

MODELING WORK GROUP GEOGRAPHICAL AREA SYNTHESIS REPORT
UPPER GREAT LAKES CONNECTING CHANNEL STUDY

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INTRODUCTION

Two types of models were developed in the Upper Great Lakes Connecting Channels Study (UGLCCS). The first type of model will be referred to as a mass balance calculation. The second type of model will be referred to as process-oriented. Both types of modeling efforts are valuable for indicating needed research, remedial and regulatory actions. With sufficient data, mass balance calculations are useful for determining (1) whether an area is a source or a sink of contaminants, and (2), the relative importance of known and unknown contaminant sources. Mass balance calculations were made for a number of water quality parameters in the St. Clair River, Lake St. Clair, the Detroit River and the Trenton Channel of the Detroit River (Table 1). The mass balances calculated for these systems represent "snapshots" of contaminant fluxes since measurements were made during short time intervals only. Annual mass balances cannot be inferred from these calculations unless specifically noted.

Process-oriented models are based on mechanistic relationships (e.g. contaminant-particle interactions) and represent a working hypothesis of how a dynamic system works. Process-oriented models are useful for (1) understanding the relative importance of processes that affect contaminant fate, and (2), given proper calibration and verification, for answering "what if" questions (e.g., if a particular contaminant is input to a system, where will it go, how long will it stay, what physical-chemical form will it be in, and what organism exposure might occur?) Models describing a variety of physical, chemical and biological processes were

developed for the St. Mary's River, the St. Clair River, Lake St. Clair,
the Detroit River and the Trenton Channel of the Detroit River (Table 2).

Table 1. Mass balance calculations performed on the Upper Great Lakes Connecting Channels.

Location	Date(s)	Parameters
St. Clair R.	Aug., Sept., Oct., 1985	Organics (concentration profiles only)
Lake St. Clair	July 21-29, 1986	Metals, Organics, ^{Total} Phosphorus
Detroit River	April 21-29, 1986 (SMB I)	Metals, Organics, Nutrients, Chlorides, Suspended Solids
	July 25-August 5, 1986 (SMB II)	Metals, Organics, Nutrients, Chlorides, Suspended Solids
Trenton Channel	May 6-7, 1986	Metals, Organics, Nutrients, Chlorides, Suspended Solids
	August 26-27, 1986	Metals, Organics, Nutrients, Chlorides, Suspended Solids

Table 2. Process models developed for the Upper Great Lakes Connecting Channels Study

Location	Type of model
St. Mary's R.	<ul style="list-style-type: none"> - 3-D steady state finite element hydrodynamic (upper river) - Steady state, depth averaged, mixing model (lower river) - Contaminant fate model (driven by hydrodynamic models, above)
St. Clair R.	<ul style="list-style-type: none"> - Unsteady flow model with flow separation around islands - Steady state, depth averaged mixing model - Contaminant fate model (water column only) - Contaminant fate model (TOXIWASP-based; water and sediments)
Lake St. Clair	<ul style="list-style-type: none"> - Water level models (hydrodynamic and empirical) - Currents (predicts meand daily currents) - Particle transport model - 3-D finite element flow field model - Waves and sediment settling and resuspension - Contaminant fate, 2-D model (TOXFATE) - Contaminant fate, 2-D model (TOXIWASP-based) - Contaminant fate, 1 box, kinetic model.
Detroit River	<ul style="list-style-type: none"> - 2-D plume model of water and contaminant discharge from Detroit's sewage treatment plant.
Trenton Channel	<ul style="list-style-type: none"> - 3-D hydrodynamic and toxicity transport model

METHODS

Mass Balance Calculations

Mass is a conservative property. As such, a mass balance framework can be applied to a control volume, where, assuming conservative behavior and steady conditions, the change in mass of the system can be described as:

$$D = W_{out} - W_{in} \quad (1)$$

W_{in} is the sum of all loads (flux) coming into the control volume (Mass/Time). W_{out} is the mass flux leaving the control volume. If all loadings into the system are accounted for and the mass flux leaving the system is known, then "D" should equal zero for a conservative substance. In general, if D is not zero, then the control volume is either a sink ($D < 0$) or a source ($D > 0$) of the substance. For substances that "leave" the system through volatilization or degradation it is important to note that a $D < 0$ does not necessarily mean that the substance is accumulating in the control volume. A process-oriented calculation would be needed to define how much substance was lost through volatilization or degradation before an accurate estimate of accumulation could be made.

In the connecting channels where advection dominates, the W terms can be computed from:

$$W = Q * C \quad (2)$$

where, W is mass flux (M/T),
 Q is flow rate (L^3/T), and
 C is concentration (M/L^3).

There are two sources of error in calculating W . First, there are analytical errors associated with measurement of Q and C . Second, errors can be introduced by inadequate temporal and spatial sampling resolution. Ideally, analytical errors would be non-existent and sampling of Q and C would be continuous at all locations. This is never the case, however, so W is always an estimate of the true load. Annual loads would ideally be calculated based on continuous measurements of Q and C throughout a year period. However, Q and C measurements might have been taken on a weekly basis only. Annual loads calculated with weekly information will be less certain than if the measurements were continuous.

Contaminant concentration data are sometimes reported as non-detectable or below the detection limit. This does not imply that the contaminant is not present in the sample, but merely that it cannot be quantified. Given a high flow condition and non-detectable concentrations, a significant portion of a contaminant mass balance can be overlooked if non-detectable concentrations are treated as zero concentration. Therefore, a method for handling non-detectables in all mass balances was devised. Details of the method used are supplied in Appendix I.

Comparability of loading estimates from Canada and the U.S. was also an issue due to the use of different analytical techniques and methods of

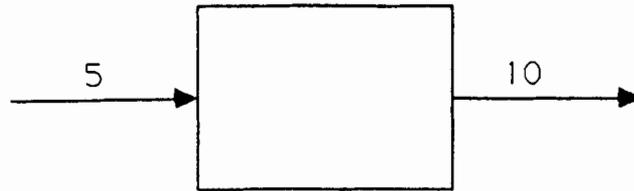
Mass Balance Calculations

Situation

Cartoon

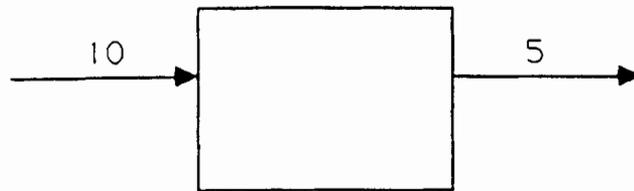
Interpretation

Upstream and downstream flux known; external loads unknown



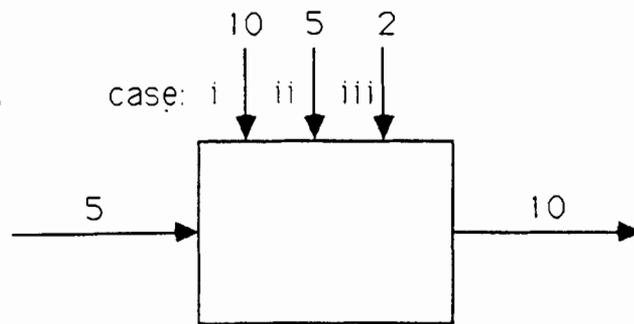
Study area is a source of contaminant (net flux = 5).

Upstream and downstream flux known; external loads unknown



Study area is a sink for contaminant (net deposition = 5).

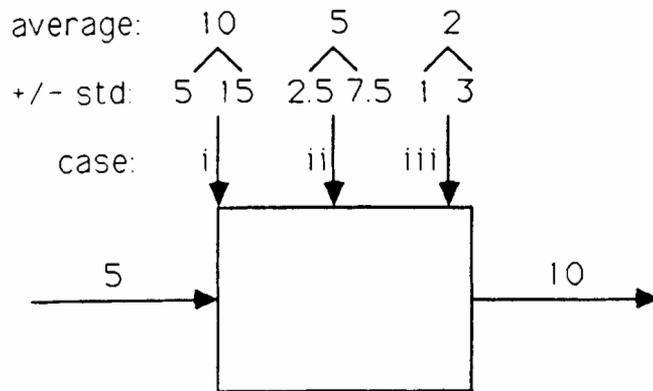
Upstream and downstream flux known; external loads known.



Case

- i Net deposition of 5; study area is a sink
- ii No net deposition
- iii Net export of 3; study area is a source

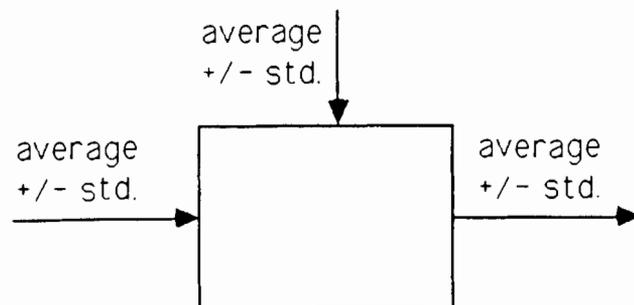
Upstream and downstream flux known; external loads approximated.



Case

- i No deposition - deposition of 5;
- ii In-place source of 2.5 - net deposition of 2.5
- iii In-place source of 4 to 2

Upstream and downstream flux approximated; external loads approximated.



Can be difficult to interpret; depends on temporal resolution of samples.

Figure 1

reporting. This issue was never fully resolved. The loads used in mass balance calculations that follow were those that the Point and Non-Point Source Workgroups furnished to the Modeling Work Group. No modifications or corrections to their numbers were made by the Modeling Work group.

All mass balance calculations that could be made were summarized as shown in Figure 2. With this type of diagram the relative importance of loads can be visualized, the relative contributions of U.S. and Canadian sources can be evaluated, unknown loads can be identified, and the source-sink question can be answered for the time period in question. In the mass balance diagrams the width of the arrow shafts indicate the relative importance of the average load and loss terms. Average loading terms are subdivided into Canadian and US contributions. A detailed breakdown of loading figures can be obtained from the Point and Non-Point Source Work Group reports. At the bottom of the figures is a box that provides an interpretation of the mass balance data. Statistical conclusions are given in this box although all data leading to the interpretation are not.

Comparison of mass balance diagrams for the same contaminant in the same physical location during different mass balance periods can be made directly. For instance, the Cadmium mass balance diagrams for Detroit River system mass balances I and II can be compared directly since all fluxes are normalized to the highest flux.

Process Models

Process-oriented models represent working hypotheses of how a system is causally linked, and through simulation, can be used to investigate the relative importance of the various processes that control the behavior of the simulated system. As such, process models can provide a framework for identifying needed field measurements and experimental studies. Process models have the potential for being used in more than one system because they are theoretically based. Process models developed in the UGLCCS range from purely physical models of water movement to temporally and spatially complex contaminant fate and behavior models. Verification of the latter models has been difficult due to lack of necessary and sufficient data. Nevertheless, these models are based on well documented cause and effect relationships, and therefore, could be used to speculate upon the possible fate of new contaminant introductions and related organism exposures in the connecting channels.

The output from process models is subject to uncertainty. Sources of uncertainty for these models include loading information, boundary conditions, initial conditions, parameter estimates (e.g., coefficient values used in process equations), and conceptual problems (e.g., are the boxes and arrows used the right ones?) Although the Modeling Work Group sought to conduct complete uncertainty analyses on all UGLCCS process models, time constraints and the computer resources needed for Monte Carlo type simulations became limiting factors for most modelers. However, uncertainty analysis of models still may take place after the UGLCCS is over. Through sensitivity analyses, modelers were able to identify some

parameters and processes that may require further research in order to improve contaminant fate models.

ST. MARY'S RIVER

Mass balance calculations

-As agreed to at the beginning of the study, no mass balance calculations would be done for the St. Mary's River.

Process-oriented models

-The following section was originally written by Y.S. Hamdy for inclusion in the St. Mary's Synthesis Report. No modifications have been made to it.

PROCESS MODELS(A) Physical: Hydrodynamics, Wind, Waves and Currents

For the purpose of the modelling study, the St. Marys River has been divided into an upper reach (above the regulatory works) and a lower reach (below the regulatory works).

Upper St. Marys River

The primary factors involved in the flow distribution in the Upper River are gravity, wind, bed friction and the associated pressure forces. One of the causes of water movement in the deep channels of the Upper St. Marys River is the inertial forces exerted by the large inflows from Lake Superior through the narrow mouth at Pointe Aux Pins. In the localized shallows of the Leigh Bay and Pointe Aux Pins Bay, an appreciable influence on the water circulation is exerted by wind stresses.

One objective of the modelling project was to describe the hydrodynamics of this area using mathematical models. A three dimensional steady state finite element model was applied to this area. The mathematical formulations were based on the three dimensional equations for conservation of mass and momentum. The principal assumptions used were:

- i) The pressure was assumed to vary hydrostatically.
- ii) The rigid-lid approximation was made, i.e. the vertical velocity at the undisturbed water surface was assumed to be a constant value of zero.
- iii) Eddy coefficients were used to account for the turbulent diffusion effects. The vertical coefficient was assumed constant while the horizontal coefficients were assumed to be zero.
- iv) The dimensions of the study area were small compared to typical weather systems, so that the geostrophic wind is assumed uniform over the entire area.

The resulting equations are discussed in detail by Liggett and Hadjitheodorou (1969) and Ibrahim and McCorquodale (1985). The basic equations contain three empirical constants, i.e. the vertical eddy diffusion coefficient, the wind drag coefficient and the bottom slip coefficient, which cannot be determined from theory alone but must be tuned by means of proper field data set in such a way that agreement between the model and prototype is sufficiently "satisfactory". A sensitivity analysis involving a large number of computer runs was made for these coefficients in order to assist with the calibration process.

The model was calibrated and verified using current meter data from the following sources:

- i) the U.S. Corps of Engineers;
- ii) the Ontario Ministry of the Environment;
- iii) Integrated Exploration Limited; and
- iv) aerial photographs taken of the area.

The model indicates that the Upper River is highly responsive to wind speed and direction. Its dynamic behaviour is important in the shallow bays where gyres readily form. Examples of gyres formed under no wind and north wind (19 km/hr) conditions are shown in Figures 1 and 2.

Some of the contaminants (e.g. PAHs) in the Bays are associated with the movement of fine-grained sediment particles; it is expected that the gyres will play a significant role in the transport of contaminants from the area of the slag dump to Leigh and Point aux Pins Bays. The model has indicated that up to two strong gyres can be formed simultaneously.

Combined with existing field data on current measurements in this area, the calibrated model provides a better understanding of the cause and effect relationship between the wind and the circulation patterns in the Upper River. This will eventually lead to the construction of more detailed fate models for management purposes. In addition, the model may provide new insights to the complex hydrodynamics of the Upper River for those who are involved in collecting field data for the area.

Lower St. Marys River

The Lower River is a nonuniform natural channel with slightly over half of its width dredged to a minimum depth of 28 feet (8.5 metres) for the passage of ships. The velocity field data on the Lower River is available from the U.S. Corps of Engineers. The data indicate the presence of some dead zones and re-circulation zones in the river due to natural or man-made protuberances from the shoreline.

The Lower River is simulated by KETOX (McCorquodale and Yuen 1987) which is a model that has a steady-state depth averaged hydrodynamic submodel coupled to a convection-diffusion (mixing) submodel. KETOX has evolved from the earlier modified K-E model which had been applied to the St. Clair River, Detroit River and Niagara River. The KETOX model has the following features:

- i) It provides a forward marching solution to the continuity and momentum equations for the river (Rastogi and Rodi 1978);
- ii) It provides solution for the lateral dispersion coefficients across each cross-section of the river based on the turbulence transport equations (K and E);
- iii) It can accept discharges from multiple outfalls;

The hydrodynamic component of KETOX was calibrated using U.S. Corps of Engineers (COE 1984) field data based on current meter measurements and drogue surveys.

