity of inorganic mercury to fish but, paradoxically, mercury accumulation increases in survivors (Heisinger et al., 1979).

#### CHRONIC TOXICITY

Prolonged exposures of fathead minnow eggs and fry to selenium concentrations of 1.0 mg/L or higher reduced times to hatch, but had no effect on percent hatched (Halter et al., 1980). Survival times were reduced relative to controls at all selenium exposure levels, but even controls exhibited some mortality. There is a possibility of other lethal factors interacting with selenium in this study.

Chronic exposures of rainbow trout to 130  $\mu$ g/L of waterborne selenium caused elevated mortality rates and incidence of deformity relative to controls and the next lowest concentration tested (60  $\mu$ g/L) (Goettl <u>et al.</u>, 1976). Exposure of trout to lower concentrations resulted in subtle hematological responses at 28  $\mu$ g/L or higher (Hodson <u>et al.</u>, 1980). These results suggest that waterborne concentrations up to 70 times background levels (<0.4  $\mu$ g/L) should not have direct adverse effects on fish.

Dietary selenium may be more toxic than waterborne selenium. Prolonged feeding of rainbow trout with diets containing 13 mg/kg of selenium caused liver pathology, elevated mortality rates, decreased feed: weight-gain efficiency, and decreased growth rates (Hilton <u>et al.</u>, 1980); there were no obvious toxic effects at the next lower dietary concentration (3.7 mg/kg).

Research by Goettl and Davies (1978) has shown effects on trout growth and mortality of dietary selenium with 50% mortality occurring at 10 mg/kg (dry weight) over a one year trial. Symptoms of selenium poisoning of mammals occur at 4-5 mg/kg (dry weight) (Oldfield <u>et al.</u>, 1974).

### DIETARY REQUIREMENTS

Fish fed diets of 0.07 mg/kg showed signs of incipient selenium deficiency that included reduced growth rate and low levels of serum glutathione peroxidase activity relative to fish on diets containing 0.35 mg/kg or higher. However, acute symptoms of deficiency, such as muscle pathology, were not evident (Hilton <u>et al.</u>, 1980). Similar symptoms, plus elevated mortality rates and muscle pathology, were observed in Atlantic salmon (<u>Salmo salar</u>) fed diets deficient in both selenium and Vitamin E (Poston <u>et al.</u>, 1976). Vitamin E deficiencies were somewhat alleviated by selenium supplementation but a diet with adequate Vitamin E and only 0.04  $\mu$ g Se/g dry-weight was deficient.

### FIELD STUDIES

The high toxicity of dietary selenium has been supported by field studies of fish mortality in a reservoir (Belews Lake, North Carolina), receiving effluent containing high concentrations of selenium from a fly-ash settling pond (Cumbie and Van Horn, 1978). Fish populations were severely reduced with evidence of decreased standing stock and a total lack of reproduction in the years following the start of operation of a coal-fired power plant. Studies of conditions in the lake showed that pesticide concentrations, water levels, temperatures, population structure, impingement and entrainment, diseases and parasites could not account for the loss of fish, especially since the loss was not evident in upstream waters or remote parts of the same reservoir. Analysis of the elemental composition of fish tissues in affected and unaffected areas showed that, of 16 elements measured, only selenium was correlated to the condition of the populations. Selenium concentrations of upstream fish were in the range of 0.5-7 mg/kg (wet weight) whereas those from the affected main lake were consistently higher, with concentrations of 10-50 mg/kg. Selenium in ovaries of ripe females from the affected area was 1-3 fold higher than in muscle tissue and this was most pronounced in various sunfish (Lepomis spp), among the most affected species. Selenium concentrations in plankton were 4-20 mg/kg (dry weight) upstream in contrast to 40-100 mg/kg in the affected area (Cumbie, 1978). Waterborne concentrations averaged 150-200  $\mu$ g/L in the effluent and 5-10  $\mu$ g/L in the lake although one peak of 20 µg/L was recorded. The majority of this selenium in both effluents and lake water passed through a 0.45  $\mu$  filter and hence was available for sorption by biota and sediments (see discussion under selenium distribution in Aquatic Ecosystems). In the sediments, selenium concentrations were 6-8 mg/kg (dry weight) in contrast to 3.4 mg/kg at the control site. However, these values resulted from the mixing during sampling of a thin surface layer of contaminated sediment with underlying uncontaminated sediments. The actual concentrations in surficial sediments at contaminated sites were greater than 20 mg/kg (dry weight) compared to 1-5 mg/kg at control sites (Cumbie, personal communication).

<sup>1</sup>Dr. P. Cumbie, Duke Power Company, Charlotte, North Carolina.

Further studies of stocked bluegill (Lepomis macrochirus) showed that fish released in clean areas survived indefinitely, either in cages or in the lake. Fish held in cages in the contaminated area, however, gradually died off over a 3-4 month period, while fish released directly to the area died almost immediately. The stomach contents of caged fish showed few benthic organisms whereas those of dead fish outside the cage contained a high proportion of benthic organisms, which corresponds to this species feeding habits (Scott and Crossman, 1973). Dying fish exhibited symptoms typical of acute lethality (Ellis et al., 1937), i.e. the peritoneal cavity was distended with ascites and the fish had "popeye," (Cumbie, personal communication). Since the waterborne selenium concentration by itself was insufficient to cause mortality, the death of fish with symptoms characteristic of acute selenium toxicity indicates that dietary selenium was very high. It is highly probable that selenium was taken up from the sediments during foraging, either from ingestion of sediments directly or from ingestion of contaminated benthos. Benthos from the contaminated area contained 20-70 µg Se/g dry-weight while those from the control area contained 4-8 µg Se/g dry-weight (Cumbie, personal communication).

A study of ash-pit effluents at a Wisconsin power plant showed elevated selenium concentrations in the water of a creek receiving this effluent (Magnuson et al., 1980). However, other metals (e.g., Cr, Fe, Zn) were also elevated so that observed effluent effects on crayfish (change in respiration rate) could not be attributed solely to selenium. Crayfish caged in the ash-pit drain accumulated about 30 mg/kg dry weight of selenium in the hepatopancreas and about 0.4 mg/kg in the muscle.

#### METABOLISM

Waterborne selenium is taken up rapidly by aquatic biota with <u>Daphnia</u> <u>pulex</u> reaching equilibrium in 24 hours (Schultz <u>et al.</u>, 1980) and rainbow trout in about 30 days (Gissel-Nielsen and Gissel-Nielsen, 1978). Uptake rates by trout are a function of the exposure concentration since the relative uptake at low concentrations is greater than at high concentrations (i.e. concentration factors (tissue/water) are greater at low concentrations) (Hodson <u>et al.</u>, 1980). Since this is true for eggs, sac fry and fry, and is independent of dietary loading, it is suggested that gill membrane permeability limits selenium uptake (Hodson and Hilton, 1981).

Dietary selenium is also rapidly taken up with no plateau evident within four days. The degree of uptake was again inversely proportional to the dietary loading (Hodson and Hilton, 1981). Selenium taken up from the water or diet is found in all tissues, but the highest concentrations are in the liver, kidney and intestines (Hodson <u>et al.</u>, 1980; Hodson and Hilton, 1981). For fish exposed to waterborne selenium, gill concentrations are also high. Muscle selenium concentrations are generally lower and equivalent to whole body concentrations.

Daphnia and trout also excrete selenium. In rainbow trout, waterborne selenium is depurated at a fixed logarithmic rate with a half-life of 29 days (Gissel-Nielsen and Gissel-Nielsen, 1978), indicating a passive excretion model relying on simple diffusion kinetics. Dietary selenium is excreted more actively with half-lives inversely proportional to dietary loading (Hodson and Hilton, 1981). It is possible that inorganic selenium taken up from water is transferred from gills to tissues and stored as inorganic selenium, whereas that taken up from the diet is transformed by the liver to an organic form that is both more toxic but more easily excreted. Within tissues of Daphnia pulex, selenium is associated with low molecular weight (64%) and protein (25%) components, while lesser amounts are associated with nucleic acids and lipids (10 and 0.1% respectively). Autoradiography indicated highest concentrations of  $^{75}$ Se in cytoplasm and these results correspond to those observed in mammals (Schultz et al., 1980).

### SELENIUM DISTRIBUTION IN AQUATIC ECOSYSTEMS

Waterborne selenium has a half-life in fresh water of 25-50 days and this time may be a function of particulate density and proximity to sediments. Selenium is precipitated to the sediments but, in enclosure experiments not in contact with sediments, the selenium remains in the water column (Rudd et al., 1980). While contact with sediments appears to be necessary for precipitation, sediment type does not seem to influence disappearance rates from the water column. Several investigators have suggested that selenium may be bioaccumulated up food chains (Rudd et al., 1980; Sandholm et al., 1973; Cumbie, 1978). Microbial transformations of selenium, particularly methylation to volatile compounds (Chau et al., 1976) or reduction to elemental selenium (Silverberg, et al., 1976), may change the availability and toxicity of waterborne and sedimentary selenium to aquatic biota as well as the form stored in their tissues.

Loadings to the Great Lakes have been estimated for Lakes Huron and Superior (Table 1), but these estimates are very unreliable due to errors in measurement of both flows and low selenium concentrations. Also, potentially important sources, such as atmospheric input, have not been measured. Copeland (1970) demonstrated that areas of Lake Michigan downwind of Chicago were contaminated with selenium and suggested that the source was the combustion of fossil fuels.

Waterborne selenium concentrations are generally very low ranging from 0.001 to 5.0  $\mu$ g/L (Table 2). This wide range probably reflects variation in analytical capability rather than real concentrations. Rain water samples contain much higher selenium concentrations than lake water and their concentrations reflect proximity to urban and industrial development (Traversy et al., 1975). These data indicate that atmospheric loading of selenium to the Great Lakes could be significant. Sediments contain about 0.1-1.0  $\mu$ g/g dry weight and the concentrations are slightly higher in the lower lakes relative to Lake Superior.

