

**SEDIMENT AND BIOLOGICAL CONTAMINATION IN THE
CORNWALL-MASSENA SECTION OF THE ST. LAWRENCE RIVER.**


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ABSTRACT

The St. Lawrence River, near Cornwall, Ontario and Massena, New York, was declared an Area of Concern (AOC) by the International Joint Commission in 1985 due to high levels of contaminants in physical and biological components of the environment. A Remedial Action Plan (RAP) was established to identify specific problems and implement remedial measures. As part of the RAP process, the public at large was consulted and one of the identified concerns was the extent of mercury and PCB contamination of bottom sediments. In Chapter 1, we assess the evidence for local origin of mercury and PCB sediment contamination by looking at the spatial relationships between suspected point sources and spatial gradients in sediment contaminant levels. Using analysis of covariance, we found that models containing distance from a suspected point source as an independent variable, for five separate outfall locations, could explain 80% of the variance in mercury sediment concentrations and 58% of the variance in PCB sediment concentrations. Examining the areas downstream of each outfall separately, we found that mercury concentration decreased exponentially with distance away from the Domtar ($r^2=0.87$, $P<0.001$) and Courtauld's ($r^2 = 0.80$, $P<0.001$) outfalls in the north channel of the river and PCBs decreased exponentially with distance away from the G.M. outfall ($r^2 = 0.42$, $P = 0.004$) and from the three south channel outfalls as a group ($r^2 = 0.44$, $p<0.001$). The results strongly suggest that the Domtar and Courtauld's outfalls are (were) important local sources of mercury. Similarly, there is strong evidence that the Grass River (ALCOA), Reynold's and G.M. as a group comprise an important local source of PCBs. These results indicate that local remediation efforts have the greatest potential to improve local conditions.

The public at large in the Cornwall-Massena Area of Concern (AOC) is also concerned about the potential for mercury and PCB sediment contamination to contribute to elevated levels of contaminants in the biota. Studies within the Great Lakes basin have focused on documenting the type and extent of biological contamination. Also required is information on contaminant sources and routes of exposure. More specifically, *local* remediation efforts can yield results if (1) there are local contaminant sources and (2) these local sources are contributing significantly to contamination of the local biota. Chapter 1 addresses the first point. In Chapter 2, we address the second point by examining spatial correlations between mercury and PCB concentrations in sediments and a small nearshore planktivore, the Spottail Shiner (*Notropis Hudsonius*). We found a weak positive linear relationship between sediment and fish mercury ($r^2 = 0.26$, $p = 0.07$), and a strong positive linear relationship between sediment and fish PCBs ($r^2 = 0.90$, $p < 0.001$). These results show that localities of highly contaminated sediments are, in turn, contributing to contamination of the local biota, more so for PCBs than for mercury. We conclude that public policy designed to reduce local emissions and/or exposure will be effective.

RÉSUMÉ

La région du Fleuve St-Laurent près de Cornwall, Ontario, et Massena, New York a été déclaré un secteur préoccupant par la Commission mixte international en 1985 à cause des niveaux élevés de polluants dans les constituants physiques et biologiques de l'environnement. Un Plan d'action correctrice (PAC) a été établi dans le but d'identifier des problèmes spécifiques et de mettre en place des mesures réparatrices. Des consultations publiques, qui font partie du processus PAC, ont réussi à déterminer qu'une des inquiétudes était l'importance de contamination des sédiments du fond par le mercure et les BPC. Dans le Chapitre 1, nous évaluons l'évidence pour l'origine locale de la contamination des sédiments par le mercure et les BPC en regardant les rapports spatiales entre des sources ponctuelles soupçonnées et les gradients spatiaux des niveaux de contamination des sédiments. En utilisant l'analyse de co-variance, nous avons trouvé que les modèles comprenant la distance d'une source ponctuelle comme variable indépendante, pour cinq déversoirs séparés, pourraient expliquer 80% de la variation de la concentration de mercure dans les sédiments et 58% de la variation de la concentration de BPC dans les sédiments. En examinant séparément les régions en aval de chaque déversoir, nous avons trouvé que la concentration de mercure diminuait d'une manière exponentielle avec distance des déversoirs de Domtar ($r^2=0,87$, $p<0,001$) et de Courtauld ($r^2=0,80$, $p<0,001$) dans le lit nord du fleuve. La concentration de BPC diminuait d'une manière exponentielle avec distance du déversoir de G.M. ($r^2=0,42$, $p=0,004$) et du groupe de trois déversoirs dans le lit sud ($r^2=0,44$, $p<0,001$). Les résultats suggèrent fortement que les déversoirs de Domtar et de Courtauld sont (étaient) des sources locales importantes de mercure. De même, il y a des preuves convaincantes que la rivière

Grass (ALCOA), Reynold's, et G.M. sont ensemble une source locale importante de BPC. Ces résultats indiquent que des efforts de réparation locales sont les plus susceptibles d'améliorer les conditions locales.

Le grand public du secteur préoccupant de Cornwall-Massena s'inquiète aussi de la possibilité que la contamination des sédiments par le mercure et les BPC peut contribuer à un niveau élevé de contaminants dans la flore et la faune de la région. Des études dans le bassin des Grands Lacs se sont concentrées sur la documentation du type et de l'importance de la contamination biologique. Il faut aussi de l'information au sujet des sources des polluants et des routes d'exposition. Plus précisément, des efforts de réparation *locales* peuvent donner des résultats si (1) il y a des sources locales de polluants et (2) ces sources locales contribuent d'une manière significative à la contamination de la flore et la faune de la région. Le chapitre 1 s'adresse au premier point. Dans le Chapitre 2, nous nous adressons au deuxième point en examinant des corrélations spatiales entre les concentrations de mercure et de BPC dans les sédiments et dans un petit planctivore littoral, le queue à tache noire (*Notropis hudsonius*). Nous avons trouvé une faible relation linéaire entre le mercure dans les sédiments et dans les poissons ($r^2=0.26$, $p=0.07$), et une forte relation linéaire positive entre les BPC dans les sédiments et dans les poissons ($r^2=0.90$, $p<0.001$). Ces résultats démontrent que les régions avec des sédiments fortement contaminés contribuent à la contamination de la flore et la faune, une tendance qui est plus évident pour les BPC que pour le mercure. Nous pouvons conclure que des politiques publiques ayant pour but de réduire les émissions locales et/ou l'exposition des polluants seront efficaces.

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GENERAL INTRODUCTION

This research was carried out as part of a multidisciplinary project known as Ecosystem Recovery on the St. Lawrence. The project was co-ordinated by the Institute for Research on Environment and Economy at the University of Ottawa and funded by the Eco-Research Tri-Council Secretariat. The principal aim of the project was to identify and propose courses of action needed to rehabilitate the Cornwall basin of the St. Lawrence River and facilitate the sustainable redevelopment of the community in the Cornwall-Akwesasne region. To achieve this, scientists from a broad range of disciplines were brought together to address environmental and socioeconomic problems perceived to be impediments to ecosystem sustainability.

The Ecology and Environmental Biology Team was assembled as a component of the overall project to address problems associated with the health of the environment. A principal task assigned to this team was construction of quantitative models of the effects of anthropogenic stressors on biological response variables in the system. Additionally, it was required that research results be made relevant in terms of public policy.

The research contained in this volume contributes to the task of the Ecology and Environmental Biology group with two distinct research results. First, it was found that areas of high sediment mercury and PCBs are related to important anthropogenic stressors in the area: the locations of industrial outfalls. A useful corollary to this is that mercury and PCB sediment contamination can be attributed to *local* sources. Second, a statistical link is made between anthropogenic stressors (outfall locations and sediment contamination) and a biological response variable: levels of contaminants in a small cyprinid, the Spottail Shiner. These results inform

public policy by providing evidence that remediation initiatives conducted on a local scale will likely be effective.

RESEARCH METHODOLOGY

Chapters 2 and 3 which follow represent only a portion of the work which was carried out during the course of this thesis. Originally, broader questions were posed and a wide data search was initiated in an attempt to locate information sufficient to address these original questions. This chapter provides an overview of this process and of the information sources identified but not used in the last two chapters.

The specific relationships between locations of point sources of pollution, sediment contamination patterns and fish contamination represent a subset of answers to the the types of questions originally posed. At the outset, we intended to establish connections among a larger set of variables. The overarching theme was one of the effects of human activities on ecological variables in the system. Had we been able to gather sufficient information on a variety of both anthropogenic and ecological variables across the St. Lawrence ecosystem we would have tested to see which human activities exert the most influence on the ecology and, the other side of the same coin, which aspects of the ecology are most sensitive to human activity. What follows is a description of the data search which was conducted, the results of that search, and an assessment of why the data found were insufficient to answer the original questions.

Data Search

During the summer and fall of 1994 the following offices were visited in the St. Lawrence River corridor in order to locate existing databases of environmental information:

AGENCY	OFFICES
Ontario Ministry of Natural Resources	Cornwall, Kemptville, Napanee, Brockville
Environment Canada	Hull, Kingston, Toronto, Belleville
Canadian Center for Inland Waters (Environment Canada, NWRI)	Burlington
Centre St. Laurent	Montreal
St. Lawrence Islands National Park	Kingston

At each office the following tasks were carried out:

- information holdings searched and reviewed
- discussions held with personnel
- information gathered where appropriate
- follow-ups made after visit to obtain data that was not available at the first visit

Two of the largest listings of published environmental data in Canada were also searched:

Databases for Environmental Analysis: Government of Canada. Statistics Canada, Ottawa, 1992.

Envirosourc. Reference Directory to Information Holdings. Environment Canada. Minister of Supply and Services Canada. 1991.

These sources were thoroughly reviewed for possible databases, contacts were made for candidate sources and data was obtained where appropriate.

Data Acquisition

From the sources listed in the previous section the following databases were obtained.

They were reviewed for suitability using criteria such as spatial locations and extent of sampling points, type of variables (human activity versus ecological), and proximity to the Cornwall Area of Concern.

Anderson, J. 1988. Sediment Quality of the St. Lawrence River Near Maitland, 1984. WRB/MOE St. Lawrence River Environmental Investigations Vol. 3

Anderson, J. 1990. Assessment of Water and Sediment Quality in the Cornwall Area of the St. Lawrence River, 1985. WRB/MOE St. Lawrence River Environmental Investigations V.4

Biberhofer, J. 1988. Cornwall /Massena Surveillance Program. Water Data.

Blokpoel, H. 1977. Gulls and terns nesting in northern Lake Ontario and the upper St. Lawrence River. Can. Wildl. Serv. Progress notes No. 75.

Bonin, J., J.L.DesGranges, C.A. Bishop, J. Rodrigue, A. Gendron and J.E. Elliot. 1994. Comparative study of contaminants in the mudpuppy (*Amphibia*) and common snapping turtle (*Reptilia*), St. Lawrence River Canada. Archives of Environmental Contamination and Toxicology.

Drinking Water Surveillance Program (DWSP) Data, 1990. Raw and Treated Water Samples. Drinking Water Section, Water Resources Branch, MOE.

Erskine, A.J., B.T. Collins. 1989. The Breeding Bird Survey in Canada, 1966-83: analysis of trends in breeding bird populations. Can. Wildl. Serv. Tech. Rep. No.75.

Griffiths, R.W. 1988. Environmental Quality Assessment of the St. Lawrence River in 1985 As Reflected by the Distribution of Benthic Invertebrate Communities. OMNR. Water Resources Branch.

Juvenile Fish Database. Karl Sun. Water Resources Branch, Watershed Management, MOEE. Ontario Ministry of Natural Resources.

Kauss, P.B., Y.S. Hamdy, and B.S. Hama. 1988. Assessment of Water, Sediment and Biota in the Cornwall, Ontario and Massena, New York Section of the St. Lawrence River, 1979-1982. WRB/MOE St. Lawrence River Environmental Investigations Vol. 1

Metcalf, J.M. and M.N. Charlton, 1990. Freshwater Mussels as Biomonitors for Organic Industrial Contaminants and Pesticides in the St. Lawrence River. Sci. Total Environ., 97/98: 595-615.

MOE Sportfish Database, 1981-1991. 14 Stations Along the St. Lawrence River, From Kingston to Lake St. Francis.

Ontario Ministry of Natural Resources. Index Netting - 1985-1993.

Ontario Ministry of Natural Resources. Creel Census - 1985-1993.

Persaud, D., 1987. The In-Place Pollutants Program, Vol. III Phase I Studies. WRB/MOE.

Report Discharges From Municipal Sewage Treatment Plants in Ontario. MISA-Municipal Water Resources Branch, MOE. 1987, 88, 89, 90.

Richman, L. 1991. St. Lawrence River Sediment and Biological Assessment 1990. WRB/MOE Data Report.

Ross, R.K. 1989. A Re-Survey of Migrant Waterfowl Use of the Ontario St. Lawrence River and Northeastern Lake Ontario. Technical Report Series No. 52, Canadian Wildlife Service.

Shields, J.A., Tarnocai, C., and Valentine, K.W. Soil Landscapes of Canada. Agriculture Canada, Ottawa, 1991.

Struger, J., J.E. Elliot, C.A. Bishop. 1993. Environmental contaminants in eggs of the common snapping turtle (*Chelydra serpentina serpentina*) from the Great Lakes - St. Lawrence River basin of Ontario, Canada (1981, 1984). J. Great Lakes Res. 19(4): 681-694.

Tributary Data, 1980-1992. 12 Major Canadian Tributaries from Kingston to Lake St. Francis, Some of Which Were Sampled at 3 Varying Points Away from the St. Lawrence River.

Data Selection

The databases and studies listed above represent a large proportion of the information related to human activity and ecological variables in the section of the St. Lawrence River from Kingston to Lake St. Francis. In general, there is less information than one might expect. Most of the toxicological data have been collected in close proximity to known industrial complexes and very little sampling has been carried out in the intervening sections of the river. For example, the area in front on Dupont, near Maitland, has been heavily sampled, but almost no information can be found downstream until one gets close to the industrial section of the river near Cornwall and

Massena. Areas upstream of Dupont, where there is relatively little industrial activity, are also devoid of data.