(B) Physical-Chemical-Biological: Fate and Transport Models

The contaminant dispersion submodel of KETOX was calibrated using the 1974 Ontario Ministry of the Environment (Hamdy et al, MOE 1978) phenol loadings and ambient measurements. The model was subsequently verified with the 1983 MOE phenol field data. The calibration and verification are illustrated in Figure 3 which is a dimensionless plot of the measured and predicted phenol concentrations along the Canadian shoreline starting from the Terminal Basins outfall location for the years 1974 and 1983.

The mixing model (K-E model) for the Lower River (including the Algoma Slip and Control Structure) has been calibrated for hydrodynamics. For steady-state loading isoconcentration maps can be developed with longitudinal resolution of the order of 50 ft (15 m) and lateral resolution as low as 1 percent of the flow in the reach. This permits a reasonably accurate zone of effect or mixing zone to be defined so that various loading scenarios can be compared and evaluated.

Table 1 illustrates the longitudinal extent of the mixing zones associated with discharge from the Terminal Basins. The 1986 loadings for ammonia and cyanide (4000 and 54 kg/d, respectively) will result in a mixing zone equal to or less than 300 m where the IJC and MOE Water Quality Objectives are met. Also, there are no toxic effects within the mixing zone, although the effluent is toxic. The mixing zone associated with the phenol loadings from the Terminal Basins extends about 3 km along the Ontario shoreline. Although the frequency of occurrence of low river flow (54,000 cfs) is about 0.1%, an estimate of the mixing zone associated with the 1986 loading is predicted to provide insight into the need for urgent reductions of phenol loadings. Figure 4 indicates that transboundary pollution which was not observed during the study, may occur under the lowest flow possible.

Modelling of the mixing zone for oil and grease took into account the partitioning of the chemical to water and sediment phases. Since oil and grease constitute a major factor in the absence of Hexagenia, a level of 1 mg/kg was selected as a guideline to be not exceeded in sediment in order to protect bottom-dwelling organisms. Based on this arbitrary guideline, the zone of effect is 800 m. Similarly, the suspended solids loadings resulted in a zone of 800 m using an arbitrary guideline of 10% above background to be met at the boundary of this zone. This arbitrary guideline was selected in order to minimize the amount of the organic portion of solids. This portion is responsible for most contaminants.

Based on the estimated extent of the mixing zones which varies from 300 m for ammonia to 3 km for phenol, a regulatory zone of 300 m long for all contaminants may be used under all river and industrial flow conditions. This regulatory zone will provide adequate protection for a variety of uses along the Sault Ste. Marie, Ontario waterfront. It will also ensure that areas near Sugar Island and those around the islands situated downstream are suitable for the production of zooplankton, invertebrate species and cold water fish.

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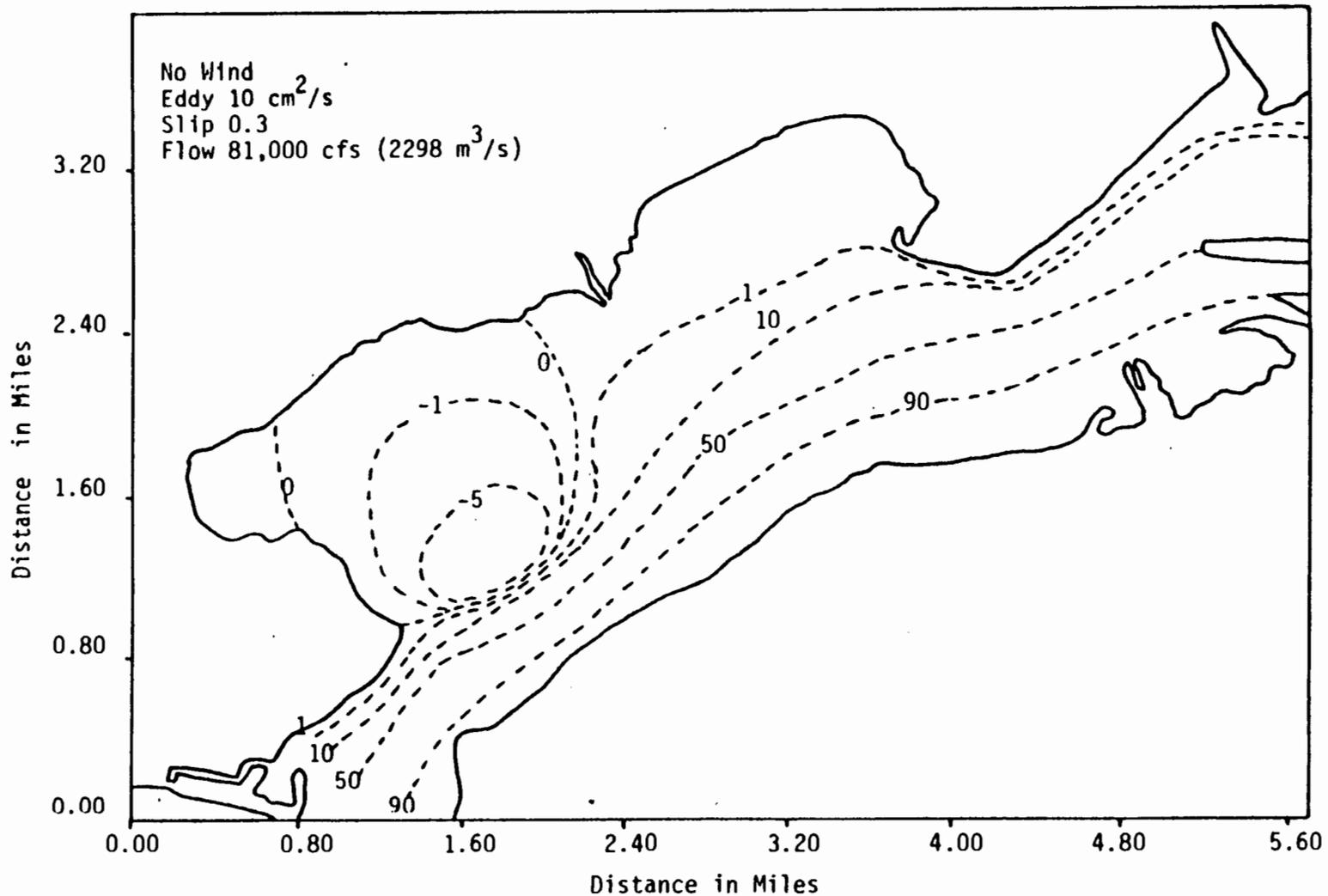


FIGURE 1 : DIMENSIONLESS STREAM FUNCTION CIRCULATION PATTERN (NO WIND)

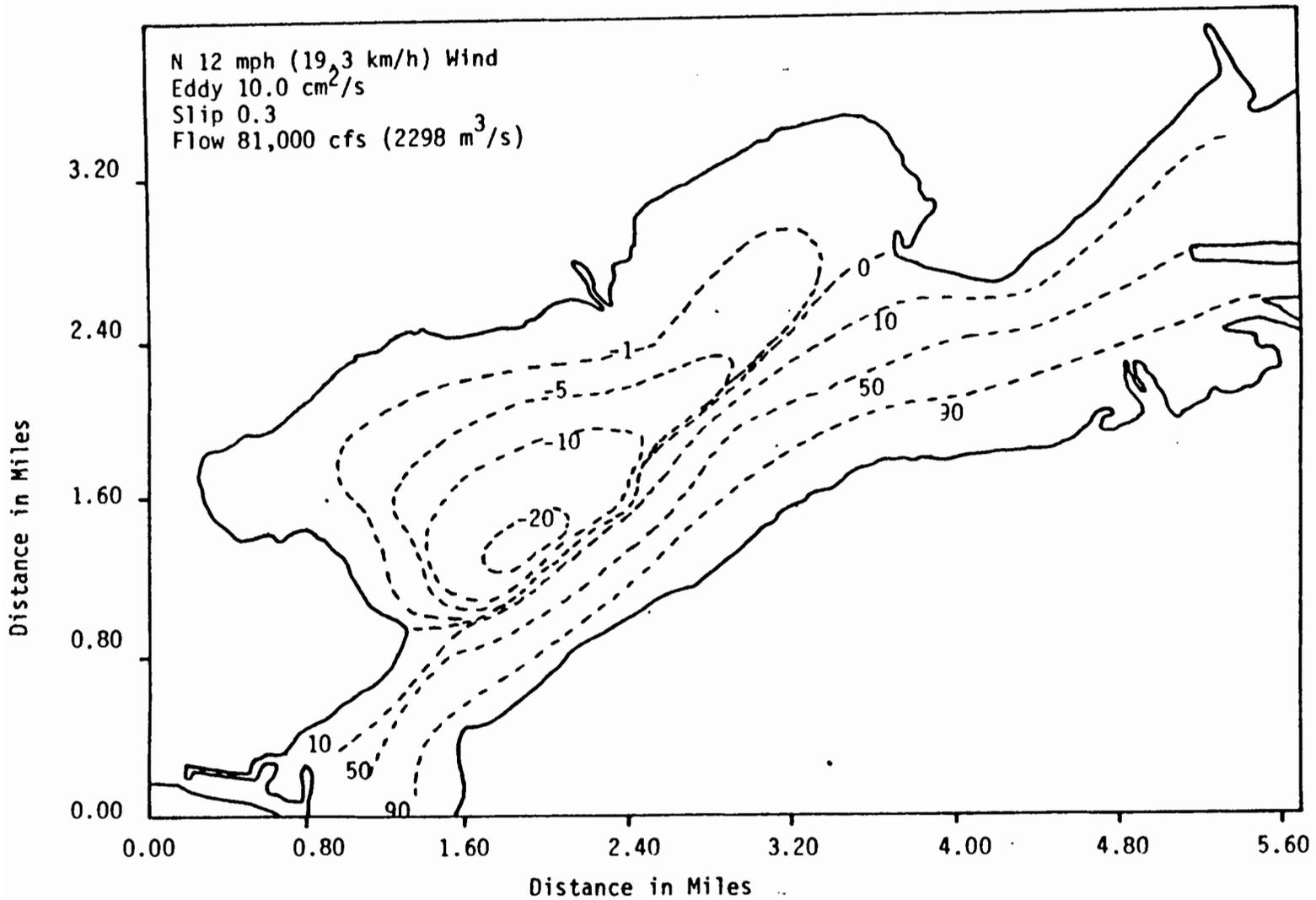


FIGURE 2 : DIMENSIONLESS STREAM FUNCTION CIRCULATION PATTERN (NORTH WIND)

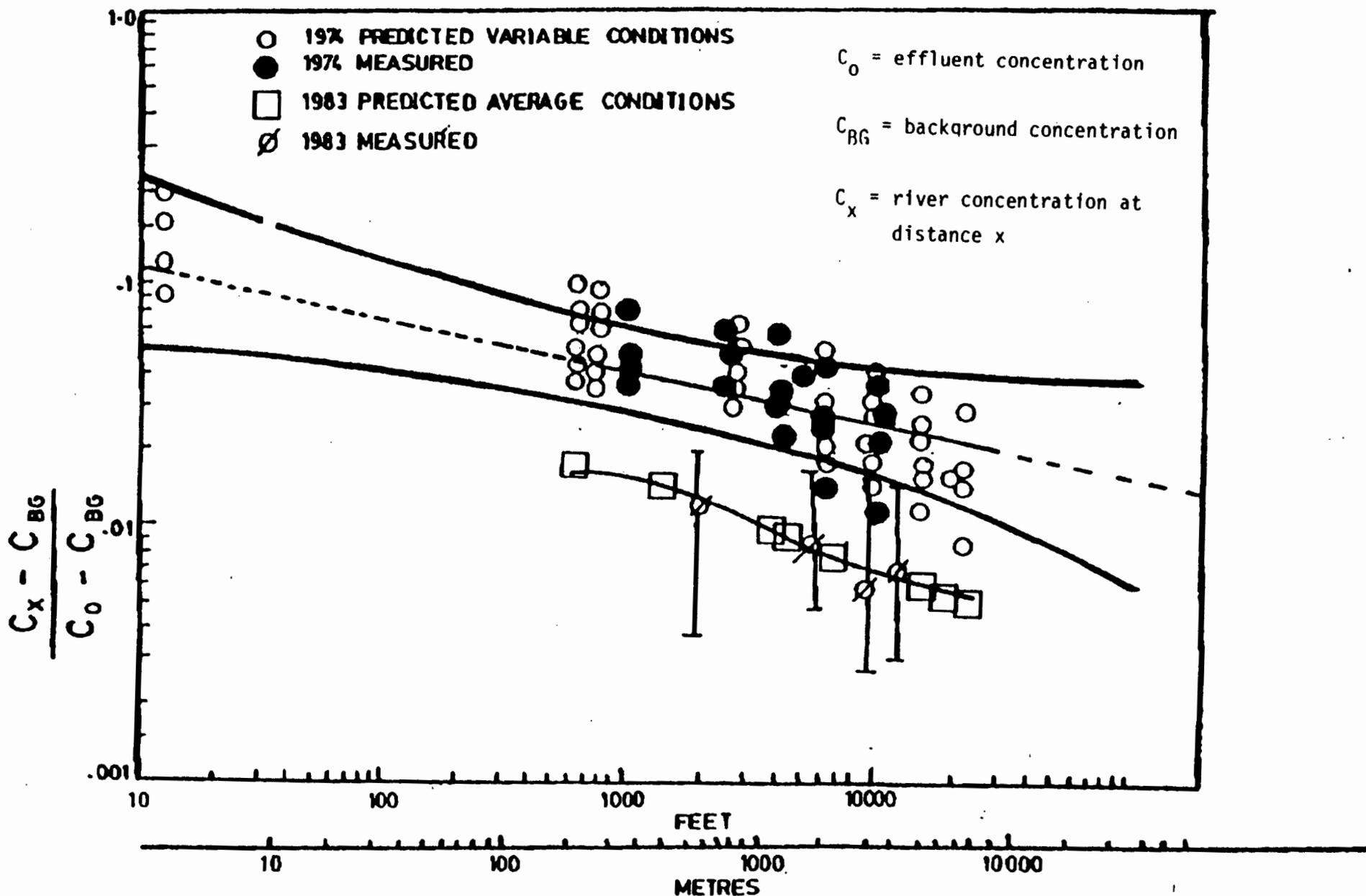


Figure 3. Predicted and Measured Phenol Concentrations versus

Distance Along the Canadian Shoreline

(1983 Verification)