Net plankton selenium concentrations vary both within and between lakes with no obvious trends that could be related to contamination (Table 3). Zooplankton, however, showed higher concentrations in Georgian Bay compared with Lakes Ontario and Erie (Table 4), perhaps due to the influence of the French River. Copeland (1970) speculated that elevated selenium levels (1-7  $\mu$ g/g dry weight) in Lake Michigan zooplankton downwind from Chicago were due to fossil fuel combustion.

### TABLE 1

### SELENIUM LOADINGS TO LAKE HURON AND LAKE SUPERIOR (kg/day)

(ULRG 1977, VOLS IIA, IIIA)

Reference La La	LAKE HURON	LAKE SUPERIOR
Municipal Discharges	<0.001	0.013
Industrial Discharges	2.09	N.M.1
Tributary inputs	145	184
Atmospheric	N.M.	N.M.
Shoreline erosion	- *	N.M.
Dredge spoil disposal	N.M.	N.M.

1 Not measured

\* All samples less than detection limit of 1 mg/kg

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4	A	D	L	E	6

### SELENIUM CONCENTRATIONS IN GREAT LAKES WATERS AND SEDIMENTS

	SUPERIOR	MICHIGAN	HURON -	GEORGIAN BAY	- NORTH CHANNEL	ST. CLAIR	ERIE	ONTARIO	REFERENCE
									S.J. S. S. S. S. S.
Rainwater									
or snow (ug/L)	<0.1-0.2			0.1-0.4		0.5	0.2-0.8	.10-0.75	Traversy <u>et</u> <u>al</u> ., 1975
Water (ug/L)			<0.1*-0.2						
			<1.0*	<1.0*	<1.0*		1-5 filtered		ULRG 1977 Vol IIA, Adam
							11-36 unfiltered		and Johnson, 1977
	<0.1		<0.1	<0.1 <0.2			<0.1	<0.1	Traversy <u>et al</u> ., 1975 Warry, 1978
Sediments-		<0.5*					0.16,0.56		Copeland, 1970
Lake and Harbours (mg/kg dry	0.63 wt)		0.90				0.79	1.00	Traversy <u>et</u> <u>al</u> ., 1975

\*detection limit

### TABLE 3

### THE SELENIUM CONTENT OF NET PLANKTON (>153µ in size)

LAKE	SITE	NO. OF SAMPLES		STANDARD DEVIATION	RANGE
Ontario	Main Duck Is. Cobourg Port Credit Port Dalhousie	5 5 5 5 5	2.52 2.74 2.04 3.34	0.08 0.09 0.09 0.06	2.4 - 2.6 2.6 - 2.8 2.0 - 2.2 3.3 - 3.4
Erie	Long Pt. Bay Erieau Wheatley Pigeon Bay Amherstberg	5 5 5 5 5 5	2.26 2.44 2.84 1.90 0.93	0.06 0.06 0.06 0.00 0.02	2.2 - 2.3 2.4 - 2.5 2.8 - 2.9 1.9 0.90- 0.95
Huron	Goderich S. Baymouth Cape Rich Burnt Is. French R.	2 5 2 3 2	1.70 0.80 2.10 1.43 1.60	0.00 0.03 0.00 0.06 0.00	1.7 0.76- 0.84 2.1 1.4 - 1.5 1.6

SAMPLED FROM THE GREAT LAKES IN 1930\*

\*D. M. Whittle, Unpublished surveillance data, Great Lakes Biolimnology Laboratory, Department of Fisheries and Oceans, Canada Centre for Inland Waters.

### TABLE 4

LAKE	SITE	NO. OF SAMPLES		STANDARD DEVIATION	RANGE
<u>Mysis</u> rel	<u>icta</u> - 1980			Mula Duck D Goverg	Ontaria
Ontario	Main Duck Is. Cobourg Port Credit Port Dalhousie	1 3 5 4	2.3 2.77 2.42 1.88	0.15 0.05 0.32	2.3 2.6 - 2.9 2.4 - 2.5 1.6 - 2.2
Huron	Goderich S. Baymouth Burnt Is. French R.	5 8 5 4	3.82 2.83 3.24 4.70	0.05 0.67 0.09 0.08	3.8 - 3.9 2.3 - 3.7 3.1 - 3.3 4.6 - 4.8
Pontopore	<u>la</u> spp 1980	1.43 1.43		Lape Riter	
Ontario	Main Duck Is.	5	2.14	0.06	2.1 - 2.2
Huron	S. Baymouth	5	3.88	0.88	3.8 - 4.0
"Zooplank	<u>ton</u> " (>500µ) - 197	3			Lanoratory Waters,
Erie	Western Basin	5	2.38	0.24	-

THE SELENIUM CONTENT OF ZOOPLANKTON SAMPLED FROM THE GREAT LAKES IN 1980\* AND 1973\*\*

\*D. M. Whittle, Unpublished surveillance data, Great Lakes Biolimnology Laboratory, Department of Fisheries and Oceans, Canada Centre for Inland Waters.

\*\*Adams and Johnson, 1977.

Variations in selenium concentrations between fish species are quite high (Table 5) but variations within species are quite small, with standard deviations generally less than 13% of the mean of any sample (Adams and Johnson, 1977). Table 5 shows that selenium concentrations within any fish species decrease from Georgian Bay/North Channel to Lake Erie to Lake Ontario. Although sample sizes are small in some cases, variation between years and between authors is remarkably low. Therefore, the trend towards higher selenium concentrations in biota from Georgian Bay relative to other lakes is probably real and may reflect the influence of mining and smelting activities in the French River drainage basin (Warry, 1978). The utility of fish as indicators of selenium contamination is supported since field work on Belews Lake (Cumbie, 1978; Cumbie and Van Horn, 1978), and on selenium contaminated Western U.S. Lakes (Kaiser <u>et al.</u>, 1979), has shown that native centrarchids and salmonids contain elevated concentrations relative to fish in low selenium areas.

A relationship between selenium levels and fish size has not been conclusively demonstrated. Adams and Johnson (1977) found a relationship between selenium concentration and weight in yellow perch, the only species with sufficient sample numbers for a comparison. Whittle (personal communication)<sup>2</sup>, however, could not find any relationship between selenium and length using the large sample sizes of smelt, walleye, rainbow, trout, lake trout, splake or coho reported in Table 5. An examination of Adam's thesis (Adams, 1976) indicates that the weight relationship was based on two distinct pools of fish of different weights. Within each pool there was no weight effect.

The selenium content of gull tissues sampled from Great Lakes colonies shows a considerable geographic variability (Table 6). Local contamination is a possible cause of these high levels but the accumulation of selenium from sources other than the Great Lakes during migrations cannot be discounted. The observed range of concentrations encompasses those seen in other biota and their significance to the health of gulls is unknown.

### HUMAN HEALTH

Selenium effects on human health are reviewed in a number of places including "Drinking Water and Health," (U.S. NRC, 1977).

Water soluble selenium has been recognized in soils and salt deposits since 1938 and concentrations in groundwater vary greatly with the proximity to excesses in rock and soil. In some springs and shallow wells, concentrations may exceed 100  $\mu$ g/L, but deep wells contain only a few micrograms/litre. Lake water concentrations may be high in areas where soil selenium concentrations are high, but the lake water concentrations vary widely (Abu-Erreish, 1967, cited in the publication mentioned above). Considerable selenium may be derived from sewage effluent; raw sewage, primary and secondary effluent may contain as much as 280, 45 and 5 mg/L, respectively.

There is little in the literature to suggest that most surface waters contain toxic amounts of selenium; in fact there may be an insufficient

<sup>2</sup>Mr. M. Whittle, Great Lakes Biolimnology Laboratory, Burlington, Ontario.