Data on ecological variables have, not surprisingly, been collected with very specific ends in mind. Practically no data exist on general parameters of wildlife populations or species diversity on a river-wide scale. On the surface, it may appear as though the Ministry of Natural Resources Sportfish Database ought to be able to provide river-wide information on fish toxicological parameters, however upon closer examination it was revealed that the link between toxicological measurements in individual fish and the exact location at which the fish was caught was not preserved. This is because the agency which caught the fish (OMNR) did not carry out the tissue analyses of each fish. This was done by the Ontario Ministry of the Environment, whose goal was to update the *Guide to Eating Sportfish in Ontario*. These analyses, however, do not require exact locations at which fish were caught, but rather base recommendations on wide general areas. Such areas are not at a spatial resolution sufficient to conduct correlations with site-specific anthropogenic variables. Thus, the differences in the goals of the two agencies have resulted in information loss which precludes certain types of analyses.

The data that were eventually selected and used in chapters 2 and 3 were chosen because they :

- 1) were geographically situated so as to be relevant to the Cornwall/Massena AOC
- 2) represent important anthropogenic activities in the area
- 3) represent an aspect of the local biota which is a food source for sportfish
- 4) represent a set of independent and dependent variables for which there are measurements in approximately the same locations

In hindsight, it is fairly clear that the data necessary to test hypotheses about relationships among anthropogenic and ecologic variables on a river-wide scale do not exist. Most information is clumped around industrial complexes, and spatial overlap among variables is rare.

Thus, the questions asked in chapters 2 and 3 are the result of applying the criteria listed above and of conditions and limitations imposed by existing data. The variables used represent the few variables in the system which are sufficient to investigate relationships between human activity and ecological variables.

**ENDOGENOUS POINT SOURCES AND SEDIMENT CONTAMINATION IN THE
CORNWALL-MASSENA SECTION OF THE ST. LAWRENCE RIVER**

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ABSTRACT

The St. Lawrence River, near Cornwall, Ontario and Massena, New York, was declared an Area of Concern (AOC) by the International Joint Commission in 1985 due to high levels of contaminants in physical and biological components of the environment. A Remedial Action Plan (RAP) was established to identify specific problems and implement remedial measures. As part of the RAP process, the public at large was consulted and one of the identified concerns was the extent of mercury and PCB contamination of bottom sediments. In this paper, we assess the evidence for local origin of mercury and PCB sediment contamination by looking at the spatial relationships between suspected point sources and spatial gradients in sediment contaminant levels. Using analysis of covariance, we found that models containing distance from a suspected point source as an independent variable, for five separate outfall locations, could explain 80% of the variance in mercury sediment concentrations and 58% of the variance in PCB sediment concentrations. Examining the areas downstream of each outfall separately, we found that mercury concentration decreased exponentially with distance away from the Domtar ($r^2=0.87$, $P<0.001$) and Courtauld's ($r^2 = 0.80$, $P<0.001$) outfalls in the north channel of the river and PCBs decreased exponentially with distance away from the G.M. outfall ($r^2 = 0.42$, $P = 0.004$) and from the three south channel outfalls as a group ($r^2 = 0.44$, $p<0.001$). The results strongly suggest that the Domtar and Courtauld's outfalls are (were) important local sources of mercury. Similarly, there is strong evidence that the Grass River (ALCOA), Reynold's and G.M. as a group comprise an important local source of PCBs. These results indicate that local remediation efforts have the greatest potential to improve local conditions.

Key words: Mercury, PCB, St. Lawrence River, Sediments, Point Source

INTRODUCTION

The St. Lawrence River has long been used by humans for transportation, hydroelectric power and as a sink for human and industrial wastes (Government of Canada, 1991). The section of the river near Cornwall, Ontario and Massena, New York was an area of intense industrial activity from the late 19th century through the 1960's and 1970's. Local pulp and paper production, synthetics manufacturing, car manufacturing and aluminum smelting are all potential local sources of contamination of water, bottom sediments and biota (RAP, 1992). Indeed, in 1985 the International Joint Commission declared this stretch of the river to be an *Area of Concern* (AOC) (IJC, 1985). Under the Great Lakes Water Quality Agreement, identification of a location as an AOC requires the implementation of a Remedial Action Plan (RAP). A RAP involves three stages: 1) definition and description of environmental problems and impaired uses; 2) selection of remedial measures and implementation plans; and 3) monitoring to determine if environmental integrity has been restored. The RAP process is driven by public consultation: environmental problem definition and hence, remediation targets are defined by members of a Public Advisory Committee who solicit the views of the public at large. The scientific community then attempts to develop a set of strategies designed to address the specific environmental concerns raised by the community.

A major community concern in the Cornwall-Massena AOC is the type and extent of sediment contamination (PAC, 1994). Kauss (1988), Anderson (1990), Richman (1991) and Sloterdijk (1991) have all reported elevated levels of certain contaminants in the AOC or in Lake St. Francis immediately downstream. Of these contaminants, mercury and PCBs have received

much attention because they have been recorded at levels exceeding provincial sediment quality guidelines and because of their potential to negatively impact important elements of the biota. Moreover, both substances can pose important human health risks (Futatsuka, 1989; Sun 1983). Sources of sediment contamination in the Cornwall-Massena AOC may be endogenous (i.e. of local origin) or exogenous. Possible local sources include industrial outfalls around Cornwall and Massena and deposition from local atmospheric emissions (RAP, 1992). Exogenous sources may include pollution generated in the Great Lakes and transported downstream. From a remediation perspective, this difference is critical: if contaminant sources are largely exogenous, then local remediation efforts will have little effect; whereas if there are important local sources, these can be targeted and local remediation efforts are more likely to improve local conditions.

In this paper, we assess the evidence for local origin of mercury and PCB sediment contamination by looking at the spatial relationships between suspected point sources and spatial gradients in sediment contaminant levels. If sediment contamination were largely of local origin, we would expect to see a distance decay pattern downstream of suspected sources. Such gradients are commonly observed near point sources of pollutants in terrestrial, atmospheric and aquatic components of the environment (Moore *et al.*, 1991; Winger *et al.*, 1993, Vallack and Chadwick, 1993; Lepsova and Mejstrik, 1988; Lepsova and Kral, 1988; Fuller *et al.*, 1990).

METHODS

The study area is located in the St. Lawrence River, downstream of the Moses-Saunders power dam and extends just east of the confluence of the St. Regis River (Fig. 1). This area falls

within the provinces of Ontario and Quebec and the state of New York. Water flows, from west to east, around Cornwall Island, forming a north and a south channel. Flow is swift, between 5 and 8 knots, and more or less unidirectional in the north channel. Water destined for the south channel is funnelled at high speed (about 8-9 knots) through a narrow opening just off the west end of Cornwall Island (Polly's Gut), and is deflected by a stone wall located directly in the channel. This creates a large vortex, spanning the width of the river, in front of Reynold's Aluminum. Downstream of the vortex, the water flow is slower and more or less unidirectional (Morin *et al.*, 1994).

Sediment contamination data for total PCBs and mercury were obtained from published sources (Kauss, 1988; Anderson, 1990; Richman, 1991). These studies used either Shipek or Ponar grabs to collect the upper 3 centimetres of sediment from the river bottom. Total PCBs, the measure used in the original studies, refers to a non-congener specific arochlor profile (arochlor 1242, 1248, 1254, 1260). Sampling locations were combined from these three studies in order to use all possible historical sampling locations in the study area. Multiple measurements were averaged at each sampling location resulting in one datum per station for each of the two contaminants. A total of 47 mercury and 39 PCB sites were used in the analysis. The sampling locations were placed on a map of the study area using SPANS geographic information system. This was done using published latitude/longitude co-ordinates where possible and estimated using published maps otherwise (Figs. 2, 3). Distances from point sources to sampling sites were measured in the GIS by taking a straight line distance from point to point.

Sediment contaminants are hypothesized to originate from five suspected point sources: Domtar Fine Papers, Courtauld's Fibres (now closed), the mouth of the Grass River (Aluminum

Company of America located just upstream), Reynolds Aluminum, and General Motors (Fig. 1). The location of the outfall pipe for each complex was placed in the GIS using the Ontario Ministry of the Environment Great Lakes Intake - Outfall Atlas (Griffiths, 1990).

The statistical relationships between the locations of the suspected point sources and the distributions of PCBs and mercury in river sediments were examined using analysis of covariance (ANCOVA), with contaminant concentration as the dependent variable and 1) downstream distance from a point source and 2) categories, from one to five, representing each point source as the independent variables. The best models were chosen by testing all possible combinations of the variables.

To visualize the spatial character of the results of the ANCOVA models, response surfaces were constructed. To do this, a field of points was defined across the study area in the GIS. Model estimates, both for mercury and PCBs, were then calculated for each point in the field. These estimates were then used to create an interpolated surface throughout the study area. The interpolation procedure used is known as potential mapping and is equivalent to creating a trend surface map from the point data (Intera Tydac, 1993). We chose this method over other, more theoretical procedures for investigating gradients, such as kriging, because the purpose was to supplement our primary analysis with a visual aid rather than analyze the data directly using a spatial technique.

Skalski (1995) argues that in studies of the spatial character of environmental contaminants, such as this one, replication of sampling sites is difficult, and true replication exists only at the level of an entire pattern. This leads to questions about the statistical independence of sample points. In our study this problem must be addressed both on a spatial and temporal scale.

Recent work on the type and movement of sediments in the study area has shown that sediments are very heterogeneous over distances of one to four meters and that they move over relatively short periods of time (Rukovena, unpublished data). Since most of the sample points used in this study are much greater than four meters apart and data has been averaged over several years, sample points used in the regression analyses probably satisfy the assumption of statistical independence.

RESULTS

Levels of mercury and PCBs measured in the studies from which our data were drawn are depicted in Figures 2 and 3. The highest levels of mercury, between 17 and 21 $\mu\text{g/g}$, occur in the north channel, downstream of the Domtar and Courtauld's outfall pipes. Here, the greatest amount of mercury is found very close to the outfall locations with levels decreasing with increasing distance downstream from each suspected point source. Mercury is lower, between 0.1 and 4 $\mu\text{g/g}$, in the south channel. The north channel levels are well above the severe effect level of 2 $\mu\text{g/g}$, set out by Ontario provincial sediment quality guidelines for metals, and a few of the south channel levels are above the lowest effect level of 0.2 $\mu\text{g/g}$ (Persaud and Jaagumagi, 1993).

The pattern is reversed for PCBs, with the highest levels, between 8 and 13.8 $\mu\text{g/g}$, occurring in the south channel close to the mouth of the Grass River, the Reynold's Aluminum outfall and the General Motors outfall (Fig. 3). PCB concentrations are comparatively low, below

1 µg/g, in the north channel. The provincial guidelines state a severe effect level of 530 µg/g and a lowest effect level of 0.7 µg/g for sediment PCBs (Persaud and Jaagumagi, 1993).

The general form of the ANCOVA model describing contaminant concentration as a function of distance from a suspected point source is:

$$\text{Ln}[\text{contaminant}] = \text{constant} + \text{Ln}(\text{Distance}) + \text{Pipe} + \{\text{Ln}(\text{Distance}) * \text{Pipe}\} \quad (\text{eq. 1})$$

where *[contaminant]* is the concentration of mercury or PCBs, *Distance* is the straight line distance from the nearest upstream outfall to the location where the contaminant concentration was measured, *Pipe* is a categorical variable representing each of the five outfall locations and *Distance * Pipe* is an interaction between the first two variables. *Pipe* tests for the magnitude of the Y intercept for each of the five point sources, which is the contaminant concentration at zero distance from a source, *Distance * Pipe* tests for the slope or rate of change of contaminant concentration as one moves away from a source.

Eighty percent of the observed variance in sediment mercury concentration is explained by the fitted ANCOVA model (Table 1). Both the continuous (distance) and the categorical (pipe) variables are significant, as is the interaction term (distance * pipe). This means that levels of mercury at the various outfall pipes differ significantly. Sediment mercury concentration then decreases exponentially with distance from the pipes, at rates that differ among pipes. Examining the areas downstream of each pipe separately, we found that significant negative relationships between concentration and distance downstream of the suspected source exist for both the Domtar and Courtauld's point sources (Fig.'s 6, 7; Table 2). No significant relationships between

mercury concentration and distance were found for the three sources in the south channel.

Sediment mercury in this area was uniformly low.

About two thirds of the variance in the PCB data is explained by the overall ANCOVA model ($r^2 = 0.58$, Table 1). Sediment PCB concentration at the outfalls differs significantly among pipes. In contrast to the mercury model, sediment PCB concentration does not decrease systematically with distance. Rather, there is a significant interaction between pipe and distance. Examining data downstream of each pipe individually, we found sediment PCB concentration decreased significantly with distance only from the last outfall in the south channel of the river, the General Motors foundry (Fig. 8, Table 2). However, if the all the PCB data in the south channel only (Domtar and Courtauld's not included) are pooled and the mouth of the Grass River is taken as distance zero, a regression of $\ln(\text{PCB})$ versus Distance produces a significant distance decay relationship (Fig. 9, Table 2). Pooling the data in this way can be considered equivalent to combining the three sources in the south channel into one diffuse point source.

A separate analysis was carried out to test whether the particular study which the data came from has an effect on the distance decay model. Coding each observation according to the study it came from and using 'study' as an independent variable shows that there is no significant effect of 'study' for either the mercury or the PCB models (Appendix C).