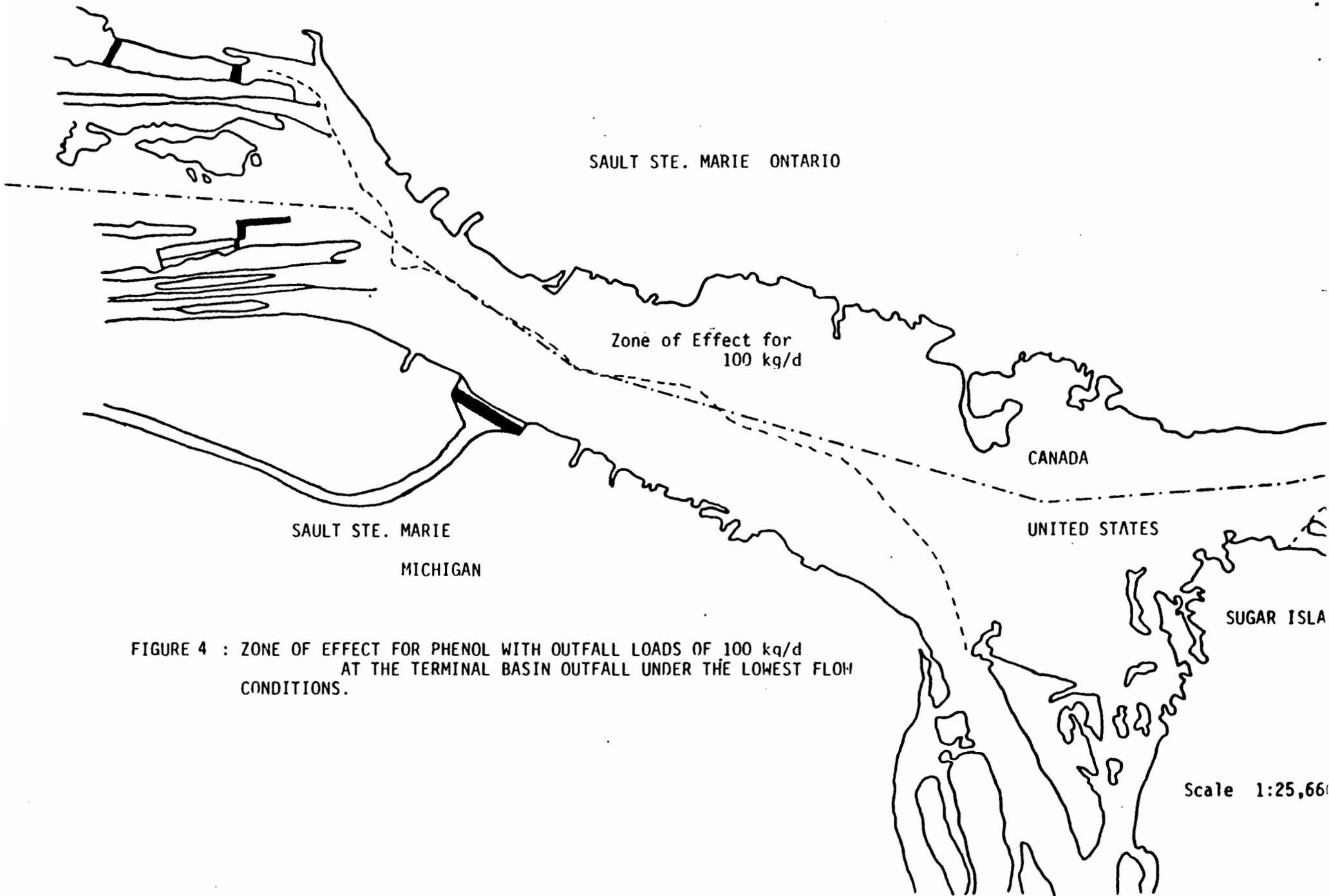


TABLE 1 - ZONES OF EFFECT PREDICTIONS

Parameter	1986 Loads (kg/d)	Length of Zone for 1986 Terminal Basins Loads (m)
Ammonia	4000	≤ 300
Cyanide	54	≤ 300
Phenol	100	3,000
Oil & Grease	1400	800
Suspended Solids	6000	800

D1300C/PM/GL-12

ST. CLAIR RIVER

Mass balance calculations

-As part of a special study of pollution in the St. Clair River, Chan et al (Water Pollution Research Journal of Canada 21: 332-343) calculated contaminant fluxes at Port Lambton. Their article is reproduced without modification on the following pages.

MEASURED AND MODELLED CHLORINATED CONTAMINANT
DISTRIBUTIONS IN ST. CLAIR RIVER WATER

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ABSTRACT

The concentration distribution of hexachlorobutadiene (HCBD), pentachlorobenzene (QCB), hexachlorobenzene (HCB) and octachlorostyrene (OCS) in water samples from transects across the upper and lower St. Clair River and the upper Detroit River were determined on four occasions in 1985. The data show a plume of these contaminants from the Sarnia industrial area. The fluxes and concentration profiles of the contaminants at Port Lambton have been modelled successfully using a simple transverse mixing model. A study on the chemical partitioning between the "dissolved" and "suspended sediment" phases shows that an important contaminant fraction is carried in the river by the suspended solids, particularly for lipophilic compounds such as HCB and OCS.

INTRODUCTION

Pollution problems in the St. Clair River have been documented by the International Joint Commission (IJC, Great Lakes Water Quality Board, 1982, 1983). The major sources of river contaminants appears to be the intensely industrialized area on the Canadian side of the river at or just downstream of Sarnia (Environment Canada and Ontario Ministry of the Environment, 1986). Both inorganic contaminants such as lead and mercury (Chau *et al.*, 1985); Thomas *et al.*, 1975) and organic chemicals such as perchloroethylene and chlorobenzenes (Bonner and Merez, 1981) have been shown to be present in elevated concentrations in the area. The contamination of the sediments has severely impacted the benthic communities along the Canadian shoreline for at least 20 kilometers downstream of Sarnia (Thornley, 1985). Significant loadings of volatile contaminants such as perchloroethylene and carbon tetrachloride from Sarnia industries have been documented (Bonner and Merez, 1981; Kaiser and Comba, 1986). More persistent contaminants such as hexachlorobutadiene (HCBD), pentachlorobenzene (QCB), hexachlorobenzene (HCB) and octachlorostyrene (OCS) have been shown to be present at elevated concentrations in native clams (Pugsley *et al.*, 1985), in caged clams (Kauss and Hamdy, 1985) and in bottom sediments (Oliver and Bourbonniere, 1985; Oliver and Pugsley, 1986). These later four chemicals appear to be useful tracers of Dow Chemical Company waste, since they are unwanted by-products of the production of chlorinated solvents and the company's earlier production of chlorine with graphite electrodes (Mumma and Lawless, 1975; Kaminsky and Hites, 1984).

Despite considerable work on sediments, biota and effluents in the area, little information is available on the concentrations of persistent chemicals in ambient waters of the St. Clair River. Some work has been done on the concentrations of volatile halogenated compounds in the river (Bonner and Merez, 1981; Kaiser and Comba, 1986) but detection limit problems have precluded detailed analysis of other chlorinated organics. In this paper, we present data for HCBD, QCB, HCB and OCS from large volume (40 L) river samples which were extracted and concentrated to 1 mL to reduce detection limits to below 0.1 ng/L. In addition,

several organochlorine pesticides and PCBs have also been determined but they will not be discussed in detail since their concentrations did not change significantly in the study area.

METHODS

(a) Sampling Locations

The sampling locations are shown in a study area map in Figure 1. The sampling locations at Point Edward (SC1 and 2), one on each side of the international border and upstream of the Sarnia petrochemical complex, were selected to provide baseline data for incoming St. Clair River water. The next set of six stations, which were located at 100 m intervals across the channel at Port Lambton (SC3-8), was about 34 km downstream of the chemical industries and about 2 km upstream of the point where the river branches. The three channels, Chenal Ecarté (SC9), the North Channel (SC10) and the South Channel (SC11) were also sampled. The remaining two stations were located at the head of the Detroit River just upstream of Windsor and Detroit (SC12 and 13) to evaluate the impact of Lake St. Clair on St. Clair River contaminant concentrations. Samples were collected on four occasions in 1985: August 7, August 27, September 23 and October 17.

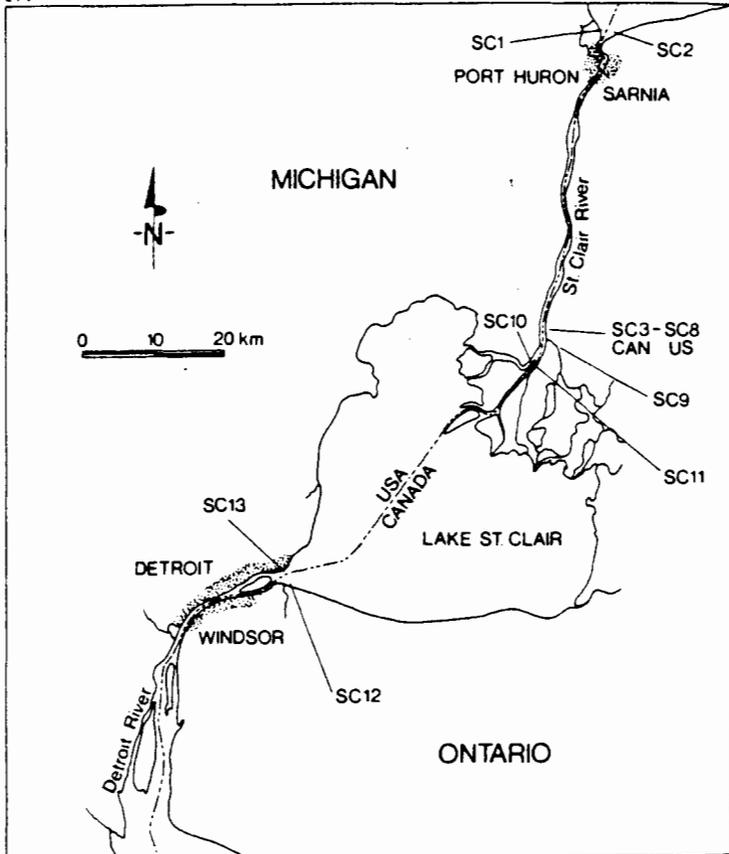


Figure 1 Map of study area and sampling locations.

(b) Field and Laboratory Procedures

At each sampling location, water was pumped aboard the research vessel Advent from mid-depth using a March 5CMD submersible pump. The water passed through a Westfalia centrifuge, which removed the suspended material, and was collected in two 20-L stainless steel containers. The water samples were transported to Burlington on the day of collection where they were kept refrigerated at 4°C until analysis. In addition, composite water samples (prepared by combining equal volumes of water from each transect station) and suspended sediments were collected from the centrifuge at the head of the St. Clair River, at Port Lambton and at the head of the Detroit River.

The water samples were extracted with dichloromethane in a counter-current continuous extractor (Goulden, 1985). Suspended sediments were soxhlet-extracted with an acetone/hexane mixture (Oliver and Nicol, 1982). The extracts underwent the normal pre-concentration and clean-up procedures before capillary gas chromatographic analysis (Oliver and Nicol, 1982). In addition to HCB, PCB, HCB and OCS, several other chlorobenzenes, organochlorine pesticides and PCBs were also analyzed (Chan and Kohli, 1986). Preliminary GC/MS studies on sample extracts from the study area confirmed the presence of the four main study compounds.

RESULTS**(a) Water Concentration Distribution**

A plot of dieldrin concentrations in the water phase from the 13 sites for the four cruises is shown in Figure 2. The dieldrin concentration is approximately the same in all samples showing the ubiquitous distribution of this contaminant in the study area. Since there does not seem to be any upward trend in the data downstream of Sarnia, the values would seem to show no significant point sources for the pesticide along the St. Clair River. Long-range transport is the likely mechanism for this "low-level" widespread contamination. Similar concentration distributions were observed for other pesticides such as α - and γ BHC and for PCBs (Chan and Kohli, 1986).

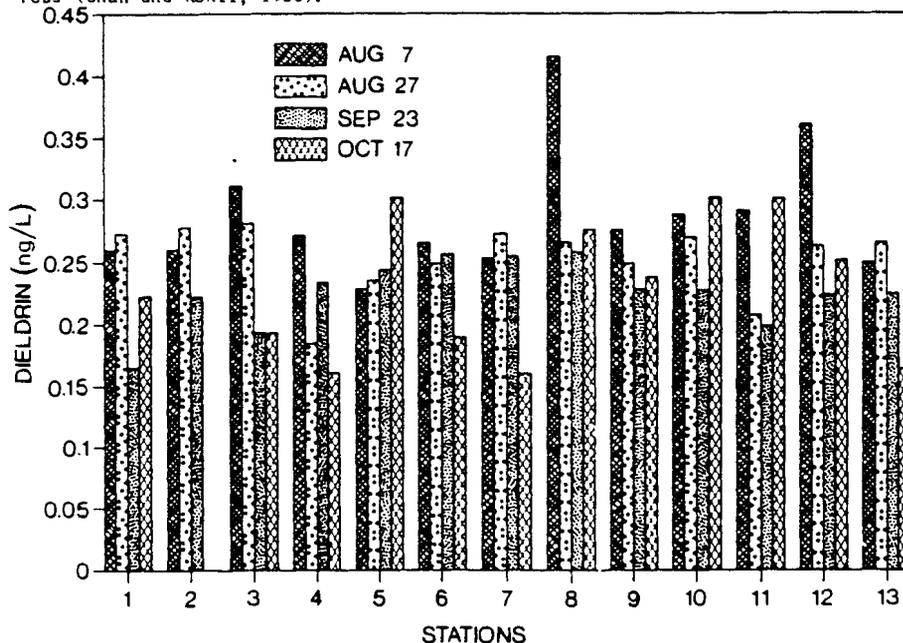


Figure 2 Dieldrin concentrations at study stations.

The concentration distribution for HCB is shown in Figure 3 and, in contrast to the behaviour of dieldrin, a marked plume from the Sarnia area is apparent. Very little HCB is present in the headwater samples. At the Port Lambton transect, peak values are observed in samples nearest the Canadian shoreline with decreasing concentrations across the river. This data shows that the plume from Sarnia has not travelled sufficient distance downstream to have spread completely and uniformly across the river. The HCB values in the three branching channels show the highest value in Chenal Ecarté (which receives nearshore Canadian water), significant levels in the South Channel, and very low concentrations in the North Channel. Diminished but measurable HCB values are observed at the head of the Detroit River, showing some Sarnia contaminant carryover but also some significant loss processes occurring in Lake St. Clair. Similar concentration distributions were observed for HCBd, QCB and OCS (see Table 1).

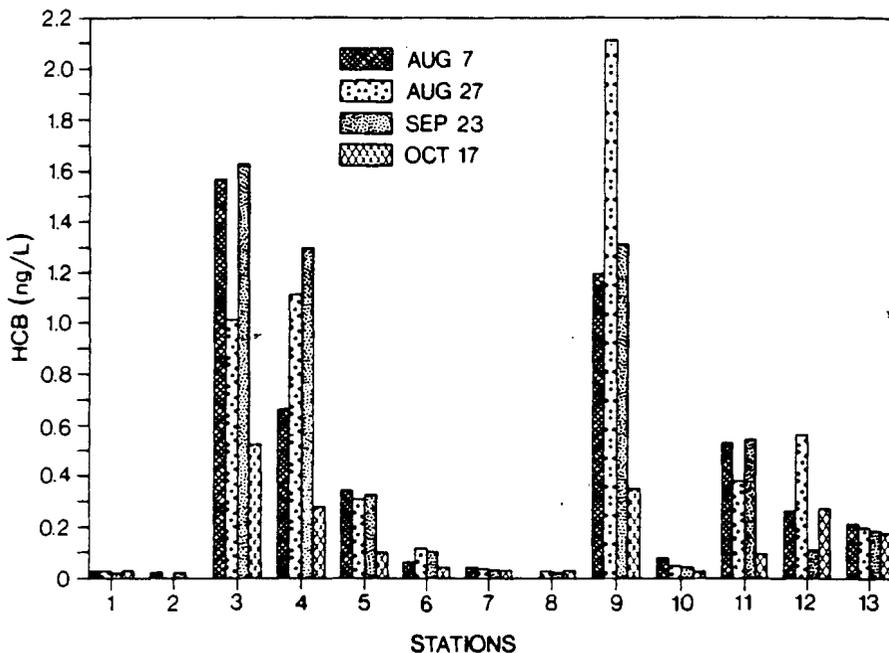


Figure 3 HCB concentrations at study stations.

(b) Calculation of Contaminant Flux at Port Lambton

Using the above concentrations and water depths, location and river discharge, the flux of a given substance across the river cross section at Port Lambton can be calculated from the equation

$$F = \int_0^w uhcdz \quad (1)$$

in which F is the flux, h is the depth, z is the cross-stream distance, w is the river width and u and c are the depth-averaged values of velocity and concentration, respectively.