### TABLE 5

Erie         1973         0.15         3         0.12 - 0.17         1           alleye         Ontario         1973         0.25         2         0.14 - 0.35         1           Erie         1973         0.25         2         0.14 - 0.35         1           Erie         1973         0.52         7         30         0.52         2           melt         1973         0.660         6         0.42 - 0.79         1           georgian Bay         1990         0.33         68*         0.26 - 0.38         2           melt         1990         0.33         68*         0.26 - 0.38         2           melt         1990         0.33         68*         0.26 - 0.38         2           melt         1990         0.31         3*         0.25 - 0.37         2           ellowperch         1973         0.64         50* 0.07         12*         0.65 - 0.38         1           feeorgian Bay-South         1973         0.64         50* 0.07         12*         0.65 - 0.45         1           feeorgian Bay         1973         0.64         3         0.69 - 0.67         1         1         1         1         1	SPECIES	LAKE	YEAR SAMPLED	MEAN CONCENTRATION (mg/g wet wt.)	NO. OF SAMPLES	RANGE	AUTHOR
Stizostedion vitreum)       Ontario       1973       0.25       2       0.14 - 0.35       1         Frie       Frie       1973       0.31       12       0.14 - 0.35       1         Beorgian Bay       1973       0.31       12       0.14 - 0.35       1         Beergian Bay       1973       0.32       7       30       0.27       0.54       2         melt       0.42       0.43       1       0.660       0.88       2         melt       1990       0.77       12       0.60       0.88       2         melt       1993       0.32       3       0.25       0.79       1         Demerus mordax       Ontario       1973       0.34       8       0.25       0.79       2         Beergian Bay-South       1990       0.77       12*       0.60       0.78       2       2         eellowperch       Erie       1973       0.34       6       0.25       0.38       1         Perca flavescans       Ontario       1973       0.63       3       0.59       0.72       2.00       1         Anterio       1973       0.53       0.26       0.38       1       1 <td>catfish (?)</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>	catfish (?)						
Stizostedion vitreum)       Ontario       1973       0.25       2       0.14 - 0.35       1         Frie       Frie       1973       0.31       12       0.14 - 0.35       1         Beorgian Bay       1973       0.31       12       0.14 - 0.35       1         Beergian Bay       1973       0.32       7       30       0.27       0.54       2         melt       0.42       0.43       1       0.660       0.88       2         melt       1990       0.77       12       0.60       0.88       2         melt       1993       0.32       3       0.25       0.79       1         Demerus mordax       Ontario       1973       0.34       8       0.25       0.79       2         Beergian Bay-South       1990       0.77       12*       0.60       0.78       2       2         eellowperch       Erie       1973       0.34       6       0.25       0.38       1         Perca flavescans       Ontario       1973       0.63       3       0.59       0.72       2.00       1         Anterio       1973       0.53       0.26       0.38       1       1 <td>lalleve</td> <td></td> <td></td> <td></td> <td></td> <td>widedorg a</td> <td>1 293</td>	lalleve					widedorg a	1 293
Erie-Western-1973/ Benerus mordax)       1574 0.27       0.52 0.27       7 0.54       30 0.27       0.54 0.27       3 0.27       3 0.28       3 0.28       0 0.42       0.73       1 0.42       0.60       0 0.42       0	Stizostedion vitreum)						
Change Left Hards							
North Channel         1973 Beorgian Bay         1973 1980         0.60 0.77         12         0.60 0.60         0.42         0.78         12           melt         0smerus mordax)         Ontario         1973 1980         0.32 0.33         3 66*         0.26         0.79         12           Erie         1973 1980         0.32 0.33         66*         0.26         0.38         12           Erie         1973 Georgian Bay-South Eerca flavescans)         0.64         12*         0.60         0.68         12           ellowperch Perca flavescans)         Ontario         1973 Georgian Bay-South Eerca flavescans)         0.74         79 0.66         0.26         0.058         13           hitefish Coregonus spp)         Ontario         1973 0.74         0.60         7         SD = 0.068         13           hitefish Coregonus spp)         Ontario         1973 0.74         0.60         7         SD = 0.04         3           hitefish Coregonus spp)         Ontario         1973 0.74         0.26         3 0.67         0.63         3 0.67         0.63         1           hitefish Coregonus spp)         Ontario         1973 0.73         0.26         3 0.69         0.35         1           hitefish Erie         1973		Erie-western-19/3/					2
Georgian Bay         1973 1980         0.70         12         0.60         6         0.42         0.79         12           Damerus mordax)         Ontario         1973         0.32         3         0.26         0.38         12           Demerus mordax)         Erie         1973         0.32         3         0.26         0.26         0.79         12           Erie         1973         0.34         8         0.15         0.45         12           Georgian Bay-South         1990         0.31         3**         0.23         0.56         0.79         12           Georgian Bay-South         1990         0.77         12*         0.60         0.89         0.25         0.37         12*         0.60         0.89         0.55         0.67         3         0.59         0.67         3         0.59         0.67         3         0.59         0.67         3         0.59         0.67         3         0.59         0.67         3         0.59         0.67         3         0.59         0.67         3         0.59         0.67         3         0.59         0.67         1         1         3         0.67         50         0.67         3		North Channel				Calce - Cump	
Internation         Ontario         1973         0.32         3         0.26         -0.38         1           Demerus mordax)         Ontario         1973         0.32         3         0.26         -0.39         1           Erie         1973         0.34         8         0.15         -0.45         1           Georgian Bay-South         1979         0.64         12*         0.69         -0.73         2           ellowperch         Perca flavescans)         Ontario         1973/74         0.74         6         0.26         -0.38         1           Perca flavescans)         Ontario         1973/74         0.74         6         0.26         -0.38         1           Correagonus Spp)         Ontario         1973         0.63         3         0.59         -0.67         1           hitefish         Goregonus Spp)         Ontario         1973         0.625         1         0.87         -2.00         1           heepshead         Maplodinotus grunniens)         Ontario         1973         0.26         3         0.19         0.35         1           Georgian Bay         1973         0.26         3         0.19         0.36         0.10							
Osmerus mordax         Ontario         1973         0.32         3         0.26 - 0.78         2           Erie         1973         0.32         68*         0.26 - 0.78         2           Georgian Bay-South         1973         0.34         8         0.15 - 0.45         2           Georgian Bay-Morth         1979         0.64         12*         0.69 - 0.73         2           ellowperch         Perca flavescans         Ontario         1973/74         0.74         6         0.26 - 0.78         2           ellowperch         Decorgian Bay-Morth         1973         0.34         6         0.26 - 0.38         1           feeorgian Bay         1973         0.34         6         0.26 - 0.38         1           feeorgian Bay         1973         0.63         3         0.59 - 0.67         1           feeorgian Bay         Lake Huron         1973         0.64         3         0.87 - 2.00         1           hitefish         Ontario         1973         0.22         1         0.87 - 2.00         1           hitefish         Ontario         1973         0.26         3         0.19 - 0.35         1           feeorgian Bay         1973         0.26 <td></td> <td></td> <td>1980</td> <td>0.77</td> <td>12</td> <td>0.60 - 0.88</td> <td>٢</td>			1980	0.77	12	0.60 - 0.88	٢
Osmer Us motoky         Ontario         iso	melt		1072	0.22	2	0 26 - 0 38	1
Erie         1973 1980         0.31 0.31         8 35*         0.15         0.43 0.23         12 0.23         0.37 2         2 0.60         12 2         0.60         0.31 2*         12 0.60         0.37 2         2 2           ellowperch Perca flavescans)         Ontario         1973 Erie-Western         1973 1973         0.64 0.63         12*         0.66         0.38 0.55         1 2*           hitefish Coregonus Spp)         Ontario         1973 Lake Huron         0.77         12*         0.60         7         50 = 0.67         1 1 50           hitefish Coregonus Spp)         Ontario         1973 N. Channel         0.22         1 1 1973         0.63         3 0.87         0.67         1 1 1 1           heepshead Aplodinotus grunniens)         Ontario         1973 Erie         0.26         3 0.19         0.36         0.19         0.35         1 1 1           heopshead Aplodinotus grunniens)         Ontario         1973 Erie         0.26         3 0.25         0.10         0.36         0.40         1 1           ock Bass Ambloplites rupestris)         Ontario         1973 Erie         0.36         0.33         0.23         0.32         0.40         1 1           oho Salmon Oncorhynchus kisutch)         Ontario Erie         1973 1973	Osmerus mordax)	Ontario					
Igeo         0.31         35*         0.23         0.59*         0.23         0.59*         0.23         22           Georgian Bay-North         1970         0.64         12*         0.60         0.59         0.57         22           ellowperch         0.77         12*         0.60         0.88         2           ellowperch         1973/4         0.74         79         50         0.66         13           hitefish         1973         0.63         0.60         7         50         0.67         1           Georgian Bay         1973         0.64         2         0.77         1.11         1           hitefish         0rtario         1973         0.55         3         0.67         2.00         1           foregonus spp         Ontario         1973         0.55         3         0.67         2.00         1           heepshead         montario         1973         0.26         3         0.19         0.35         1           ablodincus grunniens)         Ontario         1973         0.26         3         0.19         0.35         1           feess         amblogites rupestris)         Ontario         1973		Frie					
Beergin Bay-North         1960         0.77         12*         0.60 - 0.88         2           eilowperch Perca flavescans)         Ontario Erie-Western         1973 1973         0.34         6         0.26 - 0.38         1           Mitefish Corregons Spp)         Ontario Beergian Bay Lake Huron         1973 1973         0.34         6         0.26 - 0.38         1           hitefish Corregons Spp)         Ontario Beergian Bay Lake Huron         1973 1973         0.225         1         0.67 - 2.00         1           hitefish Corregons Spp)         Ontario Beergian Bay         1973 1973         0.26         3         0.19 - 0.35         1           heepshead Aplodinotus grunniens)         Ontario Erie         1973 1973         0.26         3         0.19 - 0.35         1           ock Bass Ambloplites rupestris)         Ontario Erie         1973 1973         0.38         4         0.35 - 0.40         1           itke Esox lucius)         Ontario Erie         1973 1973         0.30         3         0.23 - 0.39         1           icho Salmon Oncorhynchus kisutch)         Ontario Erie-Western         1973 1973/74         0.34         4         0.17 - 0.52         1           iahow Trout Salmo gairdmeri)         Ontario Erie-Western         1973 1973/74         0.			1980				