DISCUSSION

The results show that the predicted distance-decay pattern is observed for sediment mercury in the north channel of the river. The decay is exponential and strongly suggests that the

Domtar and Courtauld's outfalls are or were, in the case of Courtauld's, important local sources of mercury. The Domtar outfall, or the Domtar diffuser, discharges effluents from Domtar Fine Papers, ICI (formerly CIL), Cornwall Chemicals and Stanchem directly into the river. According to samples collected for the Stage I RAP report, ICI, Cornwall Chemicals and Stanchem effluents exceeded the Ontario Industrial Effluent Objective for mercury of 0.001 mg/L (RAP, 1992). Prior to 1970, high levels of mercury were discharged into the river by the CIL chlor-alkali plant and by Domtar, before their use of mercurial slimicide was phased out (Kauss, 1988). Courtauld's closed in 1989, but prior to that, its effluent contained mercury levels exceeding the Ontario Industrial Effluent Objectives (RAP, 1992). This information confirms that there have been significant industrial sources of mercury in the north channel and our results are consistent with this. The Domtar diffuser received effluents from several mercury-producing plants in contrast to the Courtauld's point source which received effluent from Courtauld's only. This explains the higher y-intercept for Domtar (Table 2). Mercury concentrations decrease very quickly downstream of the north channel outfalls, as indicated by the regression coefficients in Table 2. The industries located in the south channel, on the other hand, (ALCOA, Reynold's and G.M.), are not known to discharge mercury (Kauss, 1988). This is also consistent with our results, which show low levels of mercury and no distance-decay pattern in the south channel.

For PCBs, a distance-decay pattern is apparent in the south channel. We cannot distinguish signatures of individual point sources, but as a group, there is strong evidence that the Grass River (ALCOA), Reynold's and G.M. comprise an important local source. All three have discharged various amounts of PCB-containing effluent at some time. General Motors was perhaps the greatest contributor because of the use of PCB-based hydraulic fluid in die-casting

machines up until 1973 (Kauss, 1988). Discharge of PCBs by industries in the north channel has been insignificant, and our results confirm this.

The signatures of individual point sources are probably not distinguishable because of the flow dynamics in the area. Water flows, from west to east, at high speed through a narrow channel known as Polly's Gut, just off the west end of Cornwall Island. Much of this water is diverted by a large stone deflector located in the channel. As a result, a large vortex is created in front of Reynold's, spanning the width of the river (Morin *et al.*, 1994). Given this, one would not expect to observe a simple distance-decay from a source, but rather a deposition pattern determined by the specific forces of the water flow. Despite this complex hydrological regime, when all three sources are combined PCBs decay with increasing distance from the G.M. outfall. This indicates that the area as a whole acts as a large point source. In contrast to the north channel, the decay is linear, not exponential. Again, this is likely due to the hydrological regime of the south channel.

Atmospheric emissions are another potential source of contaminants. The chlor-alkali plant operated by ICI (formerly CIL) is known to discharge mercury into the atmosphere. Rennie (1985) showed that 90 percent of these emissions fall out within 1 kilometre of the plant. However, very little of this reaches the river itself because the nearest shoreline is greater than 1 kilometre away and because of the low frequency of north or northwest winds (RAP, 1992). There are no sources of atmospheric PCBs in the AOC (RAP, 1992). It is well recognized that contaminants from the Great Lakes can flow into the St. Lawrence River. Despite this, most of the existing data centres on areas of known contamination, usually in the vicinity of industrial activity. Very little information exists on sediment quality in reaches of the river where industrial

activity is absent. One exception is the study by Richman (1991) where two stations well upstream of the AOC were sampled. Mercury concentrations at both stations were comparable to the lowest concentrations in our dataset. Sylvestre (1987) detected low levels of PCBs in water and suspended sediments at Wolfe Island (outlet of Lake Ontario). However, it is difficult to say whether this is contributing to contamination as far downstream as Cornwall because very little contaminant data exists for the intervening stretch of the river between Lake Ontario and our study area.

In conclusion, we feel that the evidence presented in this paper supports the hypothesis that mercury and PCB sediment contamination in the Cornwall-Massena AOC is associated with local sources. Although additional data is scarce, it appears as though exogenous sources are not contributing significantly to this contamination. This indicates that remediation activities targeted at local sources have the greatest potential to improve conditions in the area.

ACKNOWLEDGEMENTS

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Table 1. Analysis of covariance for mercury and PCBs as a function of distance from all suspected point sources. $Ln(D)$ is the straight line distance from the nearest upstream outfall to the location where the contaminant concentration was measured, $Pipe$ is a categorical variable representing each of the five outfall locations and $Distance * Pipe$ is an interaction between the first two variables.

Source	SS	DF	MS	F-Ratio	P	Overall R ²
Mercury						
Ln(D)	9.08	1	9.08	9.85	0.003	-
Ln(D)*Pipe	50.06	4	12.51	13.58	< 0.001	-
Pipe	59	4	14.75	16.01	< 0.001	-
Error	34.09	37	0.92	-	-	-
Model	-	-	-	-	-	0.80
PCBs						
Ln(D)*Pipe	23.94	4	5.98	4.37	0.01	-
Pipe	18.22	4	4.55	3.33	0.02	-
Error	41.06	30	1.37	-	-	-
Model	-	-	-	-	-	0.58

Table 2. Relationship between contaminant concentration and distance downstream from individual and combined point sources.

Suspected Point Source	Model	a ± 1 S.E.	b ± 1 S.E.	df	r ² , rms, p
<i>Mercury</i>					
Domtar	$\text{Ln}(\text{Hg}) = a + b \cdot \text{ln}(D)$	18.97 ± 2.81	-2.72 ± 0.40	6	0.87, 0.56, <0.001
Courtald's	$\text{Ln}(\text{Hg}) = a + b \cdot \text{ln}(D)$	12.99 ± 1.95	-1.82 ± 0.26	11	0.80, 0.70, <0.001
<i>PCBs</i>					
G.M.	$\text{Ln}(\text{PCB}) = a + b \cdot \text{ln}(D)$	6.60 ± 2.59	-1.05 ± 0.31	14	0.42, 1.56, 0.004
<i>PCBs</i>					
Grass R., Reynold's and G.M. Combined	$\text{Ln}(\text{PCB}) = a + b \cdot (D)$	0.40 ± 0.52	-0.0003 ± 0.00007	21	0.44, 1.84, <0.001

FIGURE LEGENDS

- Figure 1. Study area and locations of the five suspected point sources examined.
- Figure 2. Sediment mercury concentrations measured at all sampling locations.
Symbol sizes vary continuously and are proportional to the concentrations.
- Figure 3. Sediment PCB concentrations measured at all sampling locations.
Symbols sizes vary continuously and are proportional to the concentrations.
- Figure 4. Interpolated response surface of estimated mercury concentrations generated by the ANCOVA model presented in table 1.
- Figure 5. Interpolated response surface of estimated PCB concentrations generated by the ANCOVA model presented in table 1.
- Figure 6. The natural logarithm of the sediment mercury concentration immediately downstream of the Domtar outfall, expressed as a function of the natural logarithm of the distance from the outfall.
- Figure 7. The natural logarithm of the sediment mercury concentration immediately downstream of the Courtauld's outfall, expressed as a function of the natural logarithm of the distance from the outfall.

Figure 8. The natural logarithm of the sediment PCB concentration immediately downstream of the G.M. outfall, expressed as a function of the natural logarithm of the distance from the outfall.

Figure 9. The natural logarithm of sediment PCB concentrations downstream of all three south channel outfalls (black triangles), expressed as a function of the distance from the mouth of the Grass River (first point source in the south channel).

FIG. 1

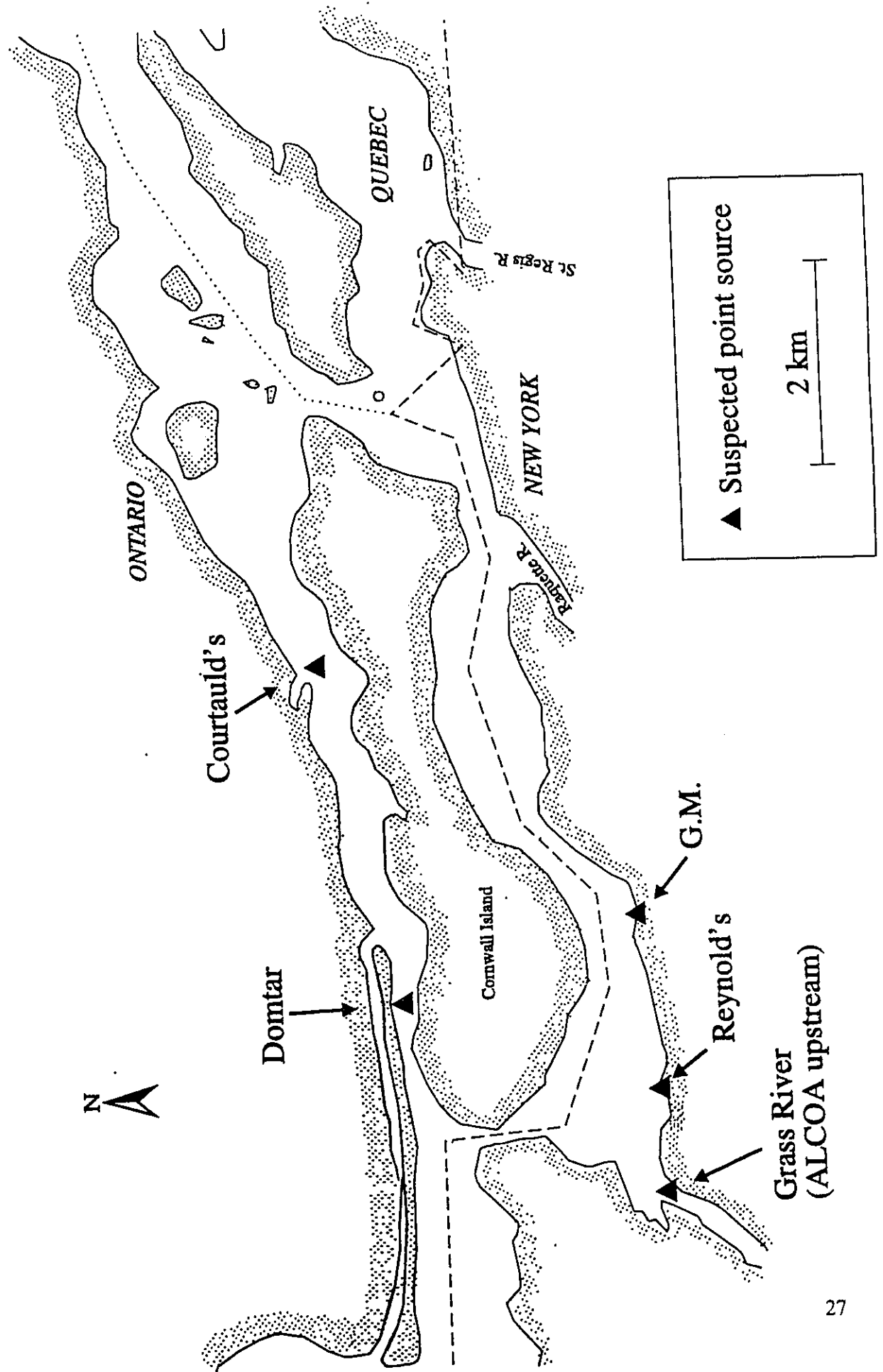


FIG. 2

Mercury Concentration ($\mu\text{g/g}$)

- 0.1
- 4
- 8
- 13
- 17
- 21

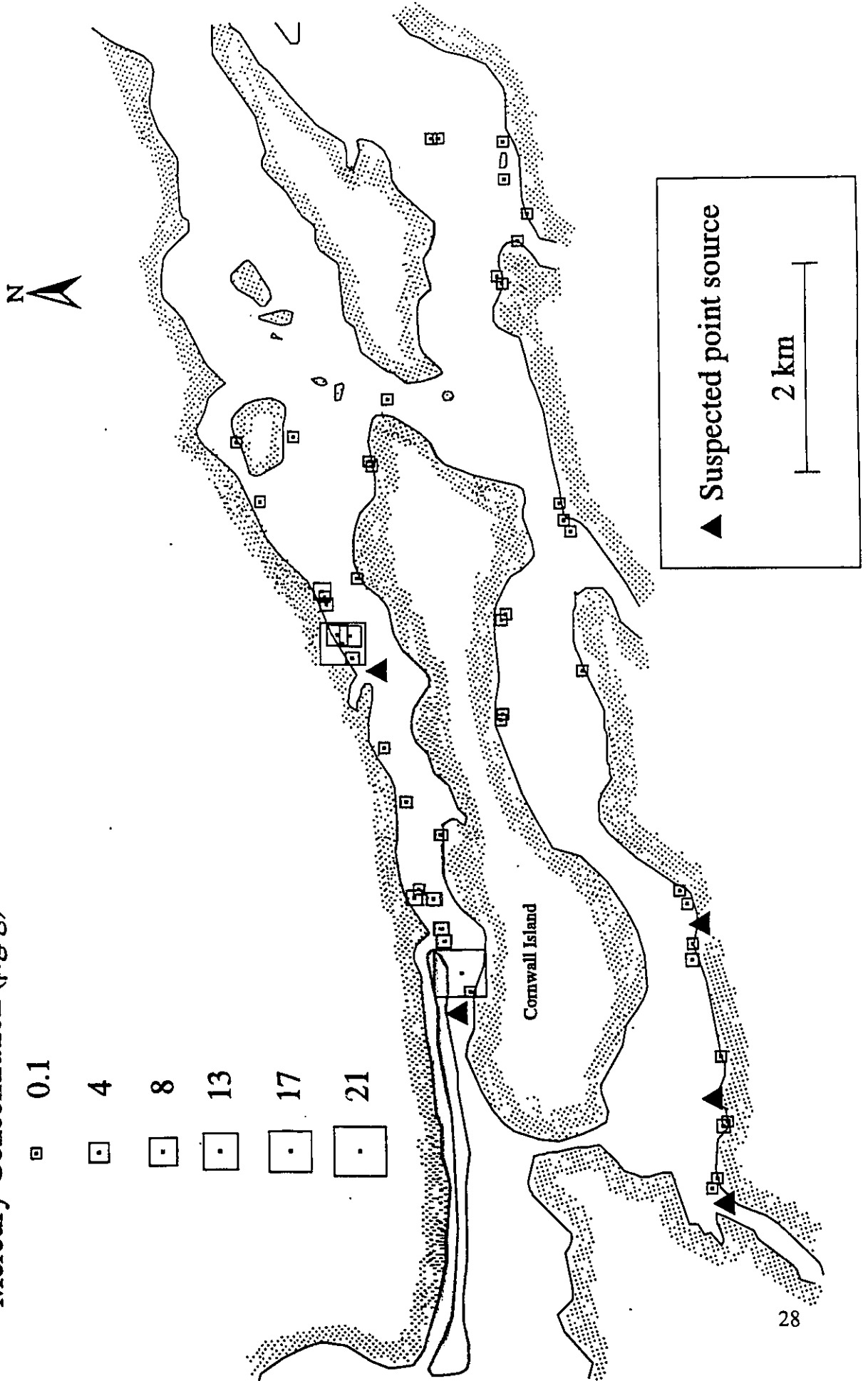


FIG. 3

PCB Concentration ($\mu\text{g/g}$)