Table 1 Contaminant concentrations, depths (h), distance from Canadian shore (z) and fractional discharge (η) at Port Lambton.

Date	Concentrations (ng/L)							
	Station	HCBd	QCB	HCB	OCS	h(m)	z(m)	η
07/08/85	SC3	3.4	0.18	1.6	0.063	2.5	6	0.0004
	SC4	3.4	0.092	0.66	0.027	16.0	140	0.35
	SC5	0.92	0.041	0.34	0.013	16.0	230	0.46
	SC6	0.11	N.D.	0.061	N.D.	12.0	360	0.72
	SC7	0.061	N.D.	0.040	N.D.	10.0	490	0.89
	SC8	0.029	N.D.	N.D.	N.D.	7.5	580	0.97
27/08/85	SC3	5.0	0.093	1.0	0.029	2.8	6	0.0004
	SC4	8.0	0.10	1.1	0.080	15.5	130	0.15
	SC5	2.2	0.030	0.31	0.018	15.5	260	0.52
	SC6	0.59	N.D.	0.12	N.D.	13.8	310	0.63
	SC7	0.13	N.D.	0.034	N.D.	10.8	400	0.78
	SC8	0.035	N.D.	0.023	N.D.	7.8	490	0.89
23/09/85	SC3	1.8	0.19	1.6	0.048	3.3	6	0.0004
	SC4	2.1	0.14	1.3	0.030	14.5	98	0.11
	SC5	1.7	0.035	0.33	N.D.	15.0	240	0.46
	SC6	1.4	N.D.	0.10	N.D.	14.0	260	0.52
	SC7	1.1	N.D.	0.027	N.D.	10.0	400	0.78
	SC8	1.2	N.D.	0.019	N.D.	8.0	540	0.93
17/10/85	SC3	1.8	0.063	0.53	0.028	3.0	6	0.0004
	SC4	1.3	0.10	0.28	0.012	16.0	92	0.095
	SC5	0.45	0.048	0.095	N.D.	16.0	210	0.39
	SC6	0.075	N.D.	0.040	N.D.	14.0	280	0.58
	SC7	0.017	N.D.	0.025	N.D.	11.0	380	0.74
	SC8	0.015	N.D.	0.028	N.D.	8.0	540	0.93

For transport problems in natural streams with irregular cross sections, it is convenient to introduce the cumulative discharge or stream-tube concept which simplifies the transport equations. This involves the introduction of a new coordinate $q(z)$, which replaces the transverse distance z . Writing

$$q(z) = \int_0^z uhdz \quad (2)$$

It can be seen that $q(z)$ represents the amount of flow between the bank and a distance z across the stream. $q(z)$ therefore varies from zero at one bank to the river's discharge Q at the other bank.

Substituting Eq. (2) into Eq. 1, one gets

$$F = \int_0^Q cdq \quad (3)$$

One can non-dimensionalize q with the river discharge Q so that the dimensionless coordinate $\eta = q/Q$ varies from zero at one bank to 1.0 at the other bank and the flux is given by

$$F = Q \int_0^1 c \eta dz \tag{4}$$

η represents a fraction of the total river discharge.

Equation (4) is used to calculate the flux of the various chemicals. However, in order to make the calculations, it is necessary to know how c varies with η . The cruise data only provides the variation of c with transverse distance z . Therefore it is necessary to calculate how the cumulative discharge q varies with z which will then provide the variation of η with z . This calculation is straightforward if velocity measurement are available. In the present case, with no velocity data, some other assumptions have to be made. Assuming that each vertical slice of the river follows Manning's resistance equation, one can write

$$\frac{u}{\bar{U}} = \left[\frac{h}{H} \right]^{2/3} \tag{5}$$

in which \bar{U} and H are the average velocity and depth respectively of the whole cross section. Using Eq. (5) it can be shown that

$$\eta = \frac{q}{Q} = \frac{1}{w} \int_0^z \left[\frac{h}{H} \right]^{5/3} dz \tag{6}$$

Therefore Eq. (6) can be used to generate the variation of η with z , using only the cross-sectional profile of the river.

The depth and cross-stream distance information from the four cruises at the Port Lampton site are plotted in Figure 4(a) from which a profile of the cross section can be drawn. Using Figure 4(a), a curve of $(h/H)^{5/3}$ versus z was constructed and, using Eq. (6), a curve of η versus z was obtained (Figure 4(b)).

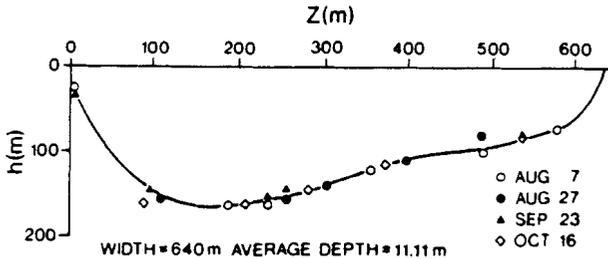


Figure 4(a) River cross section at Port Lampton depth (h) in meters versus distance from Canadian shoreline (z) in meters.

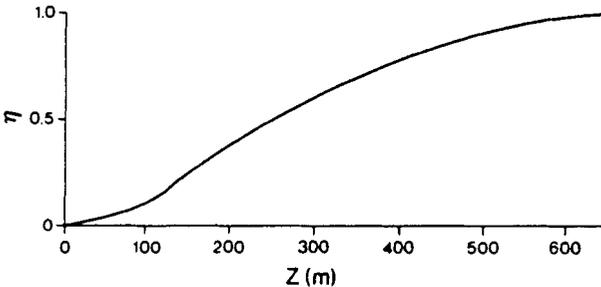


Figure 4(b) The variation in fractional discharge (η) with stream cross-sectional distance (z).

This curve shows the fraction of the total discharge which passes between the shore at Port Lambton and a given distance across the river. From this figure, the values of η where the samples were taken could be obtained and graphical integration using Eq. (4) gave the flux of each of the chemicals for each of the four days of the cruises. The flux values are summarized in Table 2. These values are in the same range as those observed by direct monitoring of Dow Chemical effluents on November 27, 1985 - HCB 140 g/d; QCB 5.4 g/d; HCBBD 230 g/d; OCS 5.4 g/d (Environment Canada and Ontario Ministry of the Environment, 1986).

Table 2 St. Clair River discharges (m^3/s) and contaminant fluxes at Port Lambton (gm/day).

Date	Discharge	HCB	QCB	HCBBD	OCS
07/08/85	6254	280	31	850	11
26/08/85	6254	240	23	1700	15
24/09/85	6032	230	26	820	6
17/10/85	6154	59	22	240	5

(c) Modelling Concentration Profiles

It is assumed that the contaminants entered the river from a point source in the Sarnia area at a rate equal to the flux values given in Table 1. Using this assumption, one can calculate the concentration profiles at various distances downstream. The solution of the mass balance equation for a conservative substance, with a point source at the origin, is given by the equation (Beltaos, 1979)

$$C = \frac{F}{Q} \frac{2}{\sqrt{2\pi\zeta}} \left\{ \exp(-\eta^2/2\zeta) + \sum_{m=1}^{\infty} \left[\exp\left(\frac{-(2m-\eta)^2}{2\zeta}\right) + \exp\left(\frac{-(2m+\eta)^2}{2\zeta}\right) \right] \right\} \quad (7)$$

in which

$$\zeta = \frac{2xe_z \int_0^1 uh^2 dn}{Q^2} \quad (8)$$

x is the distance downstream from the source and e_z is the transverse mixing coefficient for that reach of the river. For these calculations, the source is taken to be 33.5 km upstream from Port Lambton, i.e., the Dow Chemical site.

It should be noted that these organic compounds are not truly conservative substances and that losses to the atmosphere and sediments may occur. As a first approximation, this approach is probably adequate since loss coefficients for these chemicals are not available. In order to apply a more comprehensive model, which includes loss terms, much more field data would be required.

All the quantities in Eq. (8) are known except for the transverse mixing coefficient e_z . This value is either obtained from the field experiments or it may be estimated from empirically correlated e_z values for various rivers and channels (Lau, 1985). For the present case, it was decided to use one of the 16

sets of concentration data for evaluating e_z , i.e. the e_z value was varied until the concentration profile calculated from Eq. (7) matched that measured profile. The HCB data from the August 7 cruise was used for this purpose. With a flux of 280 gm/day, and a discharge of 6254 m³/s, it was found that a very good agreement between the computed concentration profile and the measured data was obtained when e_z was taken to be equal to 0.25 m²/s (Figure 5). This value of e_z was then used, together with the appropriate flux and discharge values from Table 1, to calculate the concentration profiles for the remaining 15 cases. These 15 calculated profiles were then compared with the 15 sets of measured data. The pertinent data are listed in Table 1 with the measured concentrations.

The computed profiles of c versus η and the measured data are plotted in Figures 5 to 8. Bearing in mind the variability of field data, the agreement can

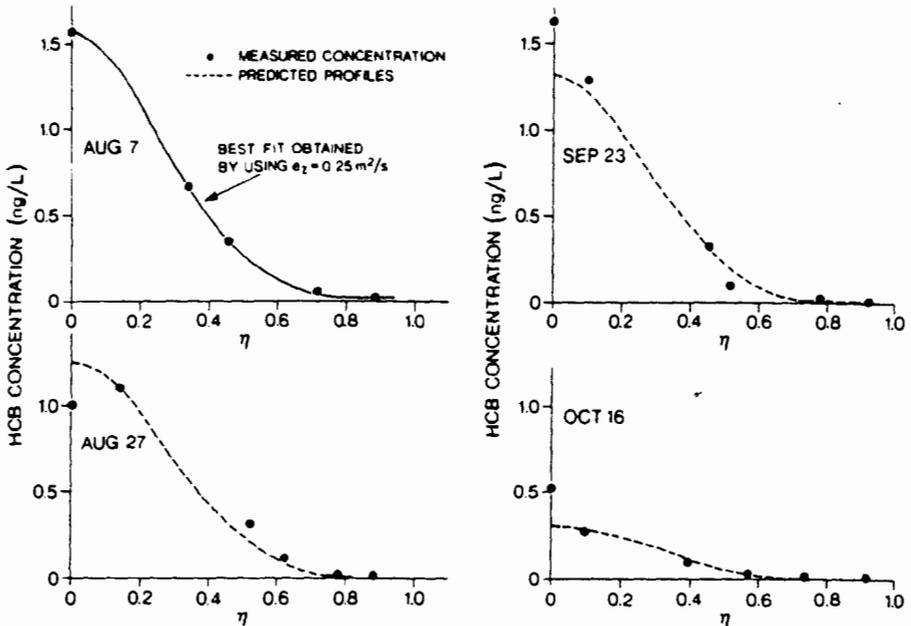


Figure 5 Predicted and measured concentration profiles at Port Lambton for HCB.

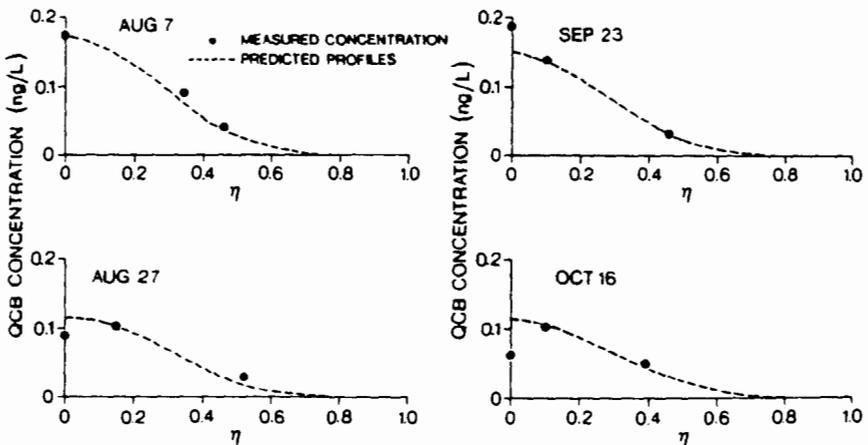


Figure 6 Predicted and measured concentration profiles at Port Lambton for QCB.

(d) Contaminant Partitioning to Suspended Sediments

In addition to measurements of the "dissolved" chemicals in the St. Clair River, suspended sediments from the river were also collected and analyzed. Equal volumes of water from stations 1 and 2 (2x20 L), from stations 3 to 8 (6x8 L) and from stations 12 and 13 (2x20 L) were combined and extracted to obtain approximate mean concentrations at these locations. Suspended sediments from ~600 L of water were recovered from across each transect and analyzed. Concentration data for whole water (dissolved + suspended solids) and for the suspended solids for the four cruises are shown in Table 3.

Table 3 The concentrations of HCB, QCB, HCB and OCS in composite samples from the head of the St. Clair River (HSCR), Port Lambton on the St. Clair River (PLSCR) and the head of the Detroit River (HDR).

Station	Whole Water (ng/L)		Suspended Sediment (ng/g)		% "Dissolved"		Solids Concentration (mg/L)	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
<u>HCB</u>								
HSCR	0.009-0.3	(0.09)	N.D.-1.1	(1.0)	89-99	(95)	0.6-2.0	(1.2)
PLSCR	0.7-6.0	(2.3)	8-44	(20)	93-97	(96)	3.3-4.2	(3.7)
HDR	0.09-0.2	(0.15)	1.7-3.5	(2.4)	82-97	(90)	3.9-6.6	(4.9)
<u>QCB</u>								
HSCR	0.009-0.017	(0.012)	1.1-3.6	(2.2)	59-94	(81)		
PLSCR	0.05-0.10	(0.072)	2.4-8.0	(4.5)	67-83	(78)		
HDR	0.05-0.07	(0.055)	3.8-6.6	(4.8)	43-67	(59)		
<u>HCB</u>								
HSCR	0.01-0.06	(0.03)	N.D.-2.9	(2.0)	80-97	(90)		
PLSCR	0.3-1.6	(0.8)	60-240	(130)	35-45	(41)		
HDR	0.2-0.3	(0.22)	15-29	(21)	50-59	(56)		
<u>OCS</u>								
HSCR	0.005-0.01	(0.008)	N.D.-0.8	(0.7)	90-93	(92)		
PLSCR	0.05-0.24	(0.12)	10-39	(23)	30-32	(31)		
HDR	0.03-0.05	(0.04)	3.8-7.0	(4.8)	39-57	(45)		

Large concentration increases in both whole water and suspended sediments are apparent below the industrial input of Sarnia at Port Lambton. The mass fluxes in Table 2 refer to only the operationally-defined "dissolved" fraction. At Port Lambton, 96% of the HCB, 78% of QCB, 41% of HCB and 31% of OCS are in the "dissolved" fraction (Table 3). This data shows that the "suspended sediment" fraction will contribute additional chemical loadings, particularly for HCB and OCS, to Lake St. Clair and the Detroit River.

The water solubility of the four study chemicals decreases in the sequence HCB>QCB>HCB>OCS, whereas, the chemicals' lipophilicity or octanol-water partition coefficients increases in the order HCB<QCB<HCB<OCS. Thus based on physical-chemical properties the degree of partitioning to suspended solids would be expected to increase in the sequence HCB<QCB<HCB<OCS as is observed.