ellowperch Perca flavescans)       Ontario       1973       0.34       6       0.26       0.38       1         bitefish Coregonus spp)       Ontario       1973       0.63       3       0.57       1.11         hitefish Coregonus spp)       Ontario       1973       0.64       7       5.0       0.04       3         hitefish Coregonus spp)       Ontario       1973       0.22       1       0.77       1.11         heepshead Aplodinotus grunniens)       Ontario       1973       0.26       3       0.19       0.35       1         ock Bass Ambloplites rupestris)       Ontario       1973       0.26       3       0.19       0.35       1         ike       Erie-Western       1973       0.26       3       0.19       0.35       1         ock Bass Ambloplites rupestris)       Ontario       1973       0.26       3       0.19       0.30       1         ike       Erie-Western       1973       0.28       2       0.10       0.39       1         ook Bass Ambloplites rupestris)       Ontario       1973       0.28       2       0.51       1       1         oho Salmon       Oncornynchus kisutch)       Ontario       1973							
Perca flavescans)         Ontario Erie-Western         1973/r4 1973         0.34 0.63         5 3         0.26 - 0.05 3         1 3         0.59 - 0.67         1 1 9           hitefish Coregonus spp)         Ontario N. Channel Georgian Bay         1973 1974         0.74 0.60         7         5D = 0.05         3 0.59 - 0.67         1 1 0.60         3           hitefish Coregonus spp)         Ontario N. Channel Georgian Bay         1973 1973         0.22 0.60         1 7         5D = 0.04         3           heepshead Aplodinotus grunniens)         Ontario Erie         1973 1973         0.26 0.45         3 0.69 - 1.07         1           heepshead Aplodinotus grunniens)         Ontario Erie         1973 1973         0.26 0.45         3 0.69 - 0.50         1 3           ock Bass Ambloplites rupestris)         Ontario Erie         1973 1973         0.26 0.25         2 0.10 - 0.39         1 1           ike Esox lucius)         Ontario Georgian Bay         1973 1973         0.38 0.25         4 0.10 - 0.39         1 1           ike Esox lucius)         Ontario Georgian Bay         1973 1973         0.30 0.30         3 0.22 - 0.51         2 0.10 - 0.39         1 1           oho Salmon Oncorhynchus kisutch         Ontario Erie-Western         1973 1973/r/4         0.34 0.82         6 SD = 0.13         3 3 0.32 - 0.66		Georgian Bay-North	1980	0.77	12*	0.00 - 0.00	L
Price (a ) latestan       1973/74       0.74       79       SD = 0.05       3         N. Channel       1973       0.63       3       0.59 - 0.67       1         Georgian Bay       1973       0.63       3       0.59 - 0.67       1         Georgian Bay       1973       0.60       7       SD = 0.04       3         hitefish       1973       0.22       1       0.77 - 1.11       1         Goregonus spp)       Ontario       1973       0.22       1       0.87 - 2.00       1         heepshead       Aplodinotus grunniens       Ontario       1973       0.26       3       0.19 - 0.35       1         Aplodinotus grunniens       Ontario       1973       0.45       4       0.36 - 0.50       1         ock Bass       nubioplites rupestris       Ontario       1973       0.38       4       0.35 - 0.40       1         wike       1973       0.25       2       0.10 - 0.39       1       1         ock Bass       Ontario       1973       0.38       4       0.35 - 0.40       1         interestrup       Ontario       1973       0.325       2       0.51 - 1.04       1         ock Bass	ellowperch	Ontania	1072	0.34	6	0.26 - 0.38	1
N. Channel       1973       0.63       3       0.69       -0.67       1         Georgian Bay       1973       0.94       2       0.77       -1.11       1         Coregonus spp)       Ontario       1973       0.60       7       SD = 0.04       3         hitefish       Coregonus spp)       Ontario       1973       0.22       1       -7       -0.11         heepshead       N. Channel       1973       0.26       3       0.89 - 1.07       1         heepshead       Aplodinotus grunniens)       Ontario       1973       0.26       3       0.19 - 0.35       1         Aplodinotus grunniens)       Ontario       1973       0.26       3       0.19 - 0.35       1         ambloplites rupestris)       Ontario       1973       0.26       3       0.19 - 0.35       1         ambloplites rupestris)       Ontario       1973       0.28       4       0.35 - 0.40       1         ike       Esox lucius)       Ontario       1973       0.30       3       0.23 - 0.39       1         icho Salmon       Ontario       1980       0.43       25       0.32 - 0.51       2         Goreorian Bay       1973	Perca Tlavescans)						3
debry Lake Huron         1974         0.60         7         5D = 0.04         3           hitefish Coregonus spp)         Ontario N. Channel Georgian Bay         1973         0.22         1         0.87         2.00         1           heepshead Aplodinotus grunniens)         Ontario Erie         1973         0.26         3         0.19         0.35         1           heepshead Aplodinotus grunniens)         Ontario Erie         1973         0.26         3         0.19         0.35         1           ock Bass Ambloplites rupestris)         Ontario Erie         1973         0.38         4         0.35         0.40         1           ock Bass Ambloplites rupestris)         Ontario Erie         1973         0.38         2         0.51         1.04         1           och Salmon Oncorhynchus kisutch)         Ontario Erie         1973         0.30         3         0.22         0.51         1.04         1           oho Salmon Oncorhynchus kisutch)         Ontario Erie         1980         0.43         25         0.32         0.51         2           arp Cyprinus carpio)         Ontario         1980         0.44         2         0.42         0.42         0.42         0.42         0.32         0.32         <				0.63			
hitefish Coregonus spp)       Ontario N. Channel Georgian Bay       1973 1973 1973 100       0.22 1 1973 1.55       1 0.87 2.00 3 0.89 1.07       1 1 1 1973 1.00         heepshead Aplodinotus grunniens)       Ontario Erie Erie-Western       1973 1973 1973 1973 0.45       0.26 4 4 0.45       0.19 4 0.065       0.19 0.055       1 1 1 0.66         ock Bass Ambloplites rupestris)       Ontario Erie       1973 1973 1973       0.38 0.25       4 0.10       0.35 0.10       0.10 10         oks Bass Ambloplites rupestris)       Ontario Erie       1973 1973       0.38 0.25       4 0.10       0.23 0.10       0.39 1       1 1 10         ike Esox lucius)       Ontario Beorgian Bay       1973 1973       0.30 0.78       3 0.51       0.23 0.51       0.39 1       1 1 10         oho Salmon Oncorhynchus kisutch)       Ontario Erie       1980 1973       0.43 0.50       25 0.32       0.32 0.32       0.60 2       2 1 1       2 1 2         arp Cyprinus carpio)       Ontario Erie       1973 1980       0.43 0.57       15 15 0.43       0.43 0.32       0.66 2       2 1 1       1 1 1         alinhow Trout Salmo gairdneri)       Ontario Nc Channel Georgian Bay       1973 1973       0.52 1 1       1 1       - 1 1       1 1 1							
Corregonus spp)         Ontario N. Channel         1973 1973         0.22 1.55 1.55         1 3 0.89 - 1.07         1 1 1           heepshead Aplodinotus grunniens)         Ontario Erie         1973 1973         0.26 3 0.45         3 4 0.36         0.19 - 0.35 1 0.35         1 1 0.35         1 0.35         1 0.39         1 1 0.33         1 0.35         0.35         0.40         1 0.33         1 0.32         1 0.33         1 0.25         0 0.10         1 0.39         1 1 0.10         1 0.39         1 1 0.10         1 0.33         0 0.23         0.32         0 0.39         1 1 0.55         1 0.33         1 0.22         0 0.33         0 0.23         0 0.32         0 0.32 <td></td> <td>Lake Huron</td> <td>1974</td> <td>0.60</td> <td>. 'a a</td> <td>50 = 0.04</td> <td></td>		Lake Huron	1974	0.60	. 'a a	50 = 0.04	
Corregionus spp)         Ontario Beorgian Bay         1973 1973         1.55 1.65 1.65         3 3         0.87 - 2.00 3         1 1.00           heepshead Aplodinotus grunniens)         Ontario Erie         1973 1973         0.26 3         3 0.45         0.19 - 0.35 4         1 0.36 - 0.50         1 3           ock Bass Ambloplites rupestris)         Ontario Erie         1973 1973         0.38 0.25         4 0.10 - 0.39         1 3           ock Bass Ambloplites rupestris)         Ontario Erie         1973 1973         0.38 0.25         4 0.10 - 0.39         1 1           ock Bass Ambloplites rupestris)         Ontario Erie         1973 1973         0.38 0.25         4 0.10 - 0.39         1 1           oho Salmon Oncorhynchus kisutch)         Ontario Erie         1973 1980         0.43 0.50         2 0.32 - 0.51         2 0.32 - 0.46         1 2 1 2           arp Cyprinus carpio)         Ontario Erie-Western         1973 1973/74         0.34 0.82         4 0.17 - 0.52         1 3 3           ake Trout Salwellinus namaycush)         Ontario         1980         0.44         176         0.33 - 0.66         2           iathbow Trout Salmo gairdneri)         Ontario         1980         0.57         15 0.43 - 0.71         2 2         0.42 - 0.85         1 3 3           ihub (?)         Ontario	hitefish		1072	0.22	1	the sentents	2
Beorgian Bay         1973         1.00         3         0.89 - 1.07         1           heepshead Aplodinotus grunniens)         Ontario Erie         1973         0.26         3         0.19 - 0.35         1           heepshead Aplodinotus grunniens)         Ontario Erie         1973         0.26         3         0.19 - 0.35         1           ock Bass Ambloplites rupestris)         Ontario Erie         1973         0.38         4         0.35 - 0.40         1           'ike Esox lucius)         Ontario Georgian Bay         1973         0.38         4         0.35 - 0.40         1           'ike Esox lucius)         Ontario Georgian Bay         1973         0.30         3         0.23 - 0.39         1           'ike Esox lucius)         Ontario Georgian Bay         1973         0.30         3         0.23 - 0.39         1           'ike Esox lucius)         Ontario Erie         1973         0.34         2         0.32 - 0.51         2           'ike Esox lucius         Dontario Erie         1973         0.34         4         0.17 - 0.52         1           'ike Esox lucius         Ontario Salvelinus campio)         Ontario         1980         0.44         176         0.33 - 0.66         2 <tht< td=""><td>Coregonus spp)</td><td></td><td></td><td></td><td>3</td><td>0.87 - 2.00</td><td></td></tht<>	Coregonus spp)				3	0.87 - 2.00	
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$ \frac{O(COPYNCHOS KISUCCI)}{Erie} \qquad 0.143 + 10 \\ Erie \qquad 1973 & 0.44 & 2 \\ 1980 & 0.50 & 23 \\ 0.32 - 0.80 & 2 \\ 0.32 - 0.80 & 2 \\ 0.32 - 0.80 & 2 \\ 0.32 - 0.80 & 2 \\ 0.32 - 0.80 & 2 \\ 0.32 - 0.80 & 2 \\ 0.32 - 0.80 & 2 \\ 0.32 - 0.80 & 2 \\ 0.32 - 0.80 & 2 \\ 0.32 - 0.80 & 2 \\ 0.32 - 0.80 & 2 \\ 0.32 - 0.80 & 2 \\ 0.33 - 0.52 & 1 \\ 0.33 - 0.66 & 2 \\ 0.43 - 0.71 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.96 & 2 \\ 0.41 - 0.9$	Coho Salmon		1000	0.42	25	0.22 0.51	2
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$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Salvelinus namaycush)	Ontario	1980	0.44	1/6	0.33 - 0.00	2
Same generation         Ontario         1980         0.65         10         0.41 - 0.96         2           Chub (?)         Ontario         1973         0.52         1         -         1           N. Channel         1973         0.59         1         -         1           Georgian Bay         1973         0.73         2         0.62 - 0.85         1	ainbow Trout	0.0	1000	0.57	15	0.43 - 0.71	2
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N. Channel         1973         0.59         1         -         1           Georgian Bay         1973         0.73         2         0.62 - 0.85         1	1 1 (0)				1	ntosneon re	1
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Counter Pay South 1072 0.70 47 0.42 - 1.20 2					2	0.62 - 0.85	1
	Splake (**)	Georgian Bay-South	1973	0.70	47	0.42 - 1.20	2