- 0.018
- 2.7
- 5.5
- 8.2
- 11.0
- 13.8

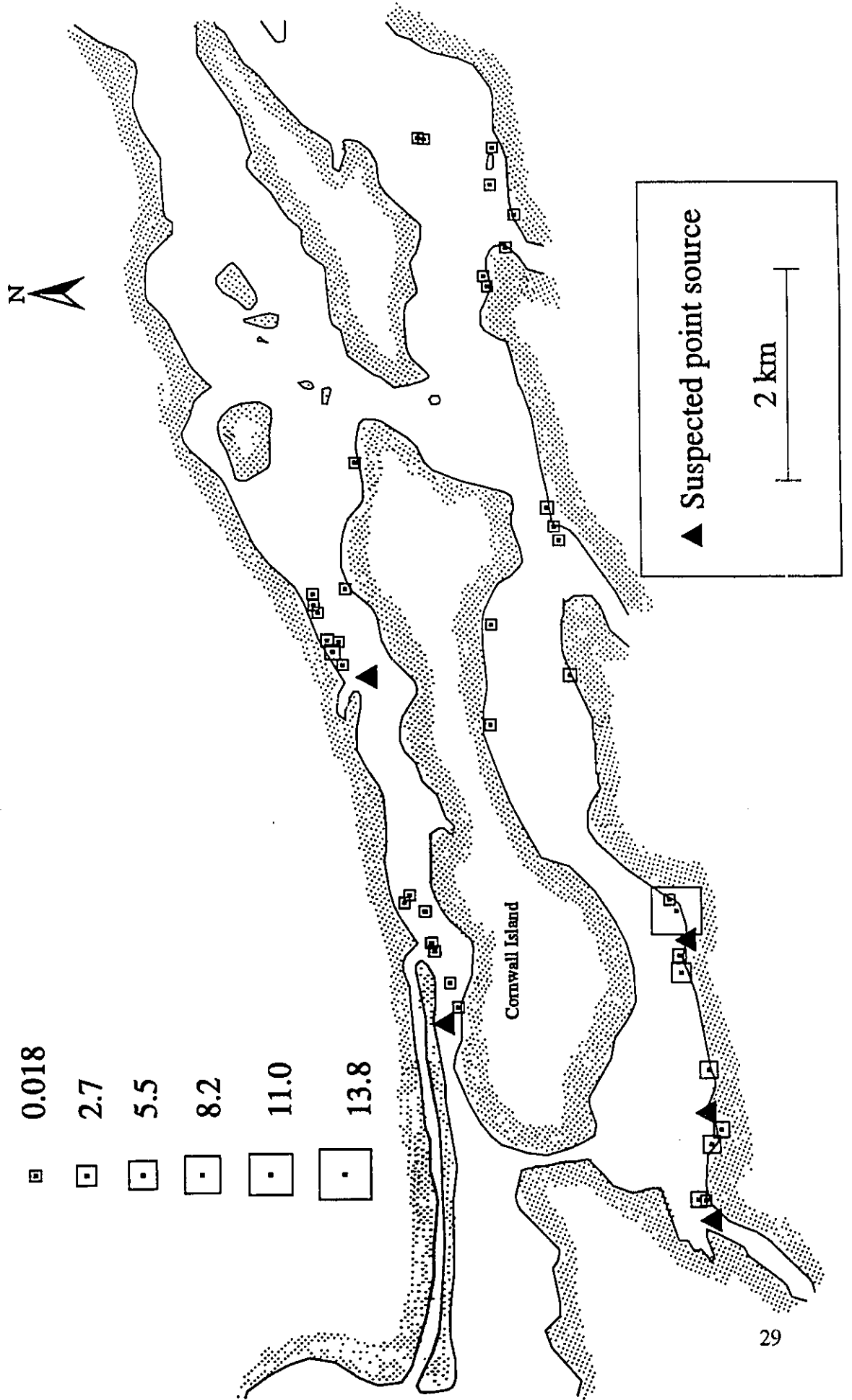


FIG. 4

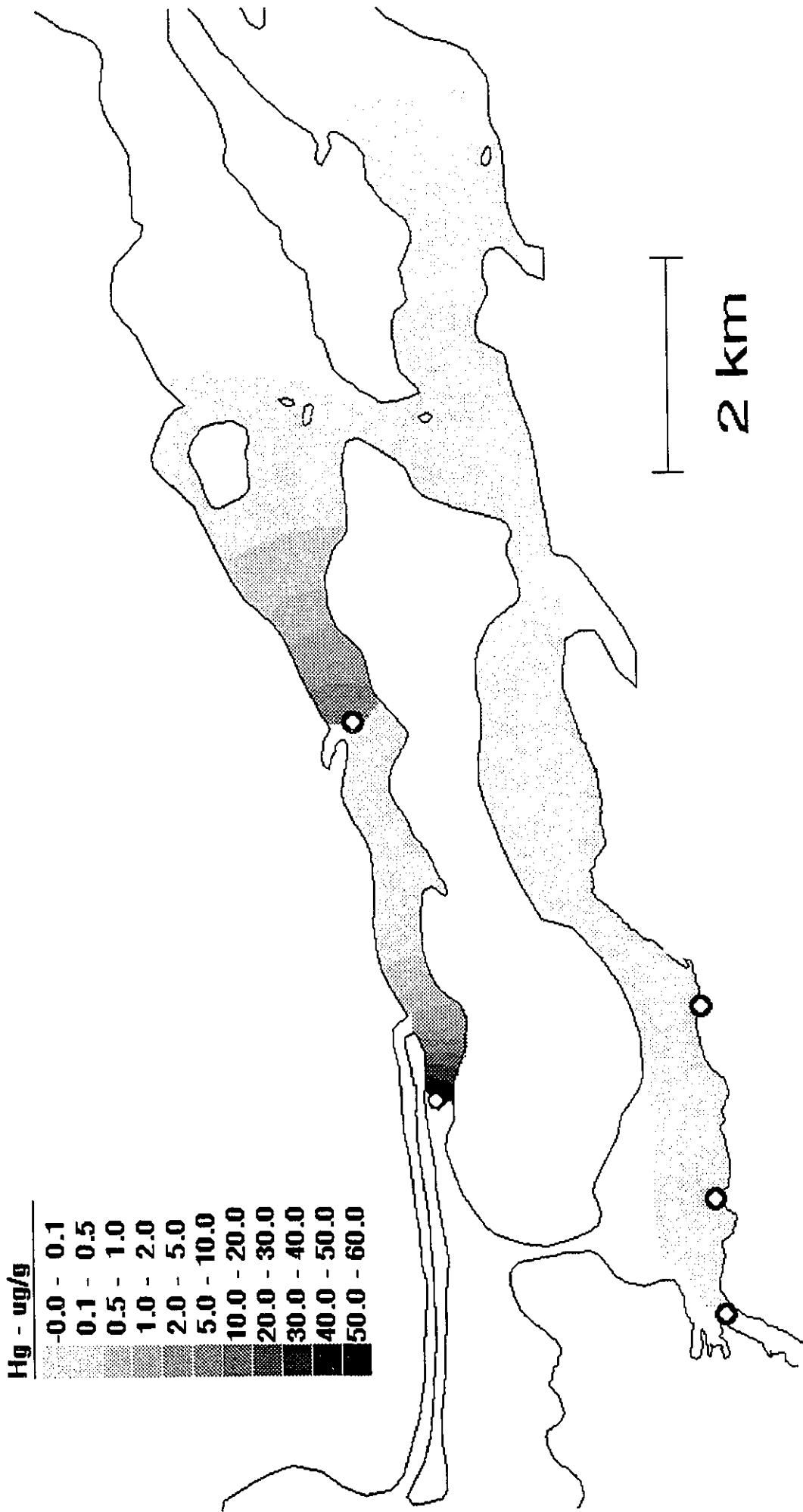


FIG. 5

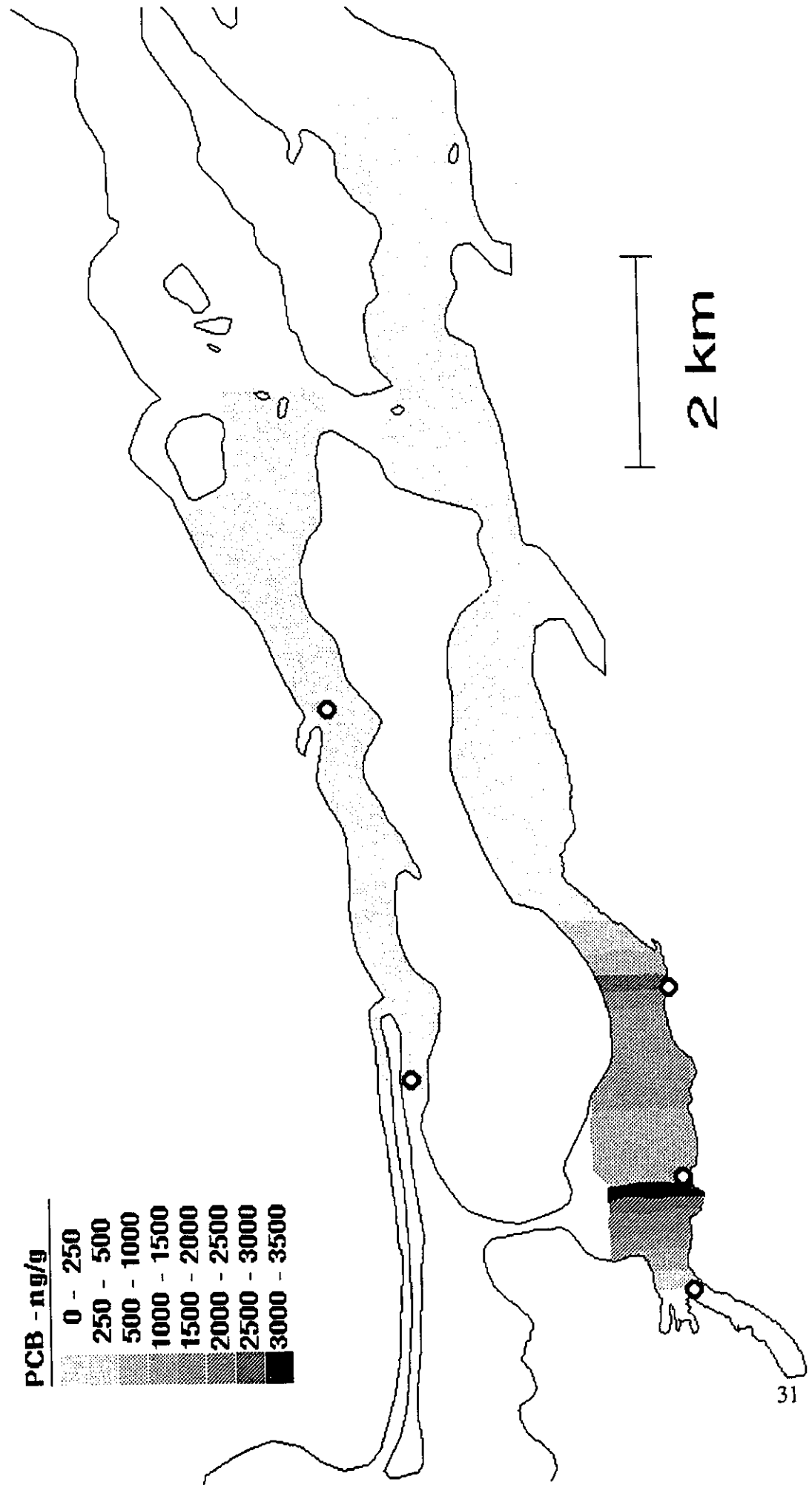


FIG. 6

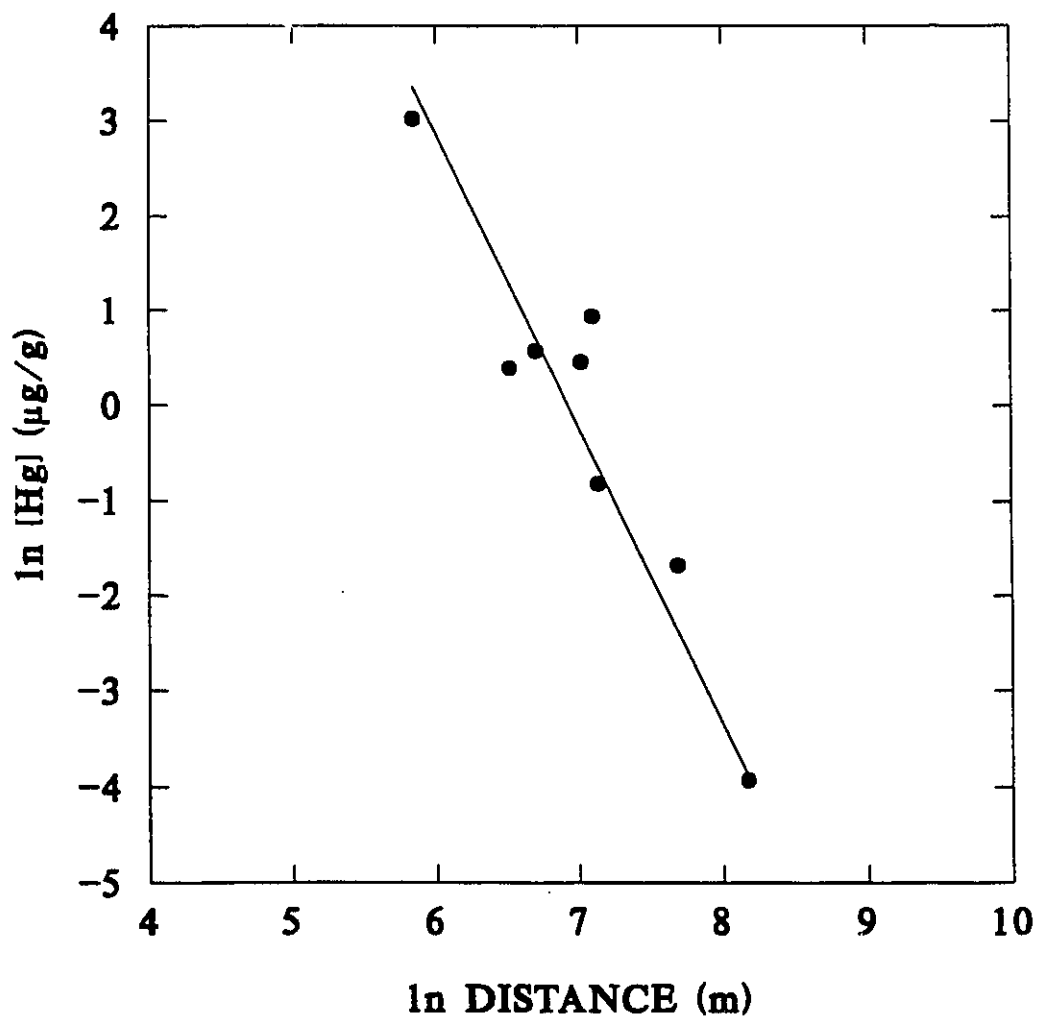


FIG. 7

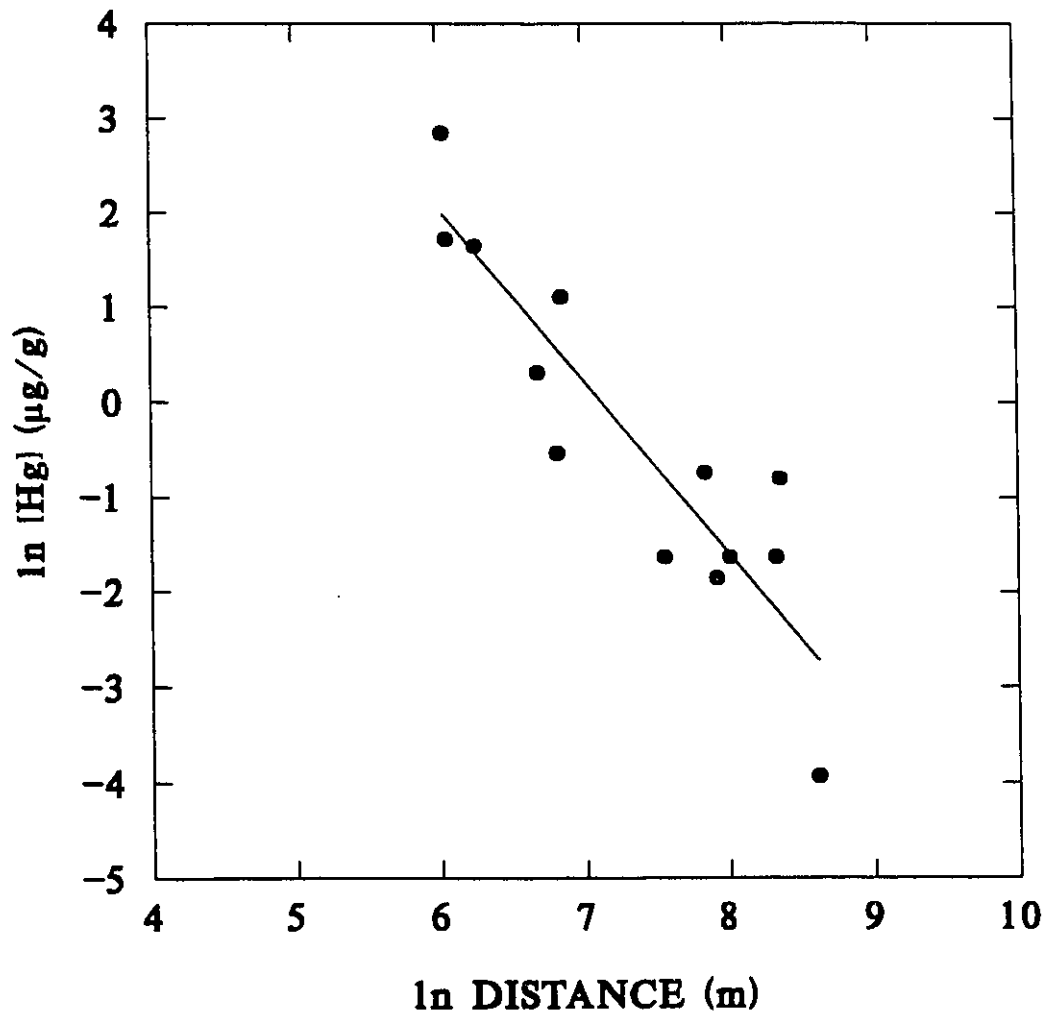


FIG. 8

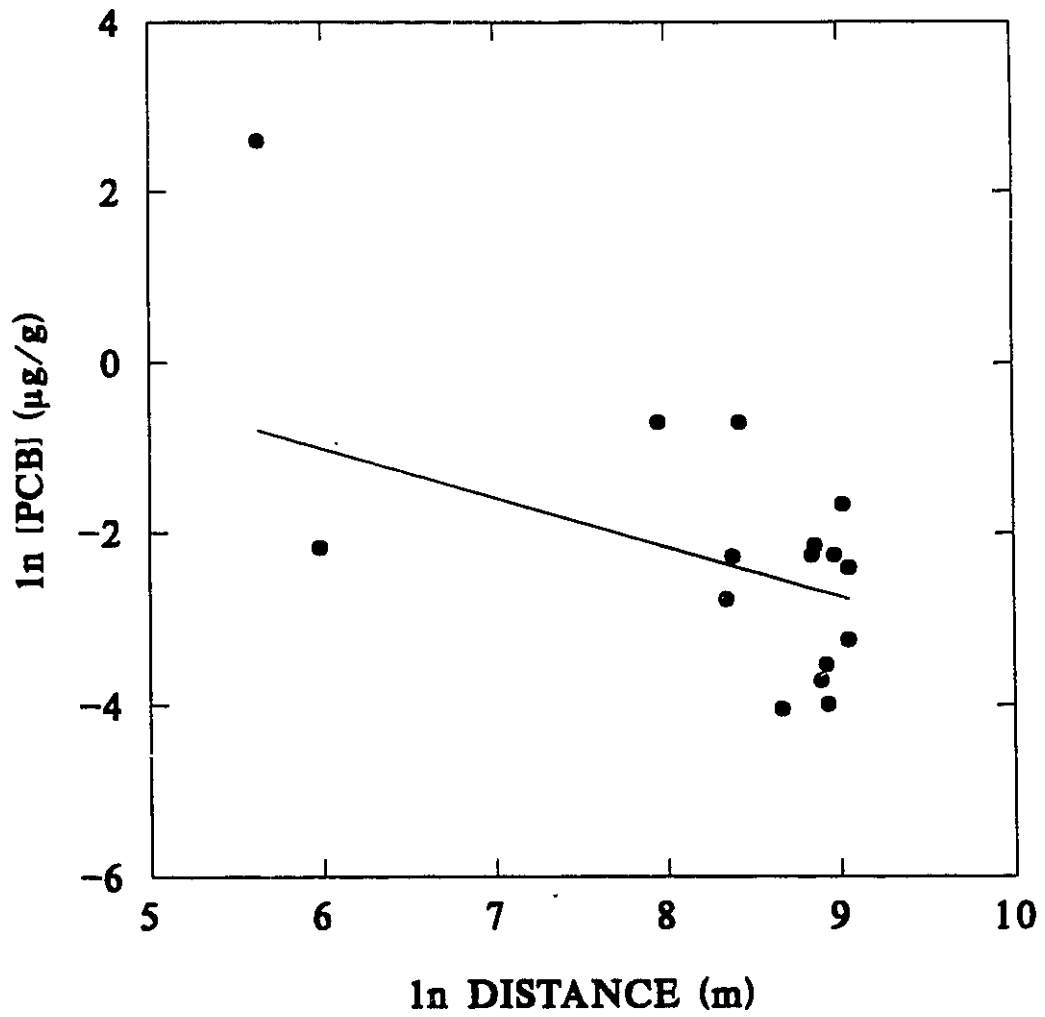
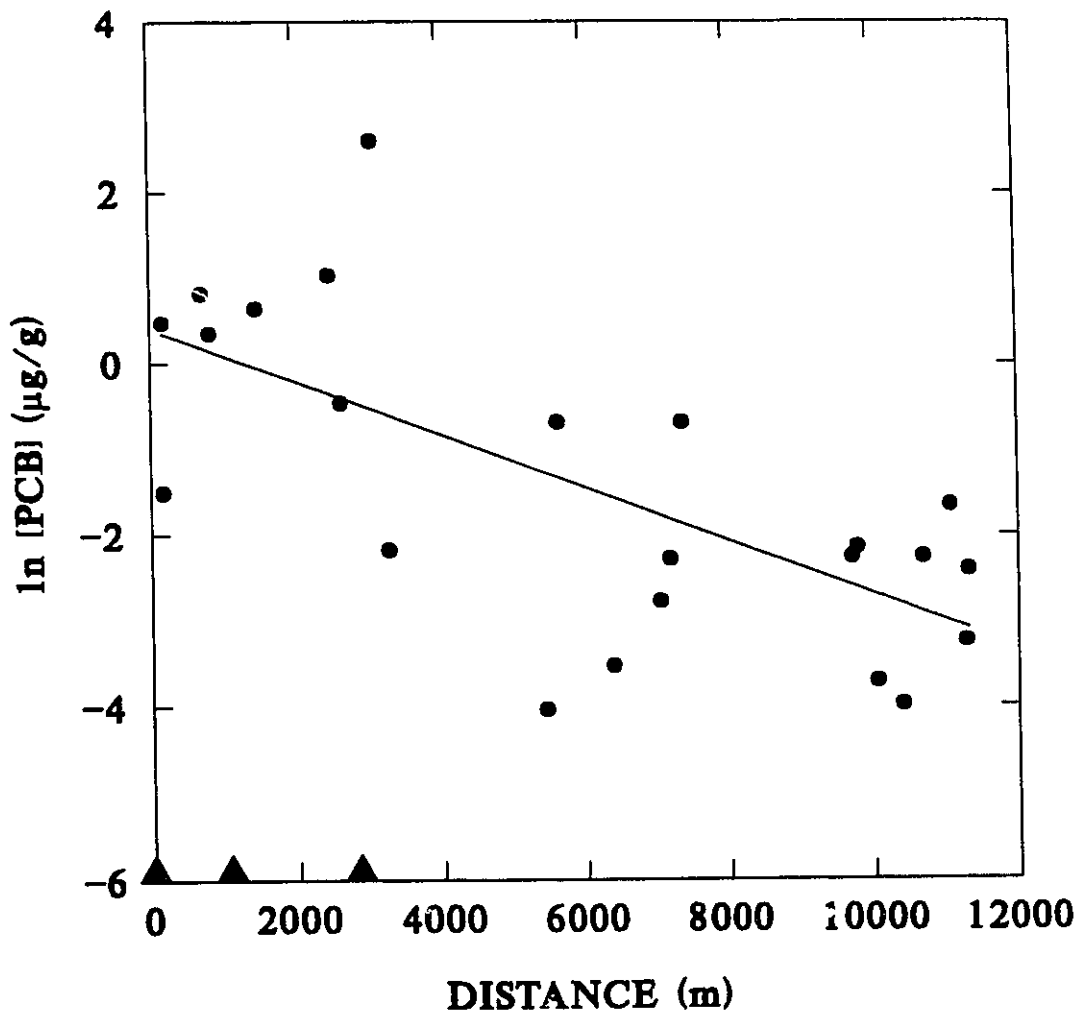


FIG. 9



Appendix A. Raw Data Used to Construct Distance-Decay Models.

Case	Pipe Hg	ln [Hg]	ln (Dist. Hg)	Pipe PCB	ln [PCB]	ln (Dist. PCB)
1	1	3.04	5.85	1	-2.23	5.30
2	1	0.41	6.52	1	-2.83	5.91
3	1	0.59	6.70	1	-3.12	6.55
4	1	0.47	7.02	1	-2.15	6.67
5	1	0.96	7.10	1	-1.35	7.00
6	1	-0.80	7.14	1	-3.44	7.11
7	1	-3.91	8.18	1	-1.19	7.15
8	1	-1.66	7.69	2	-2.01	5.64
9	1	-4.61	7.93	2	0.52	6.04
10	2	2.87	6.04	2	-2.23	6.06
11	2	1.74	6.06	2	0.01	6.23
12	2	1.67	6.26	2	-2.75	6.68
13	2	0.34	6.68	2	-2.47	6.80
14	2	-0.51	6.82	2	-2.98	6.89
15	2	1.13	6.85	2	-3.82	7.48
16	2	-1.61	7.55	2	-2.81	8.37
17	2	-1.61	8.01	3	-1.49	5.10
18	2	-1.61	8.33	3	0.50	5.15