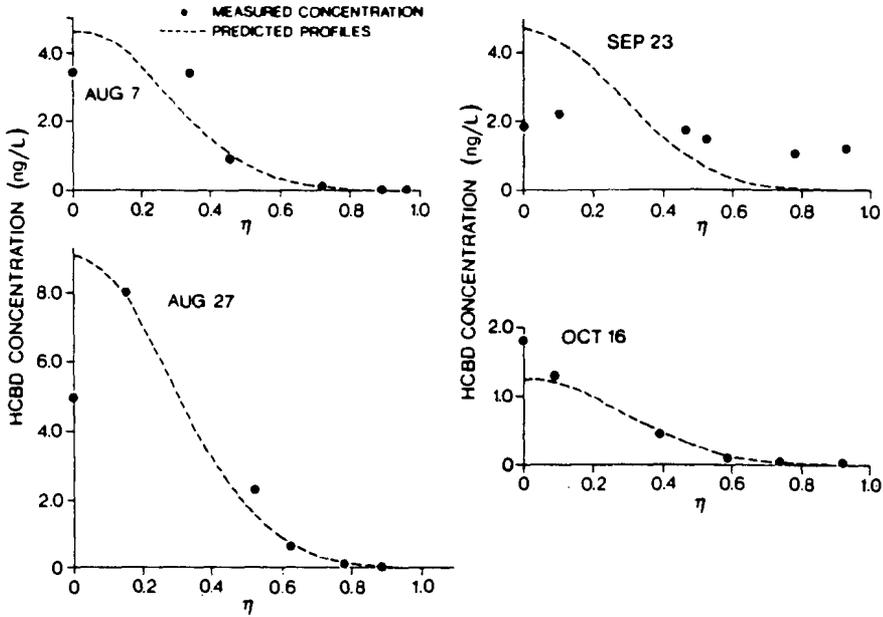


Figure 7 Predicted and measured concentration profiles at Port Lambton for HCBd.

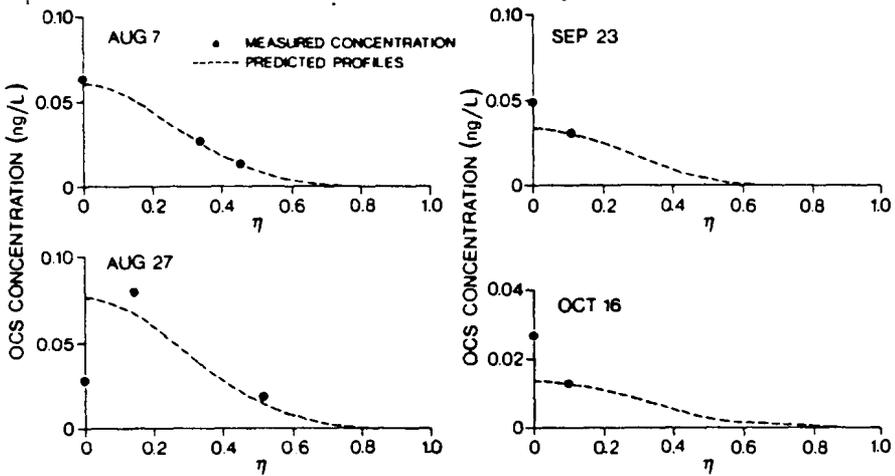


Figure 8 Predicted and measured concentration profiles at Port Lambton for OCS.

be considered quite good. The only exception is the HCBd data of September 23, which are relatively constant across the river and show no plume-like distribution. Two of the OCS distributions have only two data points each and for those it is difficult to say how well the data fit the profile.

SUMMARY AND DISCUSSION

The field data show that the plume of contaminants discharged to the St. Clair River by the chemical industry in Sarnia spreads only slowly as it moves downstream. The plume is still mainly confined to within 300 m of the Canadian shoreline at Port Lambton about 34 km downstream of the major sources. These water concentration profiles agree quite well with sediment contaminant distributions which show no transboundary movement of the Sarnia contaminants in the river (Oliver and Pugsley, 1986).

For calculation of the concentration profiles, a value of e_z of $0.25 \text{ m}^2/\text{s}$ was empirically derived by curve fitting the August 7 HCB profile at Port Lambton. This value for e_z can be non-dimensionalized with U_*H (U_* is the shear velocity) for comparison with data from other rivers. With a slope of 0.000025 and an average depth of 11.11 m, the shear velocity is equal to 0.052 m/s and the dimensionless dispersion coefficient e_z/U_*H is equal to 0.43. This value fits in quite well with published data compiled by Lau (1985). Using e_z of $0.25 \text{ m}^2/\text{s}$, the concentration profiles for the remaining 15 flux values were computed. Most of these profiles compared quite well with the measured data. Therefore, the measured concentration profiles of these chemicals at Port Lambton are compatible with the assumption that they originated at some point source in the Sarnia area. The fact that the profiles for all four chemicals fitted the calculations using the same values of e_z and x indicate that these chemicals either came from the same discharge or from discharges in the same vicinity.

The e_z value is quite close to what one would expect given the hydraulics of that river reach. Therefore, the agreement of the concentration profiles also means that the choice of the source location as 33.5 km upstream from Port Lambton is reasonable. If one had chosen the source location to be much closer to Port Lambton, the e_z value would have to be unreasonably large in order for the profiles to agree.

These concentration distributions also provide some insight for sampling. If one were to monitor the loading of these chemicals by sampling at Port Lambton, it would be wise to concentrate the sampling effort between the Canadian shore and 300 metres offshore because all the profiles indicate that the concentrations are quite negligible beyond the fractional discharge n of 0.5. From Figure 4(b), it can be seen that n equals 0.5 at x equal to 250 m. Of course, it may even be better to sample much further upstream, where the plume is smaller in size and where the concentrations will be higher.

The equations in this paper can also be used to calculate the concentration profile of the contaminant plume at various locations downstream from the source given various loading scenarios. This information would be useful for predicting the necessary loading reductions required to meet drinking water quality objectives for various towns and cities downstream of Sarnia.

The results of the water/suspended sediment partitioning study show that in future measurements should be made on both the "dissolved" and the "suspended sediment" phases or on whole water samples if contaminant fluxes or loadings are required. This is particularly true for lipophilic compounds such as HCB and OCS.

ACKNOWLEDGEMENTS

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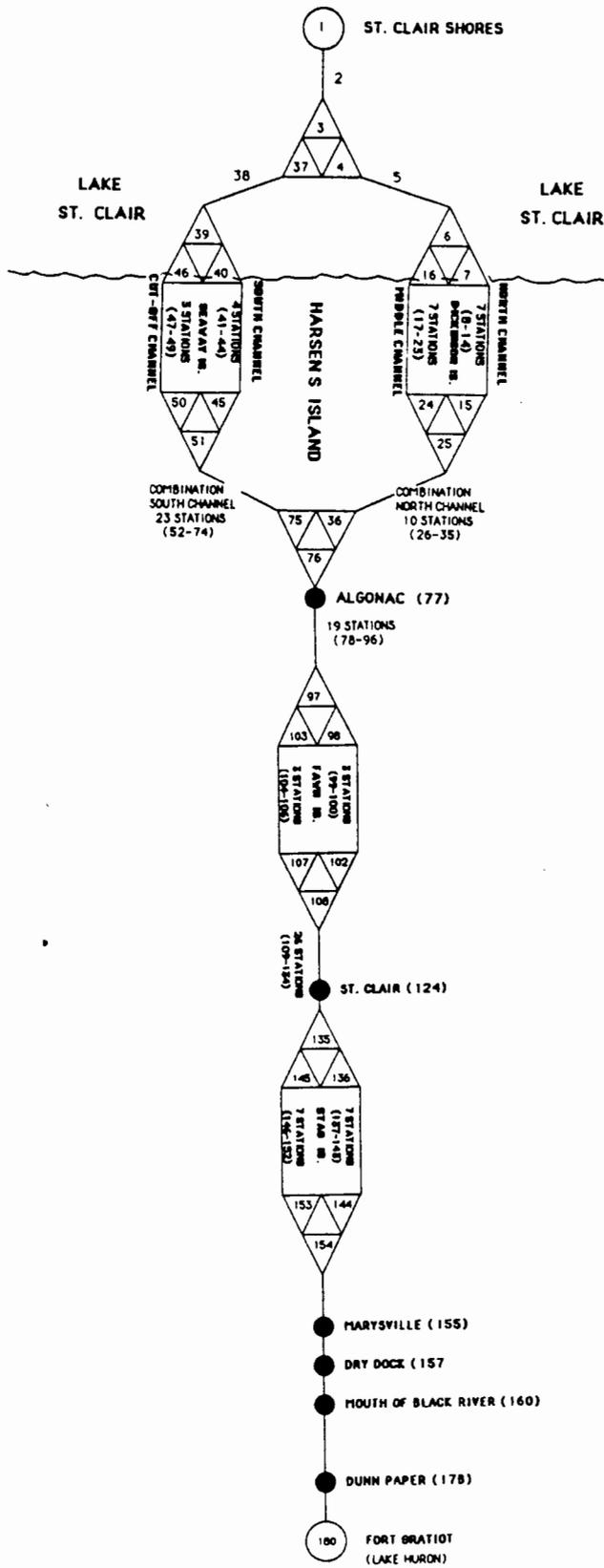
Process-oriented models

Physical: hydrodynamics, winds, waves, and currents

- An unsteady flow model of the entire St. Clair River was developed and calibrated for the entire St. Clair River, from Lake Huron to Lake St. Clair. The model provides for flow separation around Stag and Fawn Islands in the upper and middle river, and through the main delta channels in the lower river (Figure 3). The model predicts stage, discharge and velocity data on an hourly or daily basis that can be used in simulating the fate and transport of toxic substances. For instance, the model could be used to generate an input hydrological flow data set for TOXIWASP applications. The model can be run for the entire river or any preselected river reach bounded by water level gages. Details of model development and calibration are documented in the Level I Modeling Work Group report. (Derecki et al., NOAA-GLERL)

- Another hydrodynamic model was developed for the St. Clair River. This model is a steady state, depth-averaged, turbulent mixing model that was developed for complex river systems with multiple outfalls. The segmentation scheme used is shown in Figure 4. Details of model development and calibration are documented in the Level I Modeling Work Group report (Nettleton, DMOE).

Physical-Chemical-Biological models



ST CLAIR RIVER SCHEMATIC REPRESENTATION

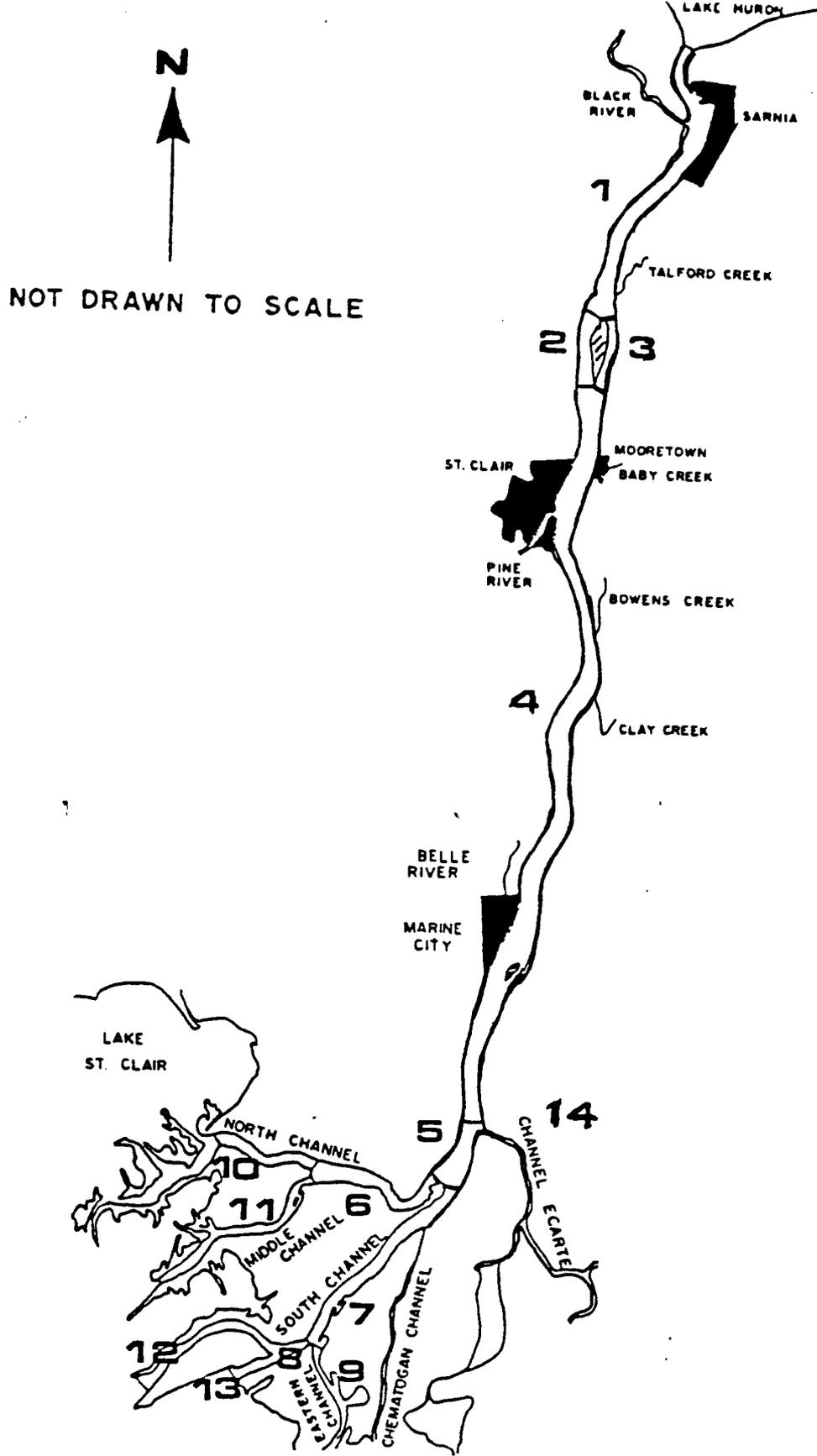


Figure 1. Definition of Major Reaches in the St. Clair River.