## THE SELENIUM CONTENT OF FISH FROM THE GREAT LAKES

1. Beal, 1974.

 D. M. Whittle, Unpublished surveillance data, Great Lakes Biolimnology Laboratory, Department of Fisheries and Oceans, Canada Centre for Inland Waters.

3. Adams and Johnson, 1977.

\* Five fish composites.

\*\* (Salvelinus fontinalis x Salvelinus namaycush

LAKE	SITE	TISSUE	NO. OF SAMPLES	MEAN VALUE	STANDARD DEVIATION
Erie	Middle Island Port Colbourne	Egg Egg	2 2	1.0 1.3	
Huron	Chantry Island Double Island	Egg Egg	2 2	<0.4 <0.4	
Michigan	Little Sister Is. Hat Island	Egg Egg	2 2	1.3 0.5	
Superior	Mamainse Island Granite Island	Egg Egg	2 2	1.0 <0.4	
Ontario	Muggs Island Snake Island Kingston	Egg Egg Adult liver Adult feather	8 9 17 17	0.56 0.72 0.311 2.60	0.15 0.14 0.114 1.22

### THE 1977 SELENIUM CONTENT IN µg/g WET WEIGHT OF HERRING GULL TISSUE IN THE GREAT LAKES\*

\*Source: D. J. Hallett pers. comm., Canadian Wildlife Service.

quantity of selenium in the water alone to provide the nutrient requirements of most animals (Cannon, cited in the publication above). Water consumed by human populations rarely constitutes a human health hazard, although finished water for domestic consumption usually is not analyzed for selenium. However, in a well-known case of an Indian reservation using well water containing high concentrations of selenate, there was a loss of hair and nails in children. In other areas with contaminated well water, it was found that the most frequent symptoms of human toxicity were gastrointestinal disturbances, bad teeth, yellowing of the skin in older persons, and sallow skin in younger persons.

The usual exposure route in man is via toxic vapors in industrial situations and selenium fumes can produce an acute respiratory distress syndrome. Chronic exposure via inhalation or ingestion may produce depression, nervousness, occasional dermatitis, gastrointestinal disturbance, giddiness, an increased incidence of dental caries and a peculiar garlic odor of the breath and sweat, due to the formation of dimethyl selenide. The principal route of excretion of selenium is via the urine. Little is known about the biochemistry of selenium in the mammalian system.

Carcinogenicity of selenium is controversial; liver tumors can be induced in chronically treated animals, although a review of the research shows that these may not, in fact, be neoplasms at all. There is no evidence of mutagenicity. Teratogenicity in humans is not an issue, but in chicks profound malformative alterations are produced at even low concentrations. There are important interactions of selenium with arsenic, mercury, cadmium, silver and thallium. For instance, mercury increases the retention of selenium in the blood, kidneys, and spleen while selenium protects against the toxicity of mercury. In tuna, batches that had little selenium contained low concentrations of mercury, and when the concentrations of mercury were high, selenium concentrations were also high.

The current drinking water standard for selenium is 10  $\mu$ g/L as total selenium (U.S. Public Health Service, 1962; Canadian Dept. of National Health and Welfare, 1979, OME, 1980).

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### MIREX

### EXISTING OBJECTIVE

For the protection of aquatic organisms and fish-consuming birds and animals, mirex and its degradation products should be substantially absent from water and aquatic organisms. Substantially absent here means less than detection levels as determined by the best scientific methodology available.

Note: The best detection levels for mirex (1977), as determined by a survey of laboratories in the Great Lakes region, are 0.005  $\mu$ g/L for water and 0.005  $\mu$ g/g for biological tissues.

### RATIONALE REVIEW

The original objective and rationale (IJC, 1977) was based upon lethal effects to crayfish (<u>Procambarus hoyi</u>) at mirex levels of approximately 0.1 µg/L and upon increased mortality to grass shrimps (<u>Palaemonetes</u> <u>vulgaris</u>) through predation by pinfish (<u>Lagodon rhomboides</u>) at 0.025 µg/L for 13 days. These effects were considered too severe to be considered subtle and hence to be the basis of an objective which would protect all aquatic life in the Great Lakes basin. Therefore, the conservative approach was adopted of recommending "zero" as the objective until such time as suitable, non-lethal effect results were available.

Since 1977 several additional mirex derivatives other than photomirex (8-monohydromirex) have been found in Lake Ontario herring gulls including 10-monohydro, 9-monohydro, 2,8-dihydro and 1,5-dihydromirex. These products are found in relatively lower concentrations than photomirex, (approximately 10%), which is the main degradation product found in Lake Ontario biota (IJC, 1978). It should be noted that the ratio of mirex to photomirex was constant in Lake Ontario herring gulls from 1974 through 1978 (Norstrom et al., 1980). It is encouraging that the concentration of mirex/photomirex has decreased at a constant rate since 1974, halving in concentration every 2.1 years through 1979 in Lake Ontario herring gulls (Weseloh et al., 1979; Hallett et al., 1980). Declining trends are also evident in Lake Ontario spottail shiners (Suns et al., Personal Communication).<sup>1</sup>

A number of papers on mammalian toxicology of photomirex and mirex have appeared since the Mirex Objective was last reviewed (IJC, 1977). Many of these have come from the laboratories of the Canadian Department of National Health and Welfare (Sundaram et al., 1980; Chu et al., 1981; Villeneuve et al., 1979b). Toxicity to male and female rats has been examined at dietary levels between 0.05 to 500  $\mu$ g/g over 28-91 days. In general, weight gain and food intake were reduced at 50  $\mu$ g/g or more in the diet at which level photomirex was lethal to 20% of the specimens over 24 days; accumulation occurred in many tissues including adipose, liver and brain; enzymatic levels were affected (both induction and disfunction) at 5  $\mu$ g/g. An independent study (Wolfe et al., 1979) employing a 15 month feeding study at 1.8  $\mu$ g/g mirex in the diets of field mice found a decrease in litter size and numbers.

<sup>1</sup>Dr. K. Suns. Ontario Ministry of the Environment, Toronto, Ontario.

Mirex and photomirex were also examined for mutagenic and teratogenic activity (Schoeny et al., 1979; Hallett et al., 1978). No such effects were observed with five <u>Salmonella</u> strains. Villeneuve et al., 1979c, using photomirex and rabbits, was unable to find teratogenic effects other than a small reduction in fetal weight despite the ability of this compound to transfer across the placenta and accumulate in the fetus.

Two recent papers report chronic, sublethal bioassays with fathead minnows (<u>Pimephales promelas</u>) (Buckler <u>et al.</u>, 1981) and daphnids (<u>Daphnia magna</u>) amphipods (<u>Gammarus pseudolimnaeus</u>) and midge larvae (<u>Chironomus plumosus</u>) (Sanders <u>et al.</u>, 1980). Fish reproduction was effected at 3-34  $\mu$ g/L and among the invertebrates tested, only the amphipod was adversely effected at low concentrations (30% reduction in adult survival at 2.4  $\mu$ g/L after 30 days exposure). This is not considered to be a subtle effect, however, and is insufficient to justify a revision of the current objective.

A survey of several laboratories performing mirex analyses in the Great Lakes basin did not indicate any general reduction in the current detection limits (0.005  $\mu$ g/g tissue, 0.005  $\mu$ g/L water). It is also apparent from the above that mammalian effects are observed at levels much above those cited in the rationale for the objective. The conclusion remains that insufficient chronic data exists to establish a safe level for the protection of all aquatic organisms. Therefore, it is recommended that no change be made to the existing objective.

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### 3. Future Considerations

The Committee believes the following list merits consideration for review during 1981-1982.

### AMMONIA

The existing objective for un-ionized ammonia does not consider the modifying effects of water quality (e.g. pH, alkalinity, temperature, and oxygen).

### ASBESTOS

### Continuing

### AQUATIC ECOSYSTEM

An attempt was made to define the demographic condition of lake trout stocks in Lake Superior during an early period of apparent steady-state yield. This period occurred prior to the time of sea lamprey invasion and the obvious effects of toxic inputs and cultural eutrophication. The data examined to date has proved insufficient for the attainment of the primary objective, although it has proven to be useful in other respects.

Further emphasis should be directed toward the formation of a task force: (1) to investigate the feasibility of pursuing a lake trout objective; (2) to consider other alternative ecosystem approaches; (3) to prepare a report with the Great Lakes Fishery Commission summarizing a practical approach to the problem.

### BENZENE

This substance is an ubiquitous high volume carcinogenic substance in the Great Lakes Ecosystem.

CHROMIUM

Continuing

COPPER

Continuing

### DIAZINON

Continuing

### DIBENZOFURANS

Polychlorinated dibenzofurans have been identified in fish and herring gulls from the Great Lakes ecosystem. The 2,3,7,8-tetrachlorodibenzofuran (TCDF) is extremely toxic and surveillance activities are underway to assess the spatial or temporal trend levels in wildlife, fish and sediments. LINDANE

Continuing

MERCURY

Continuing

MICROBIOLOGICAL INDICATOR/PATHOGEN

Recent studies in Lake Erie and Colorado indicate that an earlier recommendation (1980 AEOC) may require revision. These studies also include information on <u>Pseudomonas</u> <u>aeruginosa</u> that may be justification for a new objective specific to this pathogen.

POLYNUCLEAR AROMATIC HYDROCARBONS

Continuing

SILVER said to not three bidgs penel and antic of eben as tomethe and alog

Recent evidence suggests that silver toxicity may differ from that reported in an earlier report (1980 AEOC) and that analytical methods may be available to quantify the toxic species.

ZINC

Continuing

BENZENI

Ints substance is an ubiquitous high volume carcinogenic substance in the Great Lakes Ecosystem.

MULMOSHO

Continuing

**COPPER** 

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DIAZINON

Continuing

DIBENZOFURANS-

Polychlorinated dibenzofurans have been identified in fish and herring quils from the Great Lakes ecosystem. The 2.3.7.8-tetrachiorodibenzofuran (ICDF) is extremely toxic and surveillance activities are underway to assess the spatial or temporal trend levels in wildlife. Fish and sediments

### 4. Present Needs

The Committee has identified the following as needing additional research and believes that funding agencies should consider this list in establishing their priorities.

In particular the committee wishes to emphasize the need for developing a Great Lakes fish community data base to enable formulation of an aquatic ecosystem objective.