19	2	-0.78	8.36	3	0.84	6.58
20	2	-1.83	7.91	3	0.37	6.72
21	2	-0.71	7.84	4	0.67	6.03
22	2	-3.91	8.62	4	1.06	7.26
23	3	-3.00	4.98	4	-0.45	7.37
24	3	-2.66	5.16	5	2.62	5.63
25	3	-0.22	6.61	5	-2.15	5.98
26	3	-1.56	6.69	5	-4.02	8.66
27	4	-1.56	6.09	5	-0.67	7.95
28	4	-0.36	7.27	5	-3.51	8.92
29	4	-2.81	7.37	5	-2.75	8.35
30	5	-2.30	5.67	5	-2.25	8.38
31	5	-2.30	6.05	5	-0.67	8.42
32	5	-3.22	8.66	5	-2.23	8.84
33	5	-4.61	8.67	5	-2.12	8.86
34	5	-3.00	7.97	5	-3.69	8.89
35	5	-3.22	8.92	5	-3.96	8.93
36	5	-3.91	8.93	5	-2.23	8.97
37	5	-3.91	8.36	5	-1.63	9.02
38	5	-3.91	8.39	5	-3.22	9.05
39	5	-1.83	8.42	5	-2.39	9.05
40	5	-2.21	8.84			
41	5	-3.91	8.85			
42	5	-3.00	8.90			
43	5	-3.91	8.93			
44	5	-1.47	8.98			
45	5	-1.47	9.03			
46	5	-3.22	9.05			
47	5	-1.66	9.06			

Pipe 1 = Domtar
 Pipe 2 = Courtauld's
 Pipe 3 = Grass R.
 Pipe 4 = Reynold's
 Pipe 5 = General Motors

Note: Concentrations in $\mu\text{g/g}$
 Distances in metres

Appendix B. Original PCB Data. Numbered sample sites correspond to sampling locations of source studies.