-Two chemical transport models were developed for the St. Clair River. The hydrodynamic model used to drive chemical transport was developed by Nettleton, as described above and in the Level I Modeling Work Group report. The chemical transport models were based on the KE model framework and the EPA TOXIWASP framework. The KE model solves for the 2 dimensional depth-averaged total contaminant concentration in the water column only. The TOXIWASP model simulates the dissolved, sediment sorbed, and biosorbed concentrations of the contaminant within both the water column and the sediment bed. Both models were tested by attempting to simulate the transport of HCB in the river. HCB was chosen as a test contaminant because loading estimates and ambient river data were available. Predictions from the KE and TOXIWASP models were in good agreement with the trends and magnitudes of measured HCB water column concentrations at two distances from the DOW location (Fig. 5-7). Predicted sediment concentrations from the TOXIWASP model (Fig. 5,7) were also rather good in both trend and magnitude. Models of the fate of other contaminants awaits final assembly of the St. Clair River MISA data-base. Data will also be used in future modeling work to understand foodweb movement of contaminants and bed load contaminant transport. (Nettleton, DMOE)

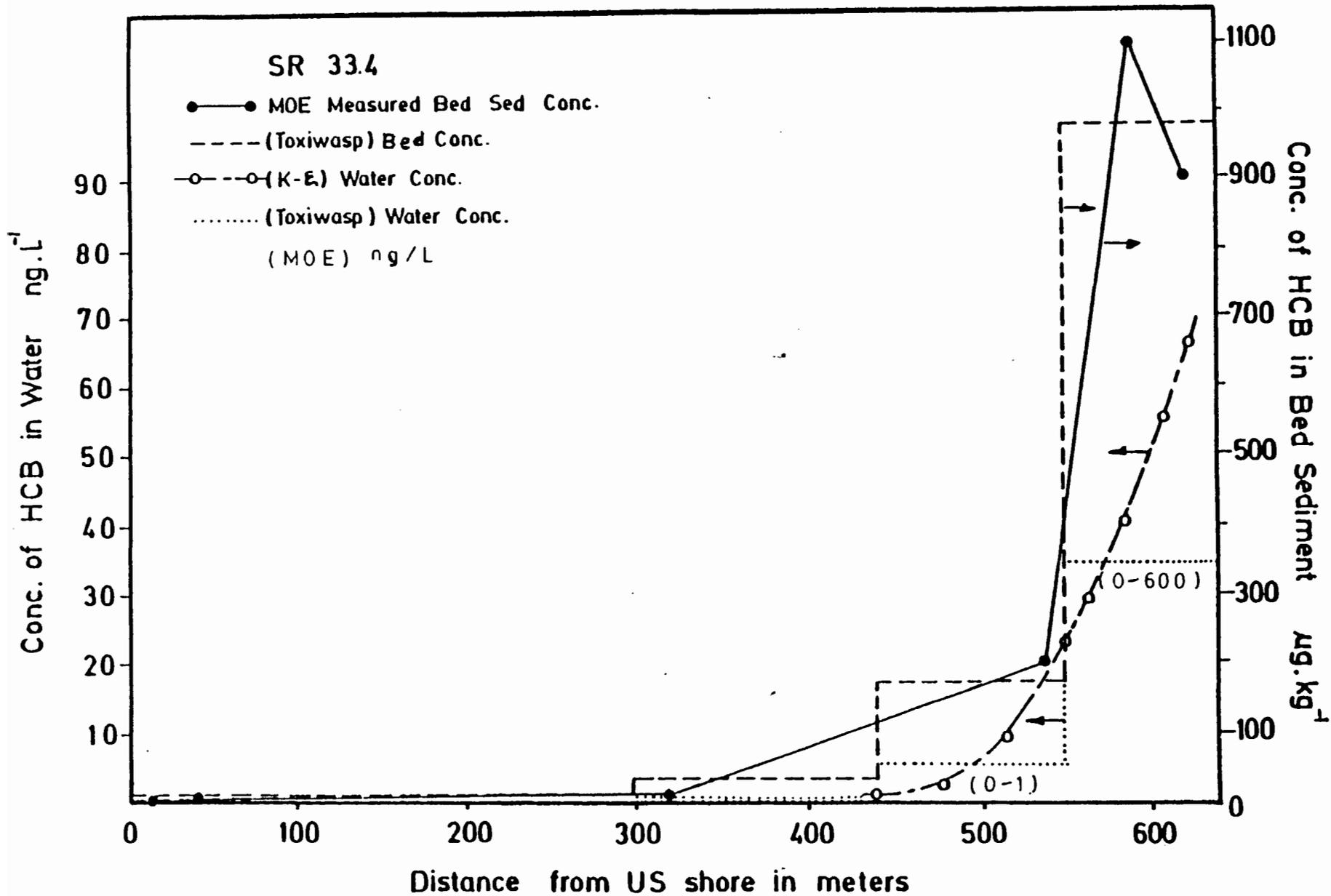


Figure 6. Comparison of MOE Field Measurements with Predictions of the Models, for a Section about 2 km downstream of Dow.

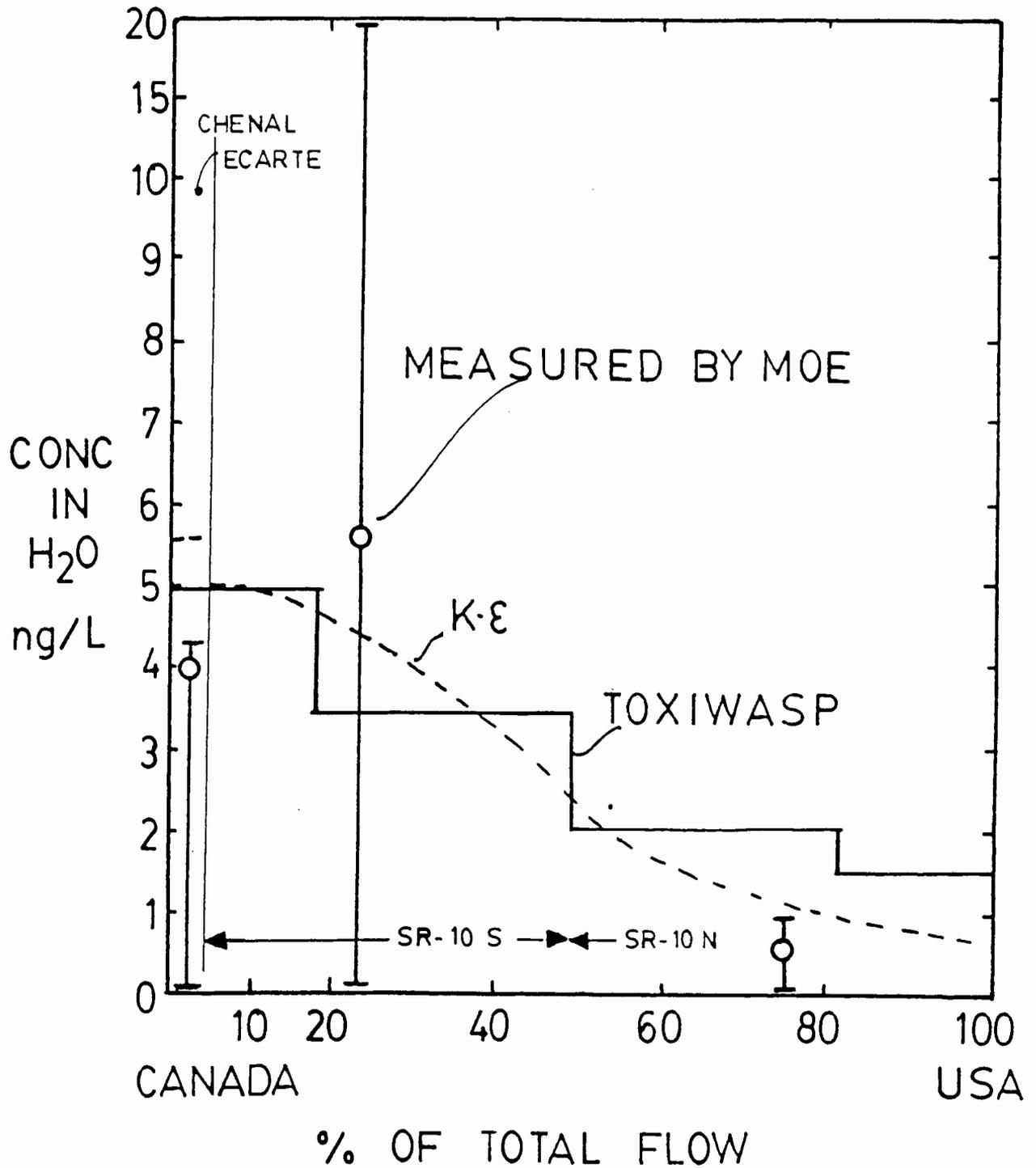


Figure 7. Comparison of MOE Field Measurements of HCB Concentrations in the Water-Column with Predictions of the Models, for a Section near Chenal Ecarte, (about 38 km d/s of Dow).

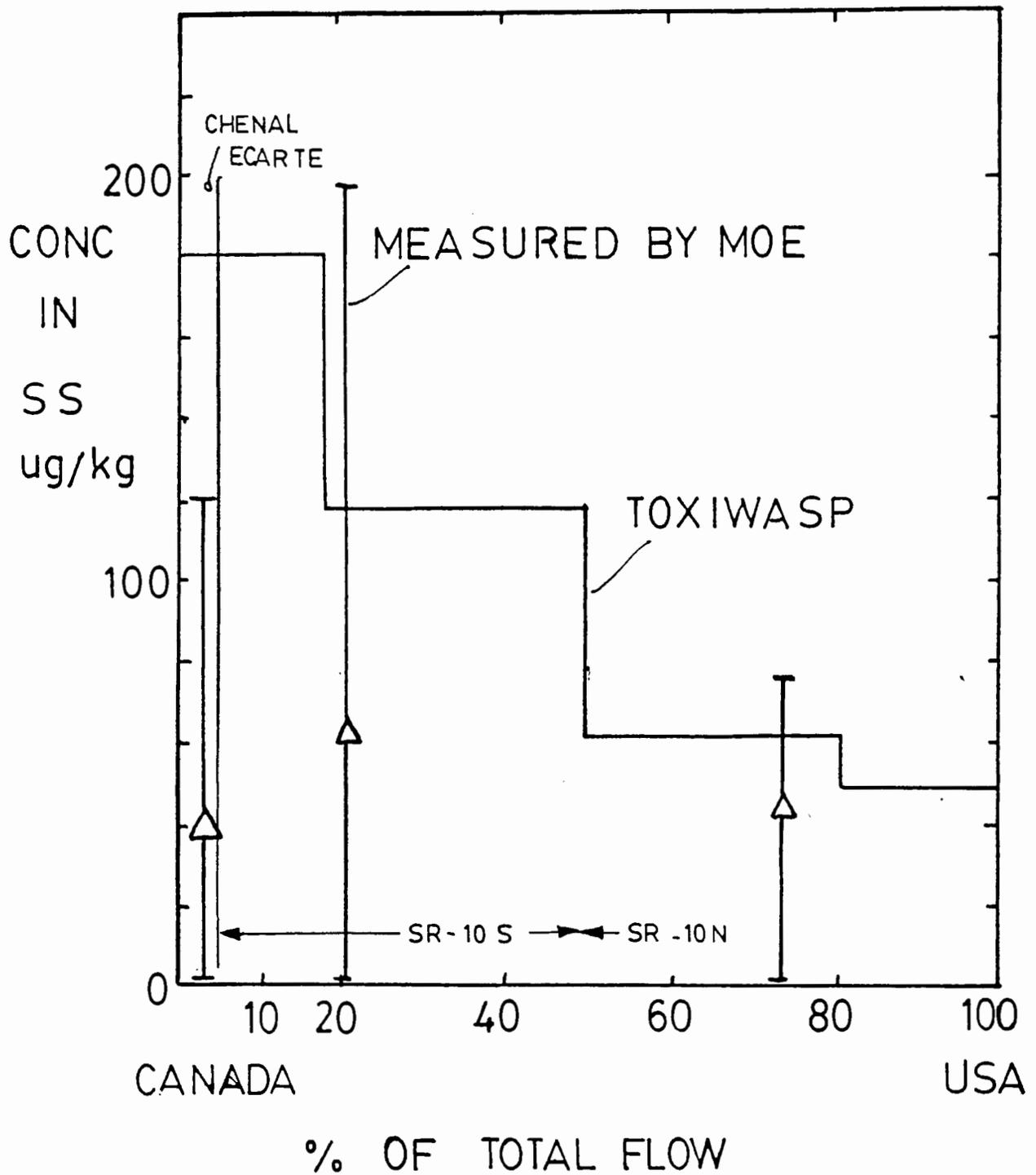


Figure 10. Comparison of MOE Field Measurements of HCB Concentrations in the Sediment with TOXIWASP Predictions, for a Section near Chenal Ecarte, (about 38 km d/s of Dow).

LAKE ST. CLAIR

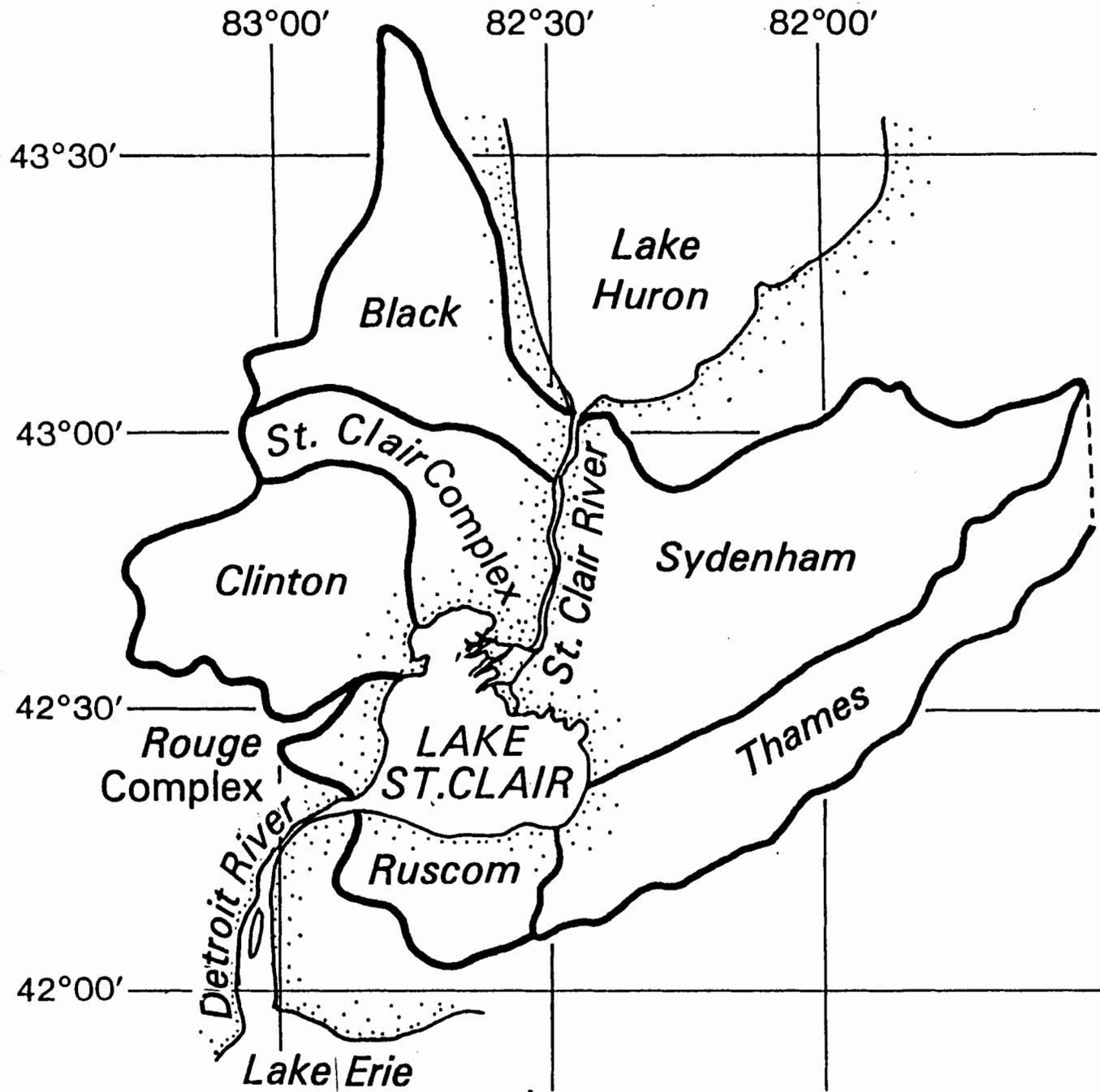
Mass balance calculations

-Four days prior to the onset of the System Mass Balance measurements in the Detroit River, measurements of contaminants entering Lake St. Clair from the St. Clair River were initiated. The intent of starting four days before making measurements on the Detroit River was to allow for passage of most of the St. Clair River water through the lake. By doing so, upstream and downstream contaminant fluxes could be compared and conclusions could possibly be drawn concerning whether Lake St. Clair is a source or a sink of contaminants. It must be emphasized that the validity of comparing upstream and downstream measurements in this mass balance calculation depends on how well the same parcel of water was sampled at the head and mouth of Lake St. Clair. Given the winds that existed during the sampling time, and output from a NOAA-GLERL particle transport model discussed below, we estimate that 60-80 percent of the water that entered the lake, exited it on day four. Therefore, downstream contaminant fluxes that are 20 to 40 percent different from upstream fluxes cannot be argued to be significant. On the mass balance diagrams that follow (Fig. 8-14), best estimates of point and non-point source inputs have also been noted. If estimates were not available, they are indicated with a "?" on the diagram. Loading information was compiled with data provided by the Point and Non-Point Source Work Groups. Ground water loading estimates are extremely preliminary and should be treated as such. The bottom line concerning these diagrams is that they should only be used to suggest possible issues

that may require further investigation. This is because of uncertainty about time lags between the head and mouth of the Lake, and the "long term average" character of some of the loading information.