### RESEARCH PRIORITY

### Analysis of Appropriate Fish Community Data Bases

There is a need to identify one or more fish community data bases for Lake Superior which will provide as minimal requirements:

- a) lake trout demographic characteristics prior to the advent of the sea lamprey and major inputs of toxic substances plus cultural eutrophication.
- b) information for other species of Lake Superior which may follow closely the pattern established by the lake trout because of similar responses to the same set of stresses. AEOC will recommend to the SAB that a Task Force be established to accomplish the above (also see Chapter 3, this report, under Aquatic Ecosytem).

### OTHER NEEDS

### Sediments as a Source of Toxic Chemicals for Aquatic Biota

Water Quality Objectives indicate that metals can be transferred from the sediments to aquatic biota to the detriment of fish or consumers of fish. There are indications that organic contaminants may similarly be transferred but probably by different mechanisms. Research is required to define and evaluate transfer mechanisms as well as conditions controlling rates and routes and in particular threshold sediment concentrations causing adverse effects in aquatic biota.

#### Metal Speciation

Research on metal speciation has clearly indicated that some metal species are more toxic to aquatic biota than others, and that 'total' is a practical rather than appropriate basis for water quality objectives. However, a major impediment to research and surveillance of metal species is the lack of practical analytical techniques to measure specific metal forms at concentrations of 0.001 to  $1.0 \mu g/L$ , therefore, research is required to develop such sensitive practical techniques.

# Air Sampling Methodology

Atmospheric deposition is a major source of contaminants to the Great Lakes ecosystem. While methods for measurement of wet deposition are available for both soluble and absorbed fractions, the same is not true for dry deposition. Techniques for the collection of such samples are urgently needed.

# Epidemiological Models

Many of the epidemiological models can give variable results depending upon which model is utilized, the number of assumptions made, and the magnitude of safety factors. While such models can not be exact, a more detailed and uniform methodology for their design must be developed. This is especially true for models involving both human health related food consumption as well as acceptable levels of contaminants in drinking water.

# Environmental Mapping

The allocation of limited use zones require the identification of sensitive inshore areas as called for in the 1978 Water Quality Agreement (Annex II, paragraph 2e). Environmental Mapping is recommended to identify biologically sensitive areas or those areas subject to intensive recreational use.

# Quantitative Structure Activity Relationships

Structure-activity relationships may significantly reduce the effort required for environmental hazard evaluation by predicting the behavior and/or toxicity of chemicals. Research is needed to define quantitative relationships either for general or specific classes of chemicals.

#### Mixtures

Objectives developed to date have addressed the biological activity of single compounds due to the lack of data dealing with multiple toxicant interactions in the aquatic environment. A document has been prepared (pages 27-33) outlining a practical approach to assessing the combined activity of metal mixtures, but the assumption of additive toxicity is not well supported. Research is required to develop a sound theoretical basis for future objectives to control mixtures.

# 5. Mixtures

#### EVALUATING THE ENVIRONMENTAL SIGNIFICANCE OF AQUEOUS MIXTURES OF METALS

Mixtures of contaminants have always been regarded with concern due to the possibility of adverse synergistic effects on aquatic biota. The following review of studies of the toxicity of metal mixtures to aquatic biota shows that "antagonism," "synergism" and "no interactions" have been observed in studies of both acute and chronic toxicity of metal mixtures. Ideally, there should be a mechanism for predicting the toxicity of observed mixtures of contaminants. However, this requires an understanding of the mechanisms of contaminant toxicity to identify those contaminants that will interact and the way in which they interact. It is unlikely that information adequate to define these mechanisms for assessing mixtures will be provided within the foreseeable future. Therefore, the review outlines a more pragmatic approach to assessing potential mixtures effects. While it is scientifically indefensible, its application to surveillance data analysis may provide an early indication of areas that are potentially harmful and to which special attention should be paid in a search for impacts and sources. AEOC recommends that this approach be considered in future assessment of water quality data already being collected, and has forwarded this approach to the Surveillance Work Group of the Water Quality Board in the hope that it might serve some utility in an examination of areas of concern.

### MECHANISM TO ASSESS THE ENVIRONMENTAL SIGNIFICANCE OF METAL MIXTURES

The following review was written to develop a mechanism to estimate the potential adverse effects on aquatic biota of mixtures of contaminants. The mixtures considered were limited to the metals, due to the availability of data on sublethal effects of mixtures, and to avoid excessive complexity. As the mechanism for dealing with mixtures is developed, more contaminants may be included.

There are two basic approaches to estimating mixture effects:

- 1. Procedural, based on experimental measurement of effects of real or defined mixtures.
- 2. Calculated, that utilize existing toxicological data on contaminants tested singly.

The latter approach was chosen because it is simpler and uses the large volume of existing toxicological data.

### RECOMMENDATION

It is proposed that the following mechanism be considered for estimating the potential toxicity of mixtures of metals in Great Lakes waters: The sum of the ratios of each metal concentration (Mi) and its respective objective concentration (Oi) should not exceed 1.0, i.e.

$$\Sigma \left[\frac{Mi}{0i}\right] \leq 1.0$$

### RATIONALE

Environmental pollution usually results in the presence of several metals simultaneously (Findlayson and Achuckian, 1979; Hutchinson and Stokes, 1975; Sprague and Ramsey, 1965). Water Quality Agreement objectives, however, are based on studies with individual metals and do not protect aquatic organisms from the combined effects of mixtures.

Most of the available literature on metal mixtures suggests that the toxicity of a mixture to aquatic biota is greater than that of any of the metals tested singly (see Konemann (1980) for a classification of the types of joint toxic action) (Table 1). Joint toxicity to algae has been observed with both binary mixtures (Braek et al., 1976; Hutchinson and Stokes, 1975) and mixtures of ten metals (Wong, et al., 1978), to ciliates with both binary and tri-metal mixtures (Grav, 1974; Parker, 1979), and to invertebrates in both lethal (Barnes and Stanbury, 1948; Russell-Hunter, 1949) and sublethal experiments (Borgman, 1980; D'Agostino and Finney, 1974). Joint toxicity to fish of mixtures was demonstrated in studies of acute toxicity (Eisler and Gardner, 1973), of subacute toxicity to eggs, alevins, and fry (Finlayson and Achuckian, 1979; Huckabee and Griffith, 1974), and of chronic toxicity during the reproductive stage (Spehar et al., 1978). A less common phenomenon in some mixtures, with some species, is a reduction in toxicity of one metal by the presence of another. For example, copper toxicity was reduced by zinc with one of four algal species tested (Braek <u>et al.</u>, 1976), and cadmium toxicity to algae and mercury toxicity to goldfish Carassius auratus were reduced by selenium (Heisinger et al., 1979; Hutchinson and Stokes, 1975).

Several models have been used to predict the toxicity of mixtures. One technique is to add together the percent reduction in growth caused by each constituent in single toxicant tests (Gray, 1974; Parker, 1979). This technique will work only if toxicity is relatively low. Another procedure involves summing the toxicant-induced mortality rates or the toxicant-induced increases, in the inverse of the growth rates observed during single toxicant exposures (Borgman, 1980). Some authors have multiplied survival (as a fraction) with one toxicant by survival with the second to estimate survival in the mixture (e.g. response) (Anderson and Weber, 1975). Also, toxicity of mixtures can be predicted from log probit plots if the slopes of these plots for individual toxicants are similar (e.g. concentration addition) (Anderson and Weber, 1975). All such models however, require complete concentrationresponse curves for each toxicant singly in order to predict toxicity at various concentrations of the mixtures. Furthermore, these concentrationresponse curves will differ between species and between toxicants. The use of such models in water quality evaluation would require excessively complicated mathematical formulas which would vary from one organism to another. A much simpler approach is required to estimate effects of metal mixtures.

The toxic unit concept, used initially for lethal studies with fish and reviewed by Sprague (1970), provides a useful basis for assessing mixtures. The concentration of a metal may be measured in toxic units, where one toxic unit is the concentration eliciting a defined response (e.g. 50% mortality). In mixtures, the defined response would be expected whenever the total concentration of all metals, each measured in toxic units, was equal to 1.0. Deviations of the observed response from the expected, using the toxic unit concept, have been called synergism or antagonism but the definitions of these terms depend on the type of model used by each author. Therefore, the toxic unit concept should not be used indiscriminantly in attempts to measure synergism or antagonism (Borgman, 1980).

The toxic unit concept overestimates somewhat (up to 10%) the lethal toxicity of cadmium-zinc mixtures to shrimp <u>Paratya tasmaniensis</u> (Thorp and Lake, 1974) but underestimates (up to 35%) the lethality of copper-mercury mixtures to brine shrimp and copepods (Corner and Sparrow, 1956). However, most lethal studies with fish indicate that the concept works fairly well (Brown and Dalton, 1970; Eaton, 1973; Sprague and Ramsey, 1965). Sprague (1970) expressed concern that toxic units might not predict lethality when concentrations of each component were <0.2 toxic units (i.e. there is a threshold concentration for lethal effects). However, he felt that toxic units might be usefully applied to sublethal responses at these low concentrations, although he had few sublethal data to investigate this possibility.

Some recent publications do, however, provide an indication of its utility at sublethal toxicant concentrations. Growth rates of zooplankton in mixtures of up to five metals can be predicted reasonably well with toxic units (Borgman, 1980) as can growth rates of ciliates if the growth rate data of Parker (1979) are analyzed in the same way as the data of Borgman (1980). Parker did not use the toxic unit concept to analyze his data. Spehar et al. (1978) observed that the number of embryos produced per female flagfish Jordanella floridae in chronic studies on cadmium and zinc mixtures was always much less in any of the mixtures compared to the control and single-metal exposures, although data variability did not permit demonstrations of statistically significant differences between the various treatments. Eaton (1973) felt that most of the chronic toxicity to fathead minnows Pimephales promelas in cadmium, copper, and zinc mixtures was due primarily to zinc. However, he tested only mixtures containing all three metals and compared his results to data on single metals reported by three different sets of authors. Therefore, it is not clear whether these two fish studies do or do not support use of the toxic unit concept. In contrast, an avoidance response by Atlantic salmon Salmo salar to mixtures of copper and zinc at very low concentrations does suggest that the toxic unit concept can be applied to fish (Sprague, et al., 1965).