Original sample site	PCBs ($\mu\text{g/g}$): Anderson (1990)	PCBs ($\mu\text{g/g}$): Richman (1991)	PCBs ($\mu\text{g/g}$): Kauss et al. (1988)
33	226		
35	1951		
55	108		
57	305		
64	93		
65	195		
66	108		
67	20		
70	108		
72	512		
73	64		
79	512		
80	30		
81	18		
82	116		
83	640		
84	1450		
87	23		
89	51		
90	64		
94	1682		
95	108		
98	135		
101	33		
103	116		
105	44		
106	59		
365			260
368			1010
369			85
371			60
378			40
382			25
383			120
384			105
390			13750
391			2880
392			2325
393			1650

Appendix C. Original Mercury Data. Numbered sample sites correspond to sampling locations of source studies.

Original sample site	Hg (µg/g); Anderson (1990)	Hg (µg/g); Richman (1991)	Hg (µg/g); Kauss et al. (1988)	Average
33			0.07	0.07
35			0.21	0.21
57			0.46	0.46
59			0.01	0.01
64			0.19	0.19
65			0.23	0.23
66			0.23	0.23
67			0.02	0.02
69			0.05	0.05
70			0.11	0.11
72			0.16	0.16
73			0.02	0.02
79			0.06	0.06
80			0.04	0.04
81			0.01	0.01
82		0.10	0.12	0.10
83		0.08	0.03	0.06
84			0.21	0.21
87			0.23	0.23
88			0.16	0.16
89			3.09	3.09
90			1.42	1.42
91			0.50	0.50
92			0.16	0.16
93			0.23	0.23
94			17.59	17.59
95			5.68	5.68
100			0.19	0.19
101			2.60	2.60
103			1.84	1.84
104			1.54	1.54
106			20.93	20.93
365	1.20	2.10		1.64
366	0.01	0.02		0.02
368	4.90	5.60		5.25
369	0.41	0.79		0.60
371	0.39	0.51		0.45
372	0.04	0.01		0.02
378	0.04			0.04
383	0.02			0.02
384	0.02			0.02
388	0.02			0.02
389	0.04			0.04
390	0.10			0.10
391	0.70			0.70
392	0.80			0.80
393	0.05			0.05

**SPATIAL CORRELATIONS BETWEEN MERCURY AND PCB CONCENTRATIONS
IN SEDIMENTS AND IN SPOTTAIL SHINERS (*Notropis Hudsonius*) IN THE
CORNWALL-MASSENA SECTION OF THE ST. LAWRENCE RIVER.**

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ABSTRACT

The public at large in the Cornwall-Massena Area of Concern (AOC) is concerned about the potential for mercury and PCB sediment contamination to contribute to elevated levels of contaminants in the biota. Studies within the Great Lakes basin have focused on documenting the type and extent of biological contamination. Also required is information on contaminant sources and routes of exposure. More specifically, *local* remediation efforts can yield results if (1) there are local contaminant sources and (2) these local sources are contributing significantly to contamination of the local biota. In this paper, we address the second point by examining spatial correlations between mercury and PCB concentrations in sediments and a small nearshore planktivore, the Spottail Shiner (*Notropis Hudsonius*). We found a weak positive linear relationship between sediment and fish mercury ($r^2 = 0.26$, $p = 0.07$), and a strong positive linear relationship between sediment and fish PCBs ($r^2 = 0.90$, $p < 0.001$). We previously examined the relationships between point sources of pollution and sediment contamination patterns in the study area which show that contaminant sources are probably local. The results presented here show that localities of highly contaminated sediments are, in turn, contributing to contamination of the local biota, more so for PCBs than for mercury. We conclude that public policy designed to reduce local emissions and/or exposure will be effective.

Key words: St. Lawrence River, sediments, Spottail Shiner, mercury, PCB

INTRODUCTION

The St. Lawrence River has long been used by humans for transportation, hydroelectric power and as a sink for human and industrial wastes (Government of Canada, 1991). The section of the river near Cornwall, Ontario and Massena, New York was an area of intense industrial activity from the late 19th century through the 1960's and 1970's. In 1985, this section of the river was declared an Area of Concern (AOC) by the International Joint Commission (IJC, 1985). This resulted in the establishment of a Remedial Action Plan (RAP). Stage 1 of the RAP, which defined environmental conditions and problems in the AOC, identified mercury and PCB sediment contamination as a major concern (RAP, 1992). Other studies in the area have documented sediment mercury and PCBs above provincial sediment quality guidelines (Kauss, 1988; Anderson, 1990; Richman 1991). More recently, it has been shown that there are localized hotspots of sediment contamination associated with the outfall pipes of specific industries in the area (Chapter 1, this volume).

The public at large is concerned about contaminants in sediments and about contaminants in sport fish, largely because of possible risks to human health and to the biota (RAP, 1992; PAC, 1995). These concerns are reinforced by current restrictions on the consumption of sport fish (OMEE, 1994). An important question is whether sediment contamination is contributing to elevated contaminant levels in the biota. Determining whether the biota is accumulating sediment toxicants has important implications for remedial action. If contamination in localized fish populations is related to local sediment contaminant levels, then locally focused remediation

efforts (e.g. dredging, emissions controls) are indicated to minimize possible long-term bioaccumulation of contaminants in the food chain.

Despite earlier research which suggested that sediment contaminants may not necessarily bioaccumulate in gill-breathing animals because pollutants remain bound to sediment particles (Neff, 1984), there is growing evidence of a link between sediment contamination and contamination in aquatic organisms. Hebert and Haffner (1991) found higher levels of organochlorines in benthic-feeding cyprinids than in a closely related surface feeder. Larsson (1986) has shown that plankton and planktivorous fish in artificial ponds accumulate PCBs directly from bottom sediments, and Malins *et al.* (1987) have demonstrated a positive correlation between frequencies of liver neoplasms in English sole and aromatic hydrocarbons in sediments. In a review article prepared for an international workshop on contaminated sediments, Willford *et al.* (1987) concluded that contaminant uptake by fish from sediments is one of the most important routes of exposure.

A number of studies have investigated aspects of toxic substances in wildlife of the Great Lakes basin, for example PCBs in snapping turtles (Struger *et al.*, 1993), organics and metals in benthos (Griffiths, 1988), PCBs, DDE and mercury in lake trout (Borgmann and Whittle, 1992), pesticides and organics in freshwater mussels (Metcalf and Charlton, 1990) and metals and organics in sport fish (OMEE, 1994). These and other studies have focused primarily on documenting type and extent of biological contamination. Also required is information on contaminant sources and routes of exposure. More specifically, *local* remediation efforts can yield results if (1) there are local contaminant sources and (2) these local sources are contributing significantly to contamination of the local biota. If both of these conditions are satisfied, then

public policy designed to reduce local emissions and/or exposure has some chance of success. These conditions are necessary (but not sufficient) conditions for successful local public policy initiatives.

This paper evaluates the second condition noted above. In a previous study (Chapter 1, this volume), we showed that in the Cornwall-Massena AOC, sediment mercury and PCB concentrations showed a characteristic distance-decay from suspected industrial effluent sources, which strongly suggests that local sources are (or have been) major contributors to sediment contamination in the area (i.e. condition 1 is, in fact, satisfied). Here we examine the relationship between sediment contaminant levels and contaminant levels in a small nearshore planktivore, the Spottail Shiner, to assess the extent to which sediment contaminants are being incorporated into the biota.

METHODS

The study area is located in the St. Lawrence River, downstream of the Moses-Saunders power dam and extends just east of the confluence of the St. Regis River (Fig. 1). This area falls within the provinces of Ontario and Quebec and the state of New York. Water flows, from west to east, around Cornwall Island, forming a north and a south channel. Flow is swift, between 5 and 8 knots, and more or less unidirectional in the north channel. Water destined for the south channel is funnelled at high speed (about 8-9 knots) through a narrow opening just off the west end of Cornwall Island (Polly's Gut), and is deflected by a stone wall located directly in the channel. This creates a large vortex, spanning the width of the river, in front of the Reynold's

point source. Downstream of the vortex, the water flow is slower and more or less unidirectional (Morin et al., 1994).

Sediment contamination data for total PCBs and mercury were obtained from published sources (Kauss, 1988; Anderson, 1990; Richman, 1991). These studies used either Shipek or Ponar grabs to collect the upper 3 centimetres of sediment from the river bottom. Sampling locations from these three studies were combined to provide a composite set of sampling locations. Multiple measurements were averaged at each sampling location resulting in one datum per station for each of the two contaminants. Contamination data for mercury and PCBs in Spottail Shiners were obtained from the Juvenile Fish Biomonitoring Program of the Ontario Ministry of Environment and Energy (Suns, 1993). Spottail Shiners were chosen as indicators for two reasons. First, because they are relatively restricted to nearshore habitats they reflect site-specific contaminant availability. Second, they are an important forage fish for predatory species and thus an important indicator of contaminant transfer to higher trophic levels. Sampling locations for both sediment and fish were placed on a map of the study area using SPANS geographic information system. This was done using published latitude/longitude co-ordinates where possible and estimated using published maps otherwise (Figs. 2, 3).

The relationship between sediment and fish contamination was investigated by averaging all sediment concentrations within a 1500 meter radius of each fish sampling site (Figs. 2,3), using only those sediment sites on the same shore of the river as the fish sampling sites. These criteria were used because young-of-the-year Spottail Shiners spend most of their time in weedbeds in shallow water, and are unlikely to cross deep water channels or travel much farther than 2 kilometres away from a home area (Scott and Crossman, 1973). These data were then

normalized by log transformation and simple linear regressions of fish contamination as a function of sediment contamination were carried out.

RESULTS

Sediment mercury in the study area ranges from under 10 ng/g to about 21 000 ng/g. The highest concentrations occur in the north channel with 29% of the observations exceeding the severe effect level set out in provincial sediment guidelines (Persaud and Jaagumagi, 1994). Fifty percent of the observations exceed the lowest effect level and 21% are below the lowest effect level. The severe effect level is defined as the level at which the sediment is considered to be heavily polluted and likely to affect the health of sediment-dwelling organisms. The lowest effect level indicates a level of contamination which has no effect on the majority of sediment-dwelling organisms. The no effect level is the level at which the chemicals in the sediment do not affect fish or sediment-dwelling organisms (Persaud and Jaagumagi, 1994). The south channel has comparatively lower levels with 76% of the sites below the lowest effect level and 24% of the sites above the lowest effect level but below the severe effect level (Fig. 2). Sampling sites with the higher measurements are considered to be some of the most contaminated sites in the Great Lakes basin (RAP, 1992). Levels of mercury in fish range from about 23 ng/g to 78 ng/g (Fig. 2). These concentrations are well below the Great Lakes Water Quality Agreement Specific Objective for the protection of aquatic life of 500 ng/g (Great Lakes Water Quality Agreement, 1978). The highest fish mercury concentrations also occur in the north channel, although spatial variability throughout the study area is low, varying only by a factor of 3 (Fig. 4).

To investigate the relationship between concentrations of mercury in fish and sediments we used simple linear regression. We found a marginally significant positive linear relationship between these two variables ($r^2 = 0.26$, $p = 0.07$, $rms = 0.08$, $n = 10$) (Fig. 4).

Sediment PCBs range from under 20 ng/g to 13 600 ng/g. The highest concentrations occur in the south channel, particularly in the western portion of the study area. About 31% of the sample sites are below the provincial lowest effect level and 68% are above the lowest effect level but below the severe effect level. Levels of PCBs in fish range from about 40 ng/g to 9 200 ng/g, a 230 fold range. The highest fish PCB concentrations are found in the south channel (western portion) (Fig. 4). All of the fish concentrations are near or above the Great Lakes Water Quality Agreement Specific Objective for the protection of aquatic life of 100 ng/g (Great Lakes Water Quality Agreement, 1978). Spottail Shiners are much more contaminated with PCBs in the south channel of the study area than at other locations throughout the Great Lakes basin where PCB levels are not elevated much above 300 to 500 ng/g (Suns *et al.*, 1993). Note that PCBs are perceived to be the most important contaminant problem in forage fish (RAP, 1992).

To investigate the relationship between concentrations of PCBs in fish and sediments we used simple linear regression. We found a highly significant positive linear relationship between these two variables ($r^2 = 0.90$, $p < 0.001$, $rms = 0.34$, $n = 10$) (Fig. 5).

DISCUSSION

Our results show that the variations in the levels of PCBs in Spottail Shiners throughout the study area are strongly related to total PCB concentrations in local surficial sediments. We

have shown earlier that the high levels of PCBs occurring in the sediments in the south channel are related to the locations of the outfall pipes of the General Motors plant, Reynold's Aluminum and the mouth of the Grass River (ALCOA located upstream) (Chapter 1, this volume). Thus, PCBs emanating from local industrial activity are the probable source of contamination of Spottail Shiners in the south channel of the St. Lawrence River in this region.