In most cases, the downstream contaminant fluxes do not differ widely from the contaminant flux entering the lake via the St. Clair River. In the cases of cadmium and particularly lead, it appears that a significant portion of the lake's total load could be coming from its tributaries. If the Thames River lead loads are reasonably accurate, then it may be a problem in a regulatory sense. Sediment records that indicate a net storage of lead over the years would corroborate this observation.

- A total phosphorus budget was developed for Lake St. Clair for 1975-1980. Phosphorus load estimates were made for point sources and hydrological areas (Fig. 15). During this period Lake Huron accounted for 52 percent of the total annual load, while hydrologic area loads accounted for 43 percent (Fig. 16). The remaining load came from the atmosphere, shoreline erosion and direct point sources. The Thames hydrologic area contributed 58 percent of the total hydrological area load, followed by the Sydenham (17 percent), the Clinton (9 percent), the Ruscom (7 percent), and the Black (6 percent). Over the six year period examined, the lake's total input and output of phosphorus were nearly equal. It was concluded that there was no significant net source or sink of phosphorus in the lake during that period. (Lang, Morton and Fontaine, NOAA-GLERL)



Process-oriented models

Physical: hydrodynamics, winds, waves, and currents

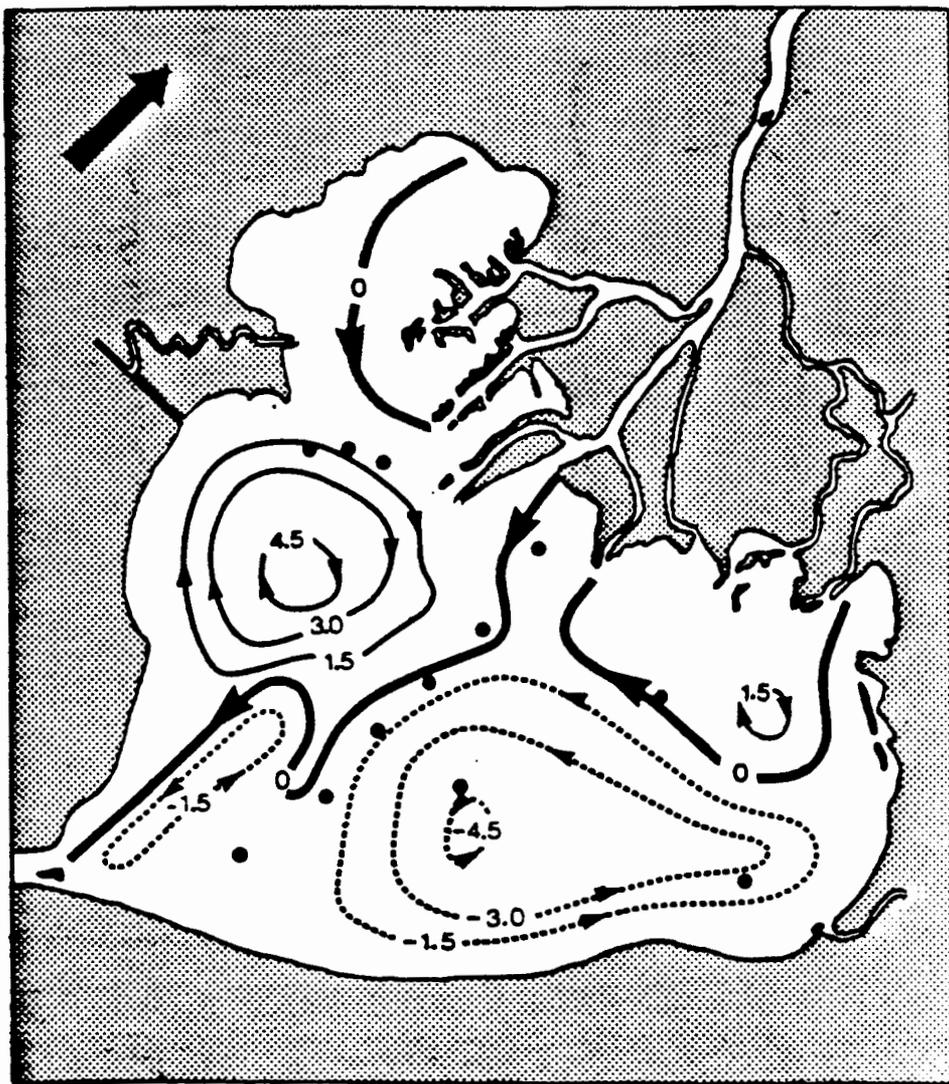
- Changes of water level caused by wind are most pronounced in shallow lakes such as Lake St. Clair. It is of practical importance, therefore, to be able to predict wind-induced water level changes since these changes can affect shorelines and contingent properties. A hydrodynamic model was developed to investigate the effects of bottom drag and wind stress on computed lake setup, and to determine the efficacy of hydrodynamic or purely empirical approaches to predicting water level changes. The latter approach simply relates setup to wind measurements, thus bypassing many of the calculations that are used in the hydrodynamic approach. No essential difference between the two approaches was found, but it was noted that for an empirical model to be developed, an adequate historical data base for the site of interest must exist. The strength of the hydrodynamic approach is that it is transferable among systems. (Simon and Schertzer, CCIW)

-To predict the fate and transport of contaminants in any body of water, the movement of that water, as affected by winds or tributaries, must be known or predictable. Because of this need, several models were developed by Canadian and US scientists to predict and understand currents in Lake St. Clair. In addition, models were developed for predicting and understanding wave dynamics in Lake St. Clair since waves can resuspend sediments and associated contaminants.

Simons and Schertzer, (CCIW) developed a model that predicts mean daily currents in Lake St. Clair. They found that an important consideration in developing the model was accounting for the effects of a shallow bottom on currents. Lack of information regarding these effects has been a major impediment to the application of hydrodynamical models to shallow lakes. They were able to develop a tentative relationship between eddy viscosity and wind stress that aided in shallow water model development. A sample prediction of streamlines for a SW wind is shown in Figure 17.

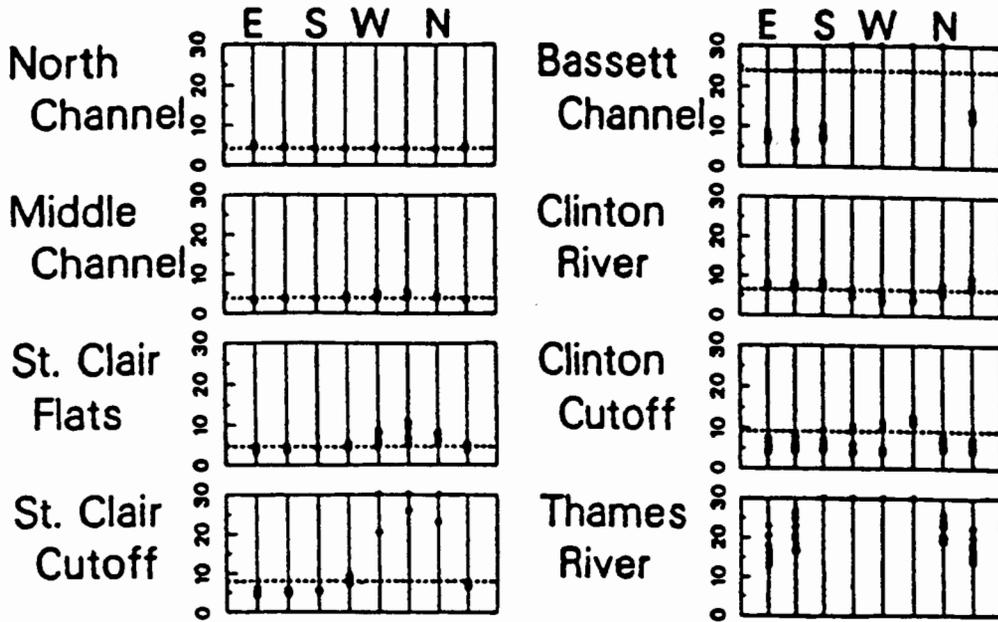
Schwab and Clites (NOAA-GLERL) developed a particle transport model for Lake St. Clair to answer the following questions: 1) What path does water entering Lake St. Clair from one of the tributaries follow through the lake before leaving at the Detroit River? 2) How long does it take? 3). How is the particle path changed by wind-induced circulation in the lake? 4) For the meteorological conditions during the summer and fall of 1985, what are the typical statistical distributions of these pathways? The model they developed calculates currents on a 1.2 Km grid and yields results that are similar to those of Simons and Schertzer, above. Their model can be used to make preliminary estimates of the spatial distribution, transport and residence times of conservative, hazardous spills in Lake St. Clair (Fig. 18). However, it should be kept in mind that this model only tracks conservative, non-dispersive tracers from the mouths of the tributaries through the lake under various wind conditions.

It can be seen that even though the average hydraulic residence time for Lake St. Clair is about nine days, the residence time for conservative



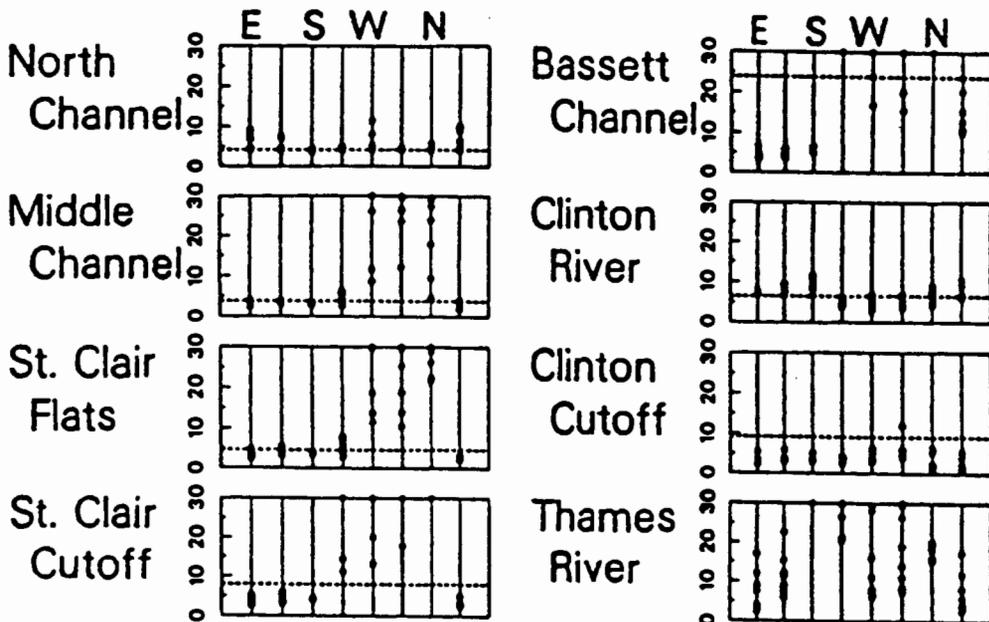
Residence Time (days) in Lake St. Clair for a 10 ms⁻¹ storm

(dashed line indicates no-wind residence time)



Residence Time (days) in Lake St. Clair for a 20 ms⁻¹ storm

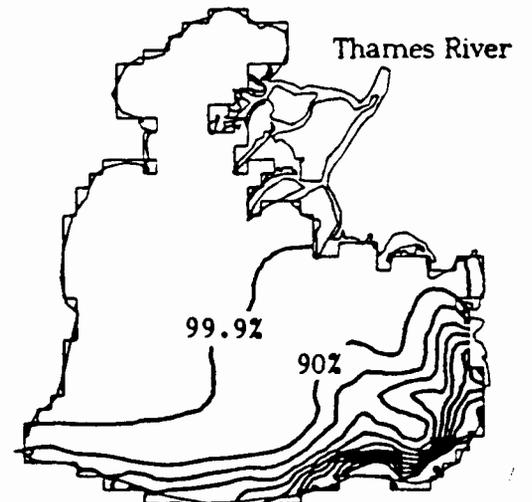
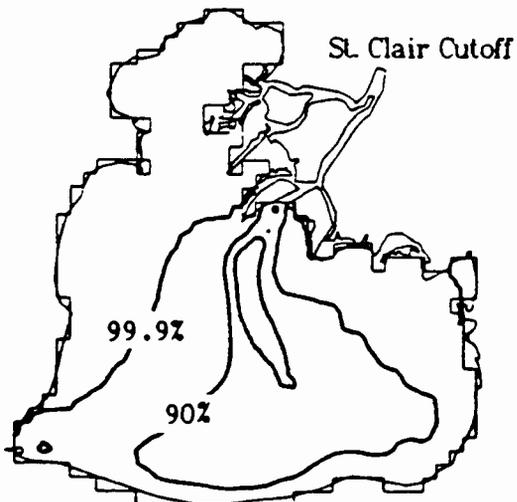
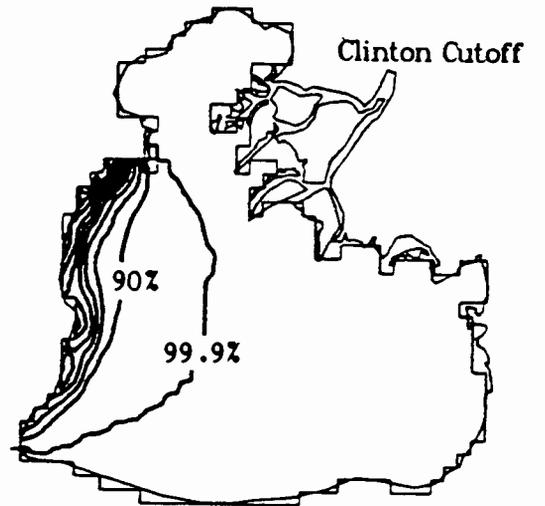
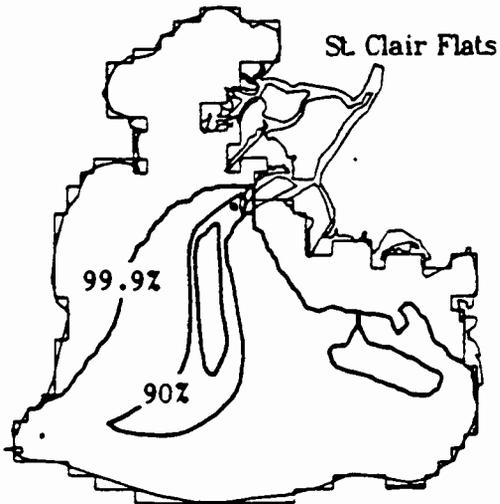
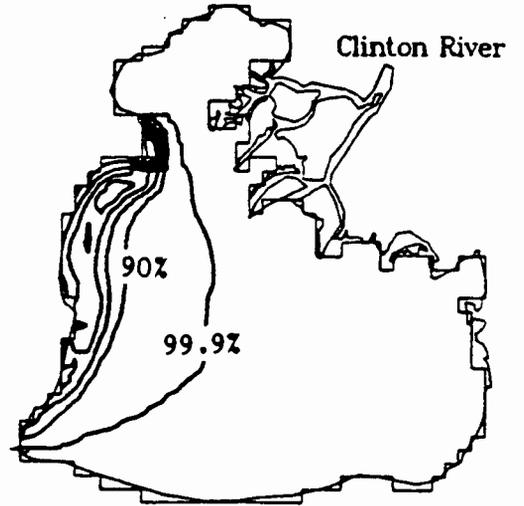
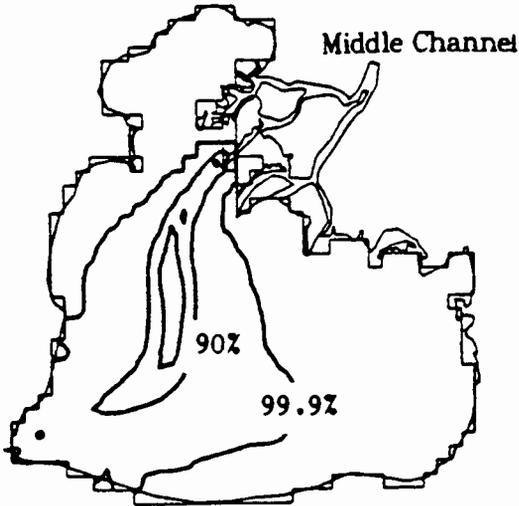
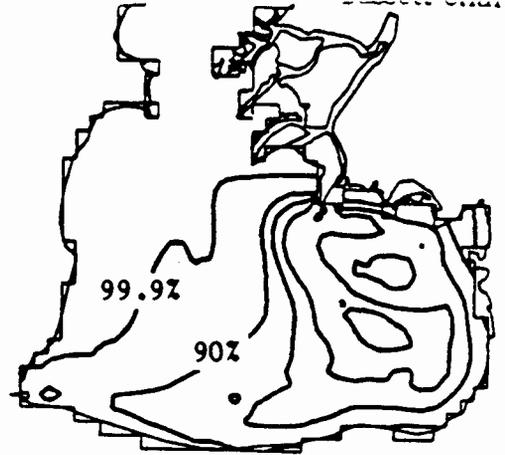
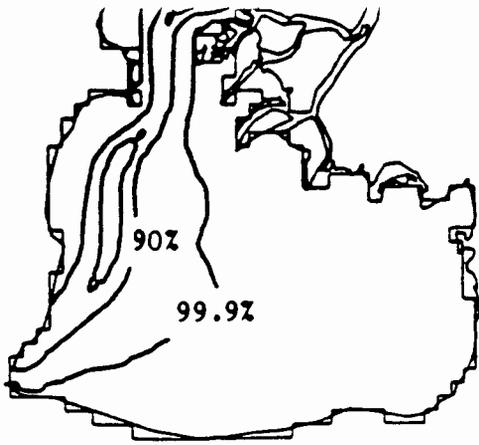
(dashed line indicates no-wind residence time)