The toxic unit concept may not be scientifically valid in that each metal may have a unique toxic action which does not necessarily add to the action of the other metals in a mixture. However, on a practical basis, the concept does seem to estimate reasonably well the effects on growth of zooplankton of metal mixtures (Borgman, 1980), i.e. the overall outcome can be predicted independently of specific toxic actions. At the present time, the toxic unit concept appears to be the only convenient method available for predicting the effects of metals in mixtures. The overall safe concentration for metals could be limited as follows:

$$\Sigma \left[\frac{\text{Mi}}{\text{Oi}}\right] \leq 1.0$$

where Mi is the observed concentration of metal "i" and Oi is the objective for metal "i", if present singly. When the sum is greater than one, it is expected that subtle adverse effects on biota would occur.

One example of a test of this approach is available. Wong et al. (1978) showed that a mixture of ten metals (concentrations in  $\mu g/L$ : As = 50, Cd = 0.2, Cr = 50, Cu = 5, Fe = 300, Pb = 25, Hg = 0.2, Ni = 25, Se = 10, Zn = 30) at the concentrations set as objectives in the 1978 Great Lakes Water Quality Agreement reduced primary production by algae by 68% from control levels in culture medium and by 78% in Hamilton Bay water. Even if each metal was present at one tenth the concentration of the objective, thereby just meeting the mixture requirement proposed above, primary production was still reduced by 40% in growth medium and 21% in Hamilton Bay water. More recent research to fully evaluate this phenomenon has demonstrated that mixtures containing zinc are the most toxic and that the "safe" concentration of zinc alone for algae is less than the Agreement objective of 30  $\mu g/L$  (Wong, 1980). Although the zinc toxicity does not explain the entire degree of toxicity in mixtures, it reduces the apparent synergism somewhat and indicates the need for sound criteria for realistic single metals and mixtures objectives.

These results show that the proposed mixtures approach may not necessarily describe the toxicity of metal mixtures, but will nevertheless provide a better estimate than strict consideration of the single metal objectives. This approach will also not predict effects of some specific metal mixtures which may be extremely toxic to some species (e.g. the synergistic toxicity of zinc and arsenic mixtures to copepods) (Borgman, 1980). However, its real value is the perspective it provides on results of water quality monitoring. For example, a hypothetical survey of metal concentrations near an urban area in Lake Ontario might contain the information depicted in Table 1.

These data indicate that the sum of the potential contributions of each metal to an adverse effect is just above the threshold level - further increases in metal concentrations would warrant concern because of the increasing probability of adverse effects. Furthermore, the majority of metals contribute little to the sum but one, lead, contributes 36%. Therefore, in the hypothetical case cited, efforts to prevent problems should focus on identifying and limiting the source of lead. An obvious weakness is that it is difficult to assess the relative importance of metals whose objective is close to the detection limit (e.g. cadmium); concentrations contributing up to 0.5 toxic units could remain undetected. Also, while some metals are in relatively high concentrations (e.g. iron) their contribution to toxic units is very small and could probably be ignored if less than 0.1 (i.e. the "no-effect level" is assumed to be 0.1).

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Metal	Observed Metal Concentration in Water (Mi) (µg/L)	Water Quality Objective (Oi) (µg/L)	Mi/Oi
Arsenic	<0.1	50	? ~ 0
Cadmium	<0.1	0.2	? ~ 0
Copper	1 1	5 ·	0.2
Chromium	1.0	50	0.02
Iron	15	300	0.05
Lead	2	5	0.4
Mercury	.05	0.2	0.25
Nickel	1 1	30	0.03
Selenium	0.1	10	0.01
Zinc	5	30	0.16
Σ Mi/Oi		of and the state of the state o	1.12

HYPOTHETICAL SURVEY OF METAL CONCENTRATIONS

A recent paper by Konemann (1980) indicates that the opposite may be true for organics. For mixtures of organic compounds whose acute toxicities can be predicted by quantitative structure/activity relationships, the resultant toxicity of the mixture can be successfully estimated by the toxic unit approach. Since mixtures of 10-50 compounds were tested, Konemann (1980) concluded that the idea of "no-effect levels", below which a component would not contribute to mixture toxicity, did not apply to organic compounds.

In summary, although it is recognized that an overall mixtures approach based on the toxic unit concept will not always be 100% accurate in predicting safe levels of metals for aquatic organisms, it will provide at least some basis for assessing the importance to aquatic biota of metal mixtures.

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# 6. Limited Use Zones

# (Mixing Zones, Problem Areas and/or Areas of Concern)

As stated within Annex II of the 1978 Great Lakes Water Quality Agreement, the parties shall, in consultation with the jurisdictions, take measures to define and describe a mechanism for allocating all existing and future limited use zones, and shall prepare an Annual Report on these measures. The definition of a limited use zone indicates only that they are those areas where specific objectives listed in Annex I do not apply. Therefore, the description or delineation of limited use zones is essential to fulfill the intent of this agreement. The importance of describing a limited use zone was observed in 1974 by the Water Quality Board when it stated "Water quality objectives describe, in part, a minimum quality of water which will not only provide for but protect any designated use. However, establishment of water objectives alone may not ensure against future losses of the beneficial uses which the parties desire to secure and protect. 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." (Appendix 'A', 1974).

The development and use of water quality objectives has always been predicated on a method for assigning the location and size of mixing zones to minimize the adverse effects on aquatic ecosystems of the dilution of pollutants from end-of-pipe concentrations to ambient lake concentrations. The 1974 Annual Report of the WQOS of the IJC outlined a set of minimum requirements for water quality within mixing zones. While these limited the severity of adverse effects within mixing zones, they did not limit the extent of adverse effects nor did they limit the total area and location of the mixing zone. Since that report, the need for a mechanism to limit mixing zones (mixing zone objective) has been reiterated annually. However, the few attempts to produce such a document have not been successful, probably due to a lack of definition of the advantages of a mixing zone objective and the lack of a clear perception of the scope and structure of such an objective. This rationale will attempt to provide these definitions, identify activities that are required to develop, support and implement a mixing zone objective, and provide guidelines for those who are charged with writing the detailed rationale.

Mixing zones are the physical expression of objectives and represent within the zone a loss of beneficial use, and, at the edge of the zone, the maximum limit of that loss. Without a description of a given mixing zone, the uses it affects adversely and monitoring to ensure that the objectives are met at its edge, there is no description, appreciation or understanding of the extent or severity of losses of beneficial uses. The net result will be inappropriate location of mixing zones, excessive density of mixing zones in a given area of lake or in given lakes, and loss of the beneficial uses the parties desire to protect. Mere identification of "problem areas" fails to describe the extent, severity, or significance of the problem and abdicates responsibility for actively limiting its impact. A further, and more serious aspect is that local environmental impact assessment on a piecemeal basis will "nickel and dime" a lake to death. The need for a mixing zone objective is obvious and the following are major, important considerations required for the formulation of such a mechanism.

- The uses to be protected must be described by the Governments of Canada and the United States on a lake by lake, and possibly on a basin by basin basis to allow identification of the extent, location and vigour with which mixing zone objectives should be applied. This step is essential and may require a reference by the Governments to the IJC.
- 2) The existing beneficial uses and resources must be identified and catalogued to recognize the potential for loss, the proportion of the whole which is lost to each mixing zone, and the long-term biological, ecological, and socio-economic costs of such a loss. Such a process, expressed in terms of biological mapping and interpretation, is the only way of establishing the significance and consequence of industrial, urban, forestry and agricultural developments. This process was first attempted at the Environmental Mapping Workshop and must be given high priority. While the development of a mixing zone objective will not be affected by a lack of a good inventory, its implementation is impossible without it.
- The concept of a mixing zone as a single isolated area of lake must 3) be discarded. Obviously the mixing zone for dilution of toxicants to ambient or objective levels will not be the same for a toxicant at three times the ambient level compared to one at three hundred times the ambient level. In other words, a given effluent containing a mixture of toxicants will have a variety of mixing zones described by simple dilution kinetics and the required specific water quality objectives. Since the beneficial uses to be protected near a given effluent will vary in their number and their relative importance (e.g. a highly valued fishery vs one which is of less value), the size of mixing zones for a given toxicant in a given effluent will also be a function of the size of area to be protected from that toxicant's effects. A good example would be that effluent components affecting bathing could be given a greater area for dilution (mixing zone) in a non-bathing, fish-producing area, than would a component affecting fish reproduction.
- 4) The mixing zone objective must contain a mechanism for describing hydraulic dispersion and mixing forces (e.g. wind stress, stratification, bottom topography, current, etc.) to allow a plotting and description of the maximum physical size in three dimensions of a given mixing zone.
- 5) The mixing zone objective must contain a mechanism for assigning relative weights to beneficial uses to be protected, based on the priorities identified by the Canada/U.S. Governments; e.g. bathing might be a higher priority in Lake Erie relative to lake trout production, whereas lake trout production in Lake Superior might be more important than in other lakes as well as the most important use within that lake.

- 6) The effects of mixtures must be recognized not only through varying mixing zone sizes for each component, but also through a means for reducing the overall size of the mixing zone according to the perceived severity of mixture interactions.
- 7) A mechanism is required for summing the overall effects of each type of impact on beneficial uses and for summing the interactive effects of different impacts. This is essential to provide a whole lake "loading concept" for mixing zones to ensure that "nickel and diming" of beneficial uses does not occur.
  - 8) An overall philosophy of conservatism must form the basis for all mixing zone assignments. It must be recognized that the lakes do not represent a resource to be divided up and traded away, but rather as a finite resource which is reduced in value by each effluent and mixing zone, with a real loss in beneficial uses. The overall philosophy must be to restrict, to the greatest degree possible, the size and impact of existing and proposed mixing zones.
  - 9) The mixing zone objective must include a mechanism for describing completely the physical, chemical and biological characteristics of existing and proposed effluents.