Based on the work of Hebert and Haffner (1991) on contaminant exposure in cyprinids, it seems likely that the Spottail Shiners are acquiring PCBs from their food. They found that the differing degrees of organochlorine contaminants in the habitats of four philopatric species of small planktivores, including the Spottail Shiner, of the same age, size, lipid content and trophic status could explain differences in body burdens of these contaminants. Further, they found that species with a close association to the bottom were more contaminated than species which feed on pelagic or terrestrial insects. This suggests that habitat and food selection play important roles in the accumulation of organochlorine contaminants in cyprinids. Spottail Shiners are facultative benthivores. As such, a large part of their diet consists of benthic cladocerans, chironomids and some algae and detritus (Hartman *et al.*, 1992). As Larsson (1986) points out, uptake of PCBs from sediments by fish can occur by two processes. First, benthic macroinvertebrates take up contaminants by ingestion of sediments or as a result of partitioning from particles or interstitial water. The invertebrates then act as the first link in the food chain and mediate contaminant transport to predatory fish. Second, bioturbation, desorption and gas convection can transport contaminants across the sediment-water interface making them available to fish for uptake by equilibrium partitioning (Larsson, 1984). Both of these mechanisms have been demonstrated in laboratory model systems (Spigarelli *et al.*, 1983; Larsson, 1984).

Bioaccumulation of PCBs in planktivorous fish is probably an important component of the distribution and dynamics of PCBs at higher trophic levels (Suns *et al.*, 1993). Spottail Shiners and other small planktivores are a primary food source for larger predatory fish such as walleye, northern pike and bass (Scott and Crossman, 1973). These game fish in the Cornwall-Massena area are also contaminated with PCBs such that restrictions are imposed on their consumption by humans (OMEE, 1994). Thus, although other routes of exposure are possible, it is likely that sport fish are being contaminated by consumption of contaminated prey.

Our results also show that the variations in levels of mercury in Spottail Shiners throughout the study area are related to mercury concentrations in local surficial sediments. We have shown earlier that the high levels of mercury occurring in the sediments in the north channel are related to the locations of the outfall pipes of Domtar Fine Papers and Courtauld's (Chapter 1, this volume). Thus, mercury emanating from local industrial activity is the probable source of contamination of Spottail Shiners in the north channel of the St. Lawrence River in this region.

The relationship between fish and sediment mercury, however, is much weaker than for PCBs. Moreover, fish mercury is well below the IJC guideline for the protection of aquatic life and much less variable than sediment mercury. Large changes in sediment mercury correspond to only very modest changes in fish mercury. This suggests that Spottail Shiners, at least, are not assimilating mercury from highly contaminated sediments to any great degree.

A possible explanation for this weak relationship is that bioavailability and mechanisms of bioconcentration are more complex for metals than for organic compounds. A number of factors have been identified as important in determining whether mercury is available to organisms. Such factors include the amount of methyl mercury versus inorganic mercury which is present in the

environment (Wood, 1968), sediment characteristics such as organic carbon content, particle size distribution, interactions with other chemicals, cation exchange capacity and the presence of selenium, among others (Richman, 1994). In general, metals show considerably lower bioavailability and more variable results than PCBs (Willford *et al.*, 1987) and simple correlations between metals in sediments and residues in biota are often only weakly significant (Luoma, 1983).

As mentioned, we previously examined the relationships between point sources of pollution and sediment contamination patterns in the study area (Chapter 1, this volume), which show that contaminant sources are probably local. Our results in this paper show that localities of highly contaminated sediments are, in turn, contributing to contamination of the local biota, more so for PCBs than for mercury. Given this, we feel that public policy designed to reduce local emissions and/or exposure will be effective. This includes dredging of sediments, where short-term exposure due to possible resuspension and transport of contaminants will likely be less damaging to the biota than long-term exposure associated with leaving contaminated sediments where they are.

ACKNOWLEDGEMENTS

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FIGURE LEGENDS

- Figure 1. Study area, including the locations (black triangles) and names of the major point sources of pollution in the region.
- Figure 2. Concentrations of sediment and fish mercury in the study area. Symbols sizes vary continuously and are proportional to the concentrations.
- Figure 3. Concentrations of sediment and fish PCBs in the study area. Symbols sizes vary continuously and are proportional to the concentrations.
- Figure 4. The natural logarithm of the mercury concentration in Spottail Shiners expressed as a function of the natural logarithm of the average concentration of mercury in sediments within a 1500 metre radius of each fish sampling site.
- Figure 5. The natural logarithm of PCB concentrations in Spottail Shiners expressed as a function of the natural logarithm of the average concentration of PCBs in sediments within a 1500 metre radius of each fish sampling site.

FIG. 1

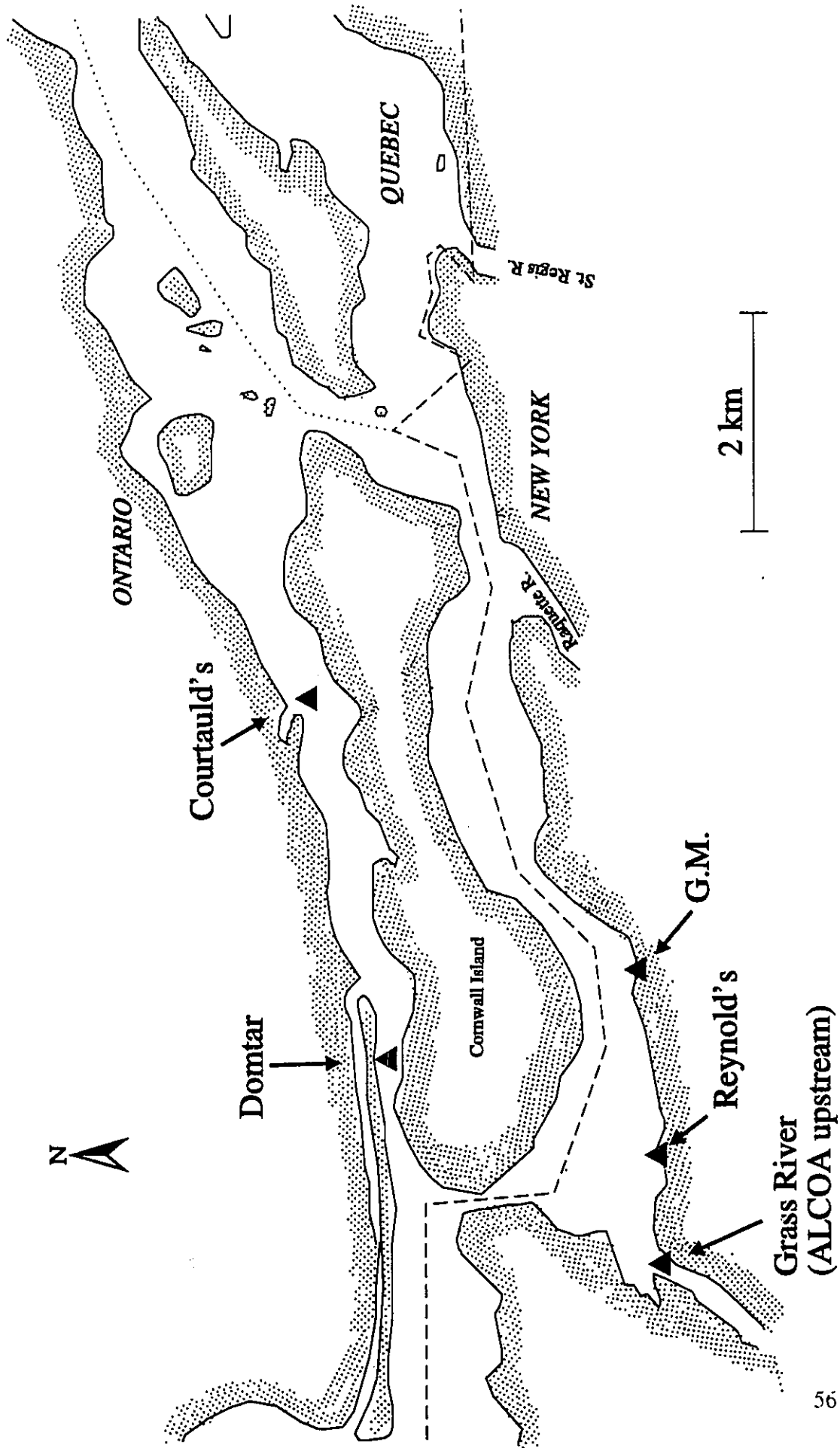


FIG. 2

Sediment Hg (ng/g)	Fish Hg (ng/g)
△ 100	□ 17
△ 4000	□ 34
△ 9000	□ 51
△ 13000	□ 68
△ 18000	□ 85
△ 21000	