particles entering the lake from the individual tributaries ranges from 4.1 days for the Middle Channel to over 30 days for water from the Thames River, depending on the wind conditions (Fig. 18). If significant contaminant loads were to enter the lake from tributaries that have long residence times, the impact of these contaminants might be greater than if they entered the lake from other tributaries.

The calculated tracks of particles were used to develop probability plots of the likelihood of a parcel of water emanating from one of the eight tributaries passing through a given area of the lake during this period. These plots quantify the wind-induced variability in the pathway that water from one of the tributaries takes through the lake. The results of these calculations are presented in Figure 19 in terms of probability contours. The outermost line is the 99.9% contour, i.e., 99.9% of the conservative particles released from that tributary remained within this contour. The next contour delineates the area in which 90% of the particles remained. Remaining contours are at 10% intervals.

Most of the water from the St. Clair River enters the lake through the North Channel (35%). According to the calculations, this water tends to flow down the western shore of the lake and never gets into the central or eastern parts of the basin. Water from the Middle Channel tends to remain in the western third of the lake, almost never entering the eastern half. Water from St. Clair Flats and the St. Clair Cutoff can be dispersed almost anywhere in the lake to the south of the shipping channel which connects the St. Clair Cutoff with the Detroit River. A small amount of the St.



Clair inflow (5%) enters through Bassett Channel. This water can pass through any part of the eastern half of the lake depending on the wind conditions. The Thames inflow tends to be confined to the eastern and southern shores before reaching the Detroit River and it can take a very long time to get there (see Fig. 18). Water from the Clinton River and Clinton Cutoff is most likely to follow the western shore of the lake southward with the most probable paths within 3 km of the western shore.

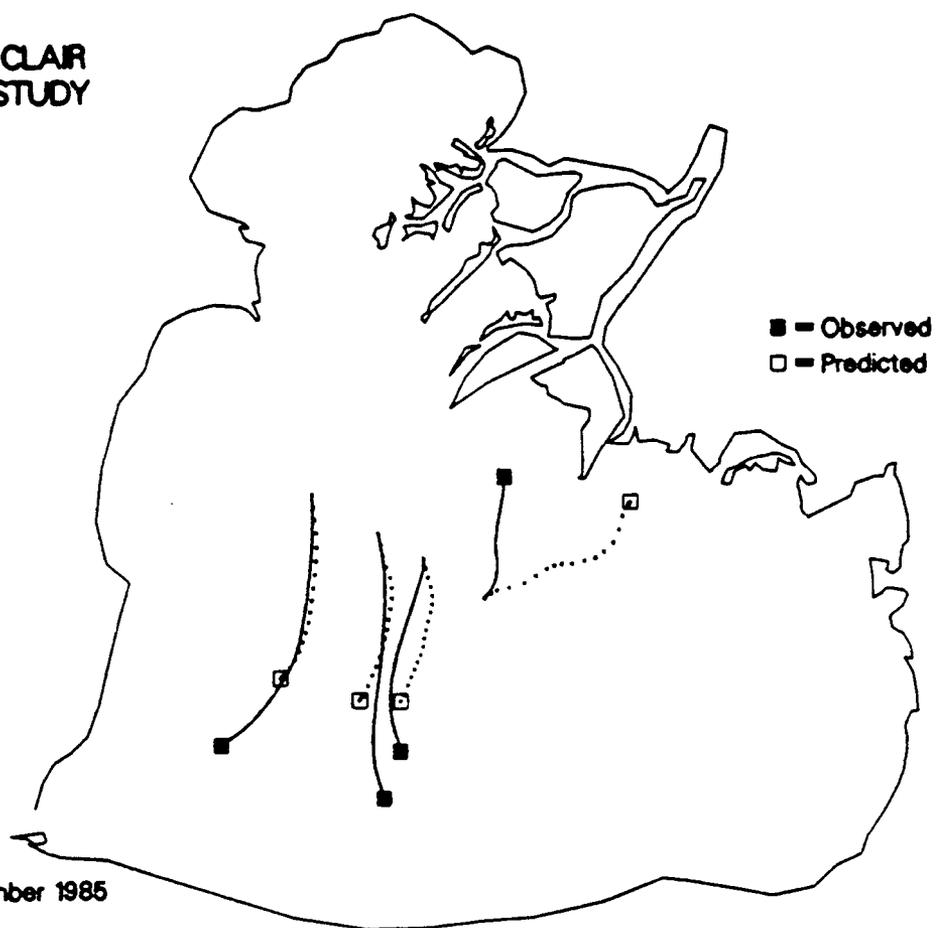
Water quality measurements made in Lake St. Clair by Leach (1972 and 1980) showed two distinctly different areas in the lake. In the southeastern part of the lake, the water quality is dominated by the Thames inflow, which is a major source of phosphate and other dissolved and suspended material. The central and western parts of the lake were more similar to Lake Huron in terms of water quality than to the southeastern part of the lake. The pattern of water mass distribution mapped in Leach's (1980) Figures 1-4 is very close to the combined patterns of the four main St. Clair River inflows and the Thames inflow in our Figure 19. Bricker et al. (1976) examined the distribution of zooplankton in the western half of the lake. They distinguished an area of biological and physiochemical similarity along the western shore of the lake that appeared to be influenced more by the Clinton River than the St. Clair River. The shape of this area matches quite well with the distribution pattern for water from the Clinton River in Figure 19.

To verify the circulation model and lend credence to currents calculated by Schwab and Clites, their model was tested by comparing model output to

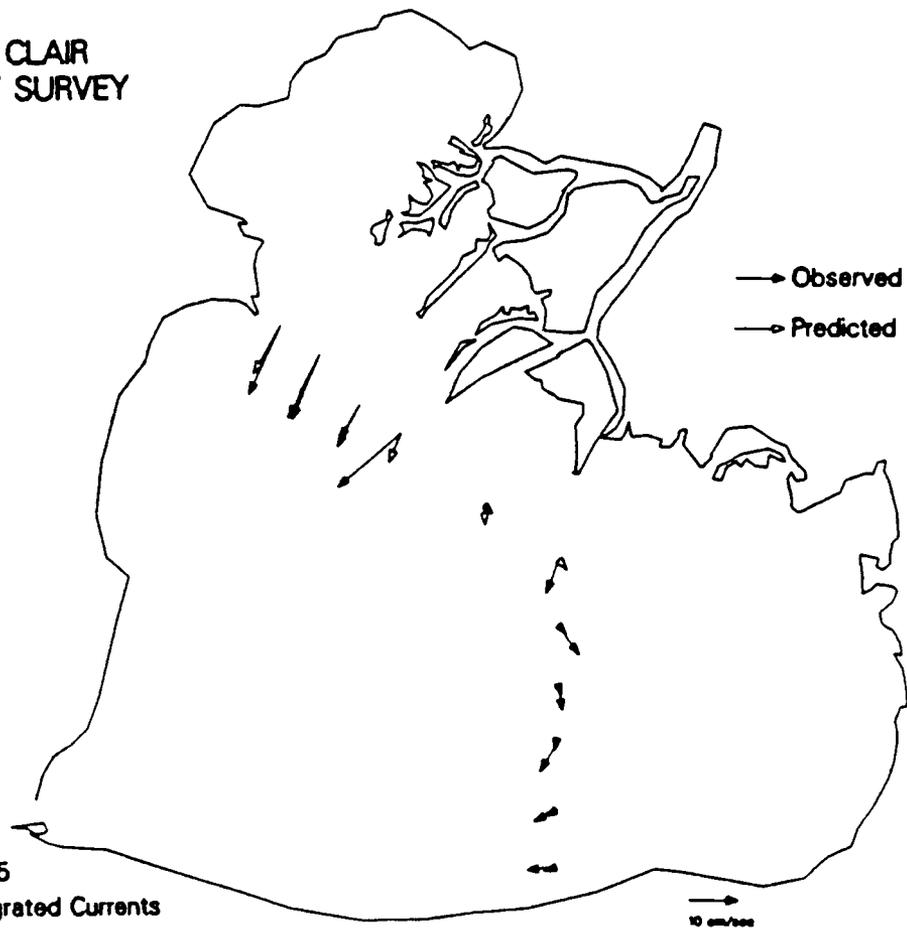
actual current data measured in Lake St. Clair in 1985. Two separate current data bases were gathered. One involved the use of 5 drifting buoys which were repeatedly launched and tracked in the lake. The other was the result of several synoptic current surveys utilizing electromagnetic current meters. Currents predicted by the circulation model were used to simulate 16 drifter tracks. Most of the tracks are about 2 days in length from various portions of the lake. In most cases, the model simulated the tracks extremely well. For the entire data set, the mean root mean square (rms) of the drifter was 25% greater than that of the calculated current track. The directions compared favorably except for a few tracks near the mouth of the Bassett Channel, where the model prediction was over 90 degrees different in direction when compared with the observed track. The comparisons between current meter measurements and model-predicted currents were even better. In nearly 100 comparisons, 60% of the variance is explained by the model prediction. The model again seems to under-predict the current speeds, here by about 30%.

- Contaminant transport depends in large part on the movement of suspended particles. Therefore, accurate computation of horizontal sediment transport should rely upon the accurate simulation of the vertical structure of the horizontal flow field. Hamblin (CCIW) developed such a three dimensional finite element model for Lake St. Clair. Model agreement with observations was good near the lake bottom but poorer near the surface (Fig. 21) and suggested that a more elaborate model would be needed to more accurately model vertical velocity profiles. The more elaborate model would include the effect of surface waves.

**LAKE ST. CLAIR
DRIFTER STUDY**



**LAKE ST. CLAIR
CURRENT SURVEY**



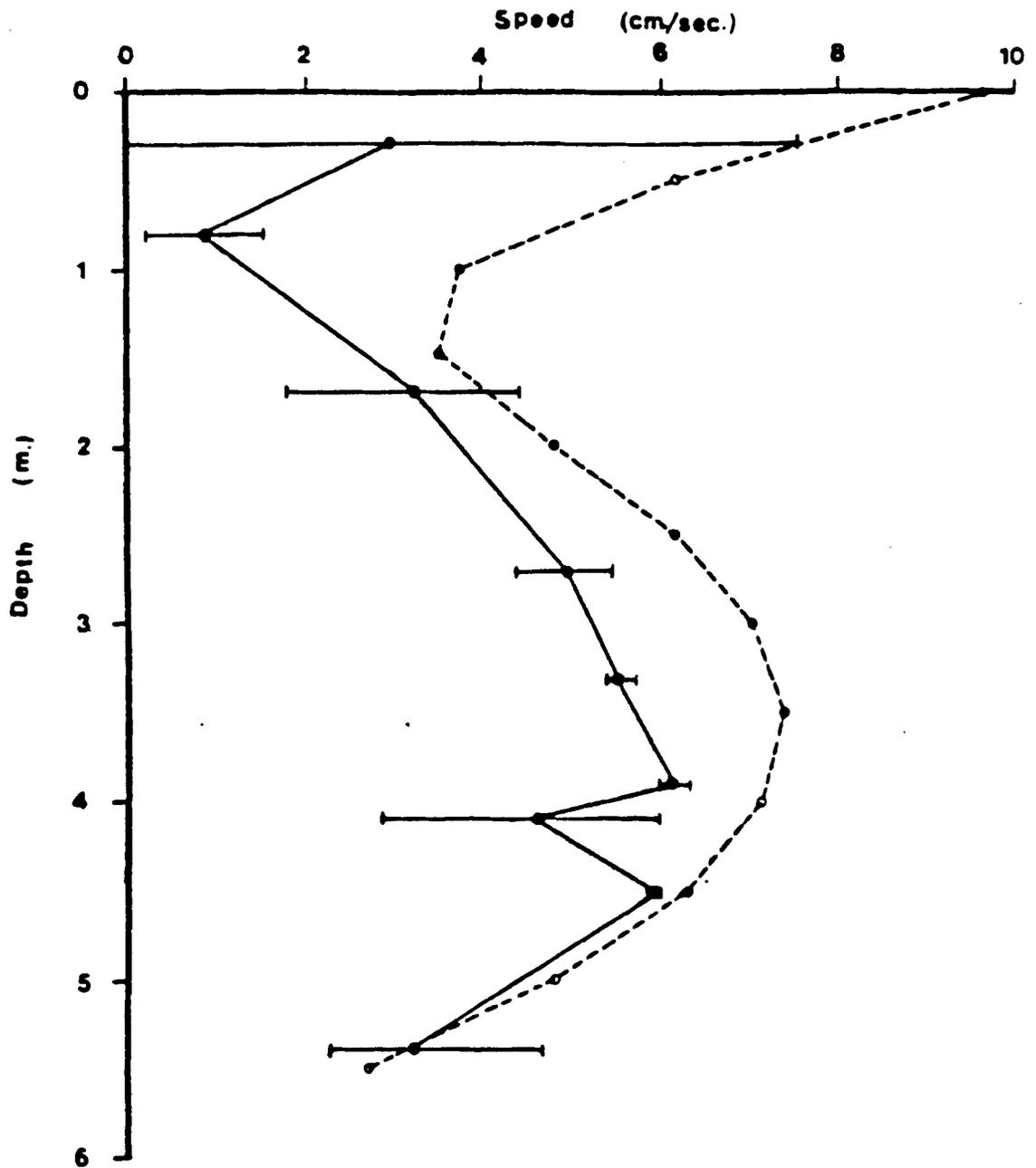