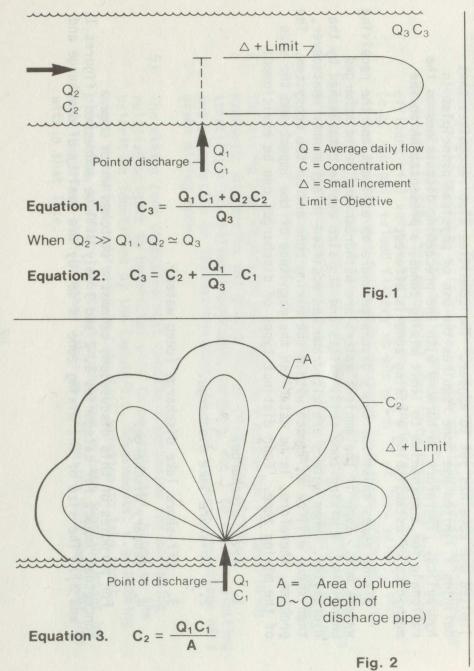
# MECHANISM OF A MIXING ZONE

To date the committee notes that an acceptable mechanism for describing a limited use zone has yet to appear. The committee also recognizes that defining a limited use zone requires the use of physical principles in hydraulics. Therefore in harmony with the preceeding discussions on the rationale for a mechanism to limit mixing zones, a presentation on the mechanics of establishing a mixing zone is offered.

Mixing zones exist for every discharge where an effluent and the receiving waters mix. Even if the ambient waters are withdrawn and are discharged unmodified, a mixing zone still exists and its size can be established by the hydraulics. When waters are withdrawn and modified in any manner whatsoever, then there will be an impact within the mixing zone and on the ecosystem. The problem, therefore, is to establish the magnitude of the impact and the size of the mixing zone. Four distinct types of discharges can be envisioned:

- 1. River discharge.
- 2. On-shore lake discharge.
- 3. Off-shore lake discharge (deep water).
- 4. Estuary discharge.

For purposes of this discussion, schematic sketches which show a conceptual impact for categories 1, 2 and 3 only will be addressed (figures 1, 2 and 3). The size of the mixing zone is set by the quality of discharge and



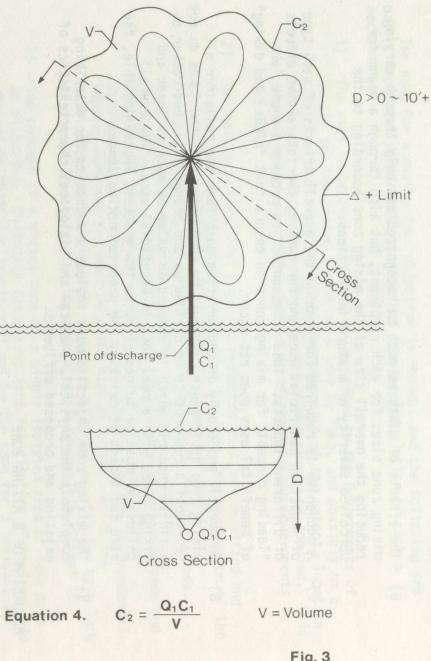


Fig. 3

the desired quality of ambient water. This difference, in terms of volume, is the mixing zone. As a simplifying assumption, the decay factor which exists for certain pollutants such as BOD-DO, temperature, and total residual chlorine, have been neglected. This represents a conservative approach.

The river situation shown in figure 1 would apply within connecting channels such as the Detroit and the Niagara River. It assumes laminar flow. Equation (1) generally applies. However, when  $Q_2$  is much larger than  $Q_1$ , the equation can be simplified as shown in equation (2). Neglecting the decay factor, the mixing zone is then a function of the dilution rate  $Q_2/Q_1$ .

Under the situation shown in figure 2, a mixing zone is the envelope of a number of plumes from the point of discharge. The shape, direction and magnitude of the plumes are a function of physical constraints, dilution rates, littoral current, weather, and time of year. The depth of the discharge point, within the envelope, is generally small; and, therefore, the surface area of the mixing zone is large. In this case equation (3) would apply.

The situation outlined in figure (3) is much more complex because it involves three dimensional flow. In this case there is usually a substantial depth (greater than 10 feet). The mixing zone is generally an envelope of plumes but must consider the entrainment of clean water through the vertical rise. This is generally the result of the jetting action of the effluent. The area on the surface generally approaches a circle while the volume generates a cone. Again, such factors as littoral current, weather and time of year, come into play. The primary difference between situation (3) and situation (2) is that now there is a vertical component in addition to the horizontal component.

The following additional assumptions are taken as given:

- a. Conditions within a mixing zone shall not be injurious to human health in the event of a temporary exposure.
- b. Conditions within a mixing zone shall not be lethal to aquatic life or wildlife which may enter the zone.
- c. The mixing zone shall be free of substances attributable to sewage, industrial wastes, other wastes, pollutant or toxic pollutant in quantities which:
  - 1. settle to form sludge deposits;
  - 2. float as debris, scum or oil;
  - 3. contaminate natural sediments so as to cause or contribute to a violation of
    - i. water quality standards outside the mixing zone or
    - ii. a condition of best usage of such waters;
  - 4. impart a disagreeable flavor or odor to flesh of fish or other aquatic life, wildlife or livestock that are consumed by man and which acquire such flavor or odor because of passage through or ingestion of waters from the mixing zone.

- d. A mixing zone shall be located so as not to interfere significantly with migratory movements, and passage of fish, other aquatic life, and wildlife. Outside the limits of the mixing zone, any waste discharge related to the mixing zone shall not interfere with potable water supply intakes, bathing areas, reproduction of fish, other aquatic life, and wildlife, nor prevent occupation of the waters by fish or other aquatic life normally inhabitating the waters prior to the addition of the waste discharge, or result in any other violation of water quality standards relating to the best usage of the water body.
- e. A mixing zone can only be defined on a case by case basis and should specify definable numerical limits considering such factors as the protected best usage, linear distances from the point of discharge, decay factors, surface area involvement and volume of receiving water within the mixing zone as well as the dilution ratio.

Based upon these assumptions, it must be determined if any mixing zone will impact a limited use zone or a desirable sensitive area. Such uses might consider spawning beds, drinking water supplies and bathing beaches. Several options to change the impact of the site-specific mixing zone are available. They include:

- 1. Modify the quality and quantity of the discharge.
- 2. Move the shore location of the discharge.
- 3. Move the discharge into deeper waters from situation (2) to situation (3).
- 4. Modify the type of diffuser mechanism.

It should be apparent from the above that the establishment of mixing zones is still an art and should not be considered a science. If the decay factor is neglected, the one common parameter than can be established is the dilution ratio. Therefore, the actual size of the mixing zone is a function of time and for complete mixing it can vary from minutes to a day depending upon the diffuser and other site-specific factors. Numbers are available, but it is extremely difficult to generalize. Each case must be considered independently in not only its size and impact but also with the best techniques of handling the situation. Attached is an examaple of a Type 3 situation with reference.

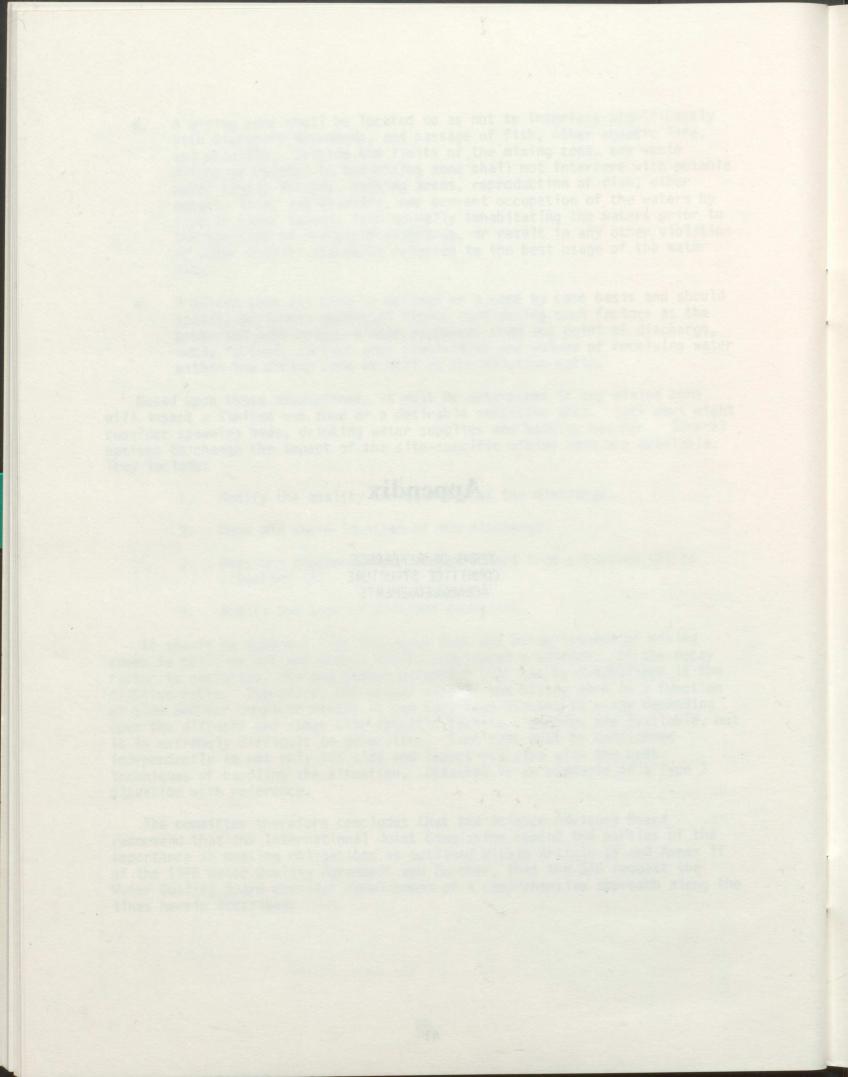
The committee therefore concludes that the Science Advisory Board recommend that the International Joint Commission remind the parties of the importance in meeting obligations as outlined within Article IV and Annex II of the 1978 Water Quality Agreement and further, that the SAB request the Water Quality Board consider development of a comprehensive approach along the lines herein described. Dard will:

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# Appendix

TERMS OF REFERENCE COMMITTEE STRUCTURE ACKNOWLEDGEMENTS

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# TERMS OF REFERENCE

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

- 1. Develop aquatic 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 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

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 scientific matters, and since the Water Quality Board will deal with the 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.

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