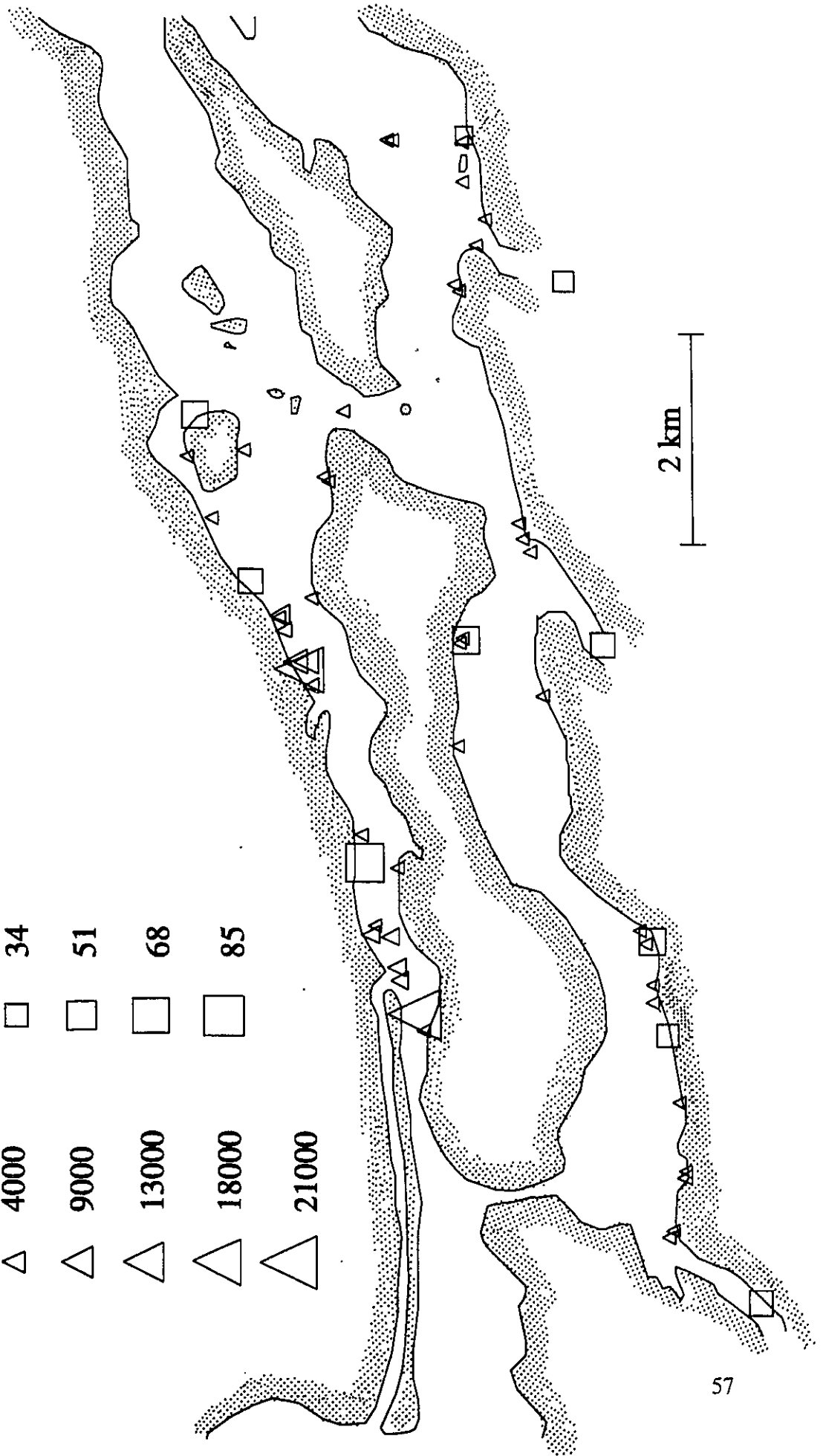


FIG. 3

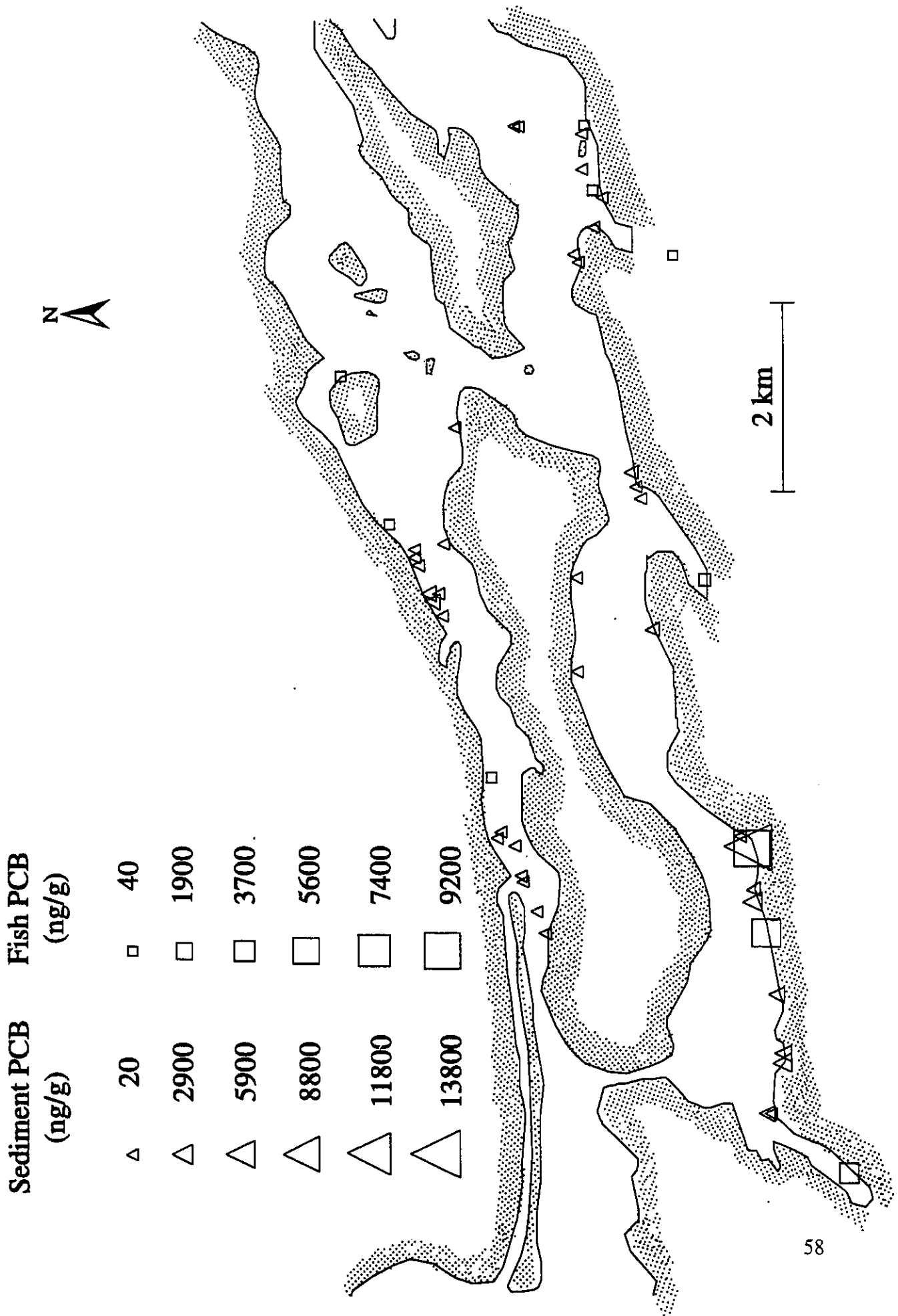


FIG. 4

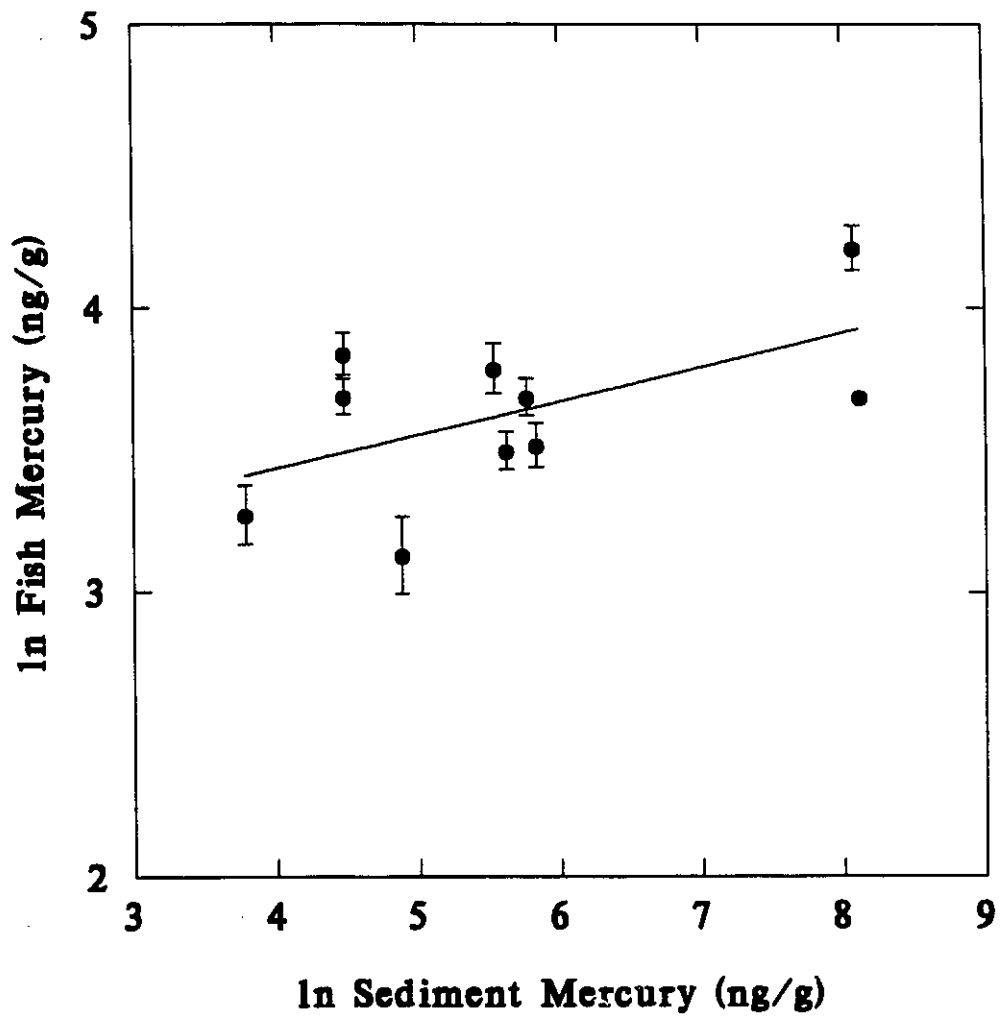
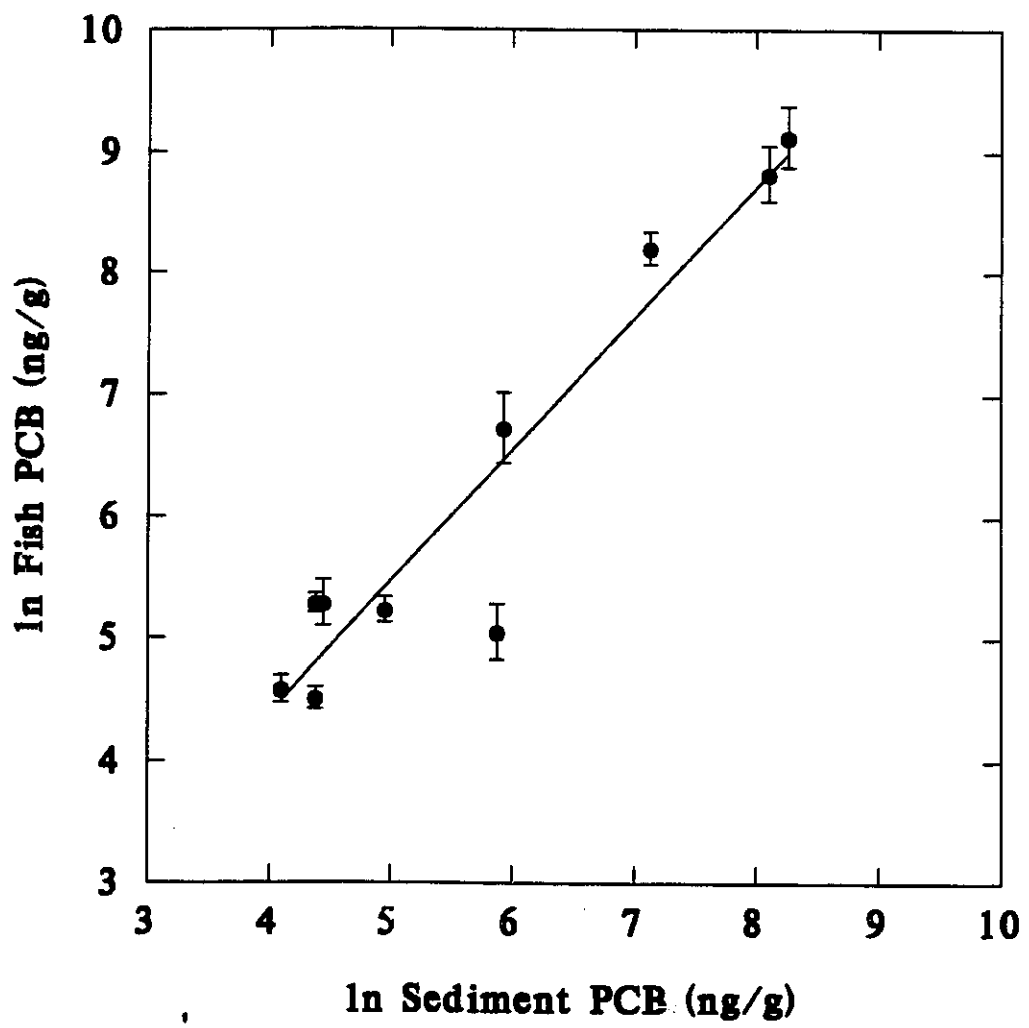


FIG. 5



Appendix A. Raw Data. Sediment and Fish Mercury and PCBs in ng/g.

CASE	SEDIMENT HG (1500 M)	FISH HG	LN SEDIMENT HG	LN FISH HG
1	2920	78	7.98	4.36
2	3040	40	8.02	3.69
3	250	45	5.52	3.81
4	290	41	5.67	3.71
5	310	34	5.74	3.53
6	230	46	5.44	3.83
7	80	41	4.38	3.71
8	80	46	4.38	3.83
9	40	27	3.69	3.30
10	120	23	4.79	3.14
CASE	SEDIMENT PCB (1500 M)	FISH PCB	LN SEDIMENT PCB	LN FISH PCB
1	142	187	4.96	5.23
2	357	156	5.88	5.05
3	60	98	4.09	4.58
4	1249	3672	7.13	8.21
5	3301	6817	8.10	8.83
6	3867	9241	8.26	9.13
7	376	837	5.93	6.73
8	85	197	4.44	5.28
9	80	197	4.38	5.28
10	80	91	4.38	4.51

Appendix B. Original Mercury Data for Spottail Shiners (ng/g).

point 1	point 2	point 3	point 4	point 5	point 6	point 7	point 8	point 9	point 10
50	40	30	50	30	30	40	50	20	30
40	40	30	40	30	40	30	40	20	20
40	40	30	40	50	40	30	50	20	20
50		40	50	30	30	40		40	
100		20	40	40	40	40		30	
50		40	60	30	30	40		30	
100		20	20	30	30	50		30	
100		30	40		60	30			
130		40	40		60	40			
130		40	40		80	40			
100		40	40		40	40			
40		60	30		50	50			
90		40	50		70	50			
70		60	50		50	40			
90		20	30			20			
20		40	30			40			
90		70	50			60			
30		40				60			
50		10							
70		30							
60		20							
70		30							
70		30							
60		20							
80		40							
80		10							
80		30							
80		20							
70		30							
90		30							
		20							
		40							
		20							
		30							
		40							
		30							
		20							
		30							
		30							
		60							
		60							
		70							
		60							
		50							
		60							
		60							

Appendix C. Original PCB Data for Spottail Shiners (ng/g).

point 1	point 2	point 3	point 4	point 5	point 6	point 7	point 8	point 9	point 10
210	218	38	2264	16000	1750	370	120	300	130
270	452	34	1938	17000	964	490	130	200	80
250	316	36	2110	16000	1590	310	100	180	90
130	294	32	2230	18000	1260	310	100	180	90
130	50	38	1890	16000	1260	430	100	180	60
130	50	110	2253	2280	1180	430	180	160	100
160	50	37	1820	1100	827	280	440	180	90
308	50	30	872	1700	23500	70	225		
331	48	90	895	6840	15600	90	50		
311	140	90	1112	1260	25600	80	60		
516	130	100	937	1460	23700	110	45		
282	160	90	1490	900	16800	70	70		
232	70	90	1327	4100	19200	1700			
218		60	1188	4540	26300	2320			
297		50	991	7840	5200	1460			
141		100	1071	3140	38000	2160			
140		40	1505	4440	13000	2100			
250		110	459	3460	35000	1050			
169		150	823	3460	22000	2070			
42		170	877		3800				
50		90	865		940				
60		80	1280		850				
40		80	1160		1530				
50		90	873		700				
209		45	769		2000				
115		45	960		990				
225		180	767		640				
160		240	7900		540				
170		160	5900		1920				
130		200	11400		6140				
120		180	5700		8200				
90		160	6300		3040				
35		200	9000		940				
30			7900						
170			6800						
130			11000						
260			6500						
90			9200						
180			12000						
105			9000						
200			9000						
250			3420						
			5300						
			4900						
			2200						
			3400						
			2440						
			2280						

Appendix D. Results of ANCOVA models testing for effect of study.

EFFECT OF STUDY ON MERCURY MODEL

LEVELS ENCOUNTERED DURING PROCESSING ARE:

PIPEHG
 1.000 2.000 3.000 4.000 5.000
 STUDYHG
 1.000 2.000 3.000

DEP VAR: LNHGP N: 55 MULTIPLE R: 0.900 SQUARED MULTIPLE R: 0.811

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
LNDHG	13.950	1	13.950	14.407	0.000
LNDHG*PIPEHG	56.216	4	14.054	14.514	0.000
PIPEHG	65.773	4	16.443	16.982	0.000
STUDYHG	2.374	2	1.187	1.226	0.304
STUDYHG					
*LNDHG	2.836	2	1.418	1.464	0.243
ERROR	39.700	41	0.968		

EFFECT OF STUDY ON PCB MODEL

LEVELS ENCOUNTERED DURING PROCESSING ARE:

PIPEPCB
 1.000 2.000 3.000 4.000 5.000
 STUDYPCB
 1.000 3.000

DEP VAR: LNPCBP N: 39 MULTIPLE R: 0.785 SQUARED MULTIPLE R: 0.616

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
LNDPCB					
*PIPEPCB	26.842	4	6.711	4.967	0.004
PIPEPCB	21.151	4	5.288	3.914	0.012
STUDYPCB	1.863	1	1.863	1.379	0.250
STUDYPCB					
*LNDPCB	1.312	1	1.312	0.971	0.333
ERROR	37.829	28	1.351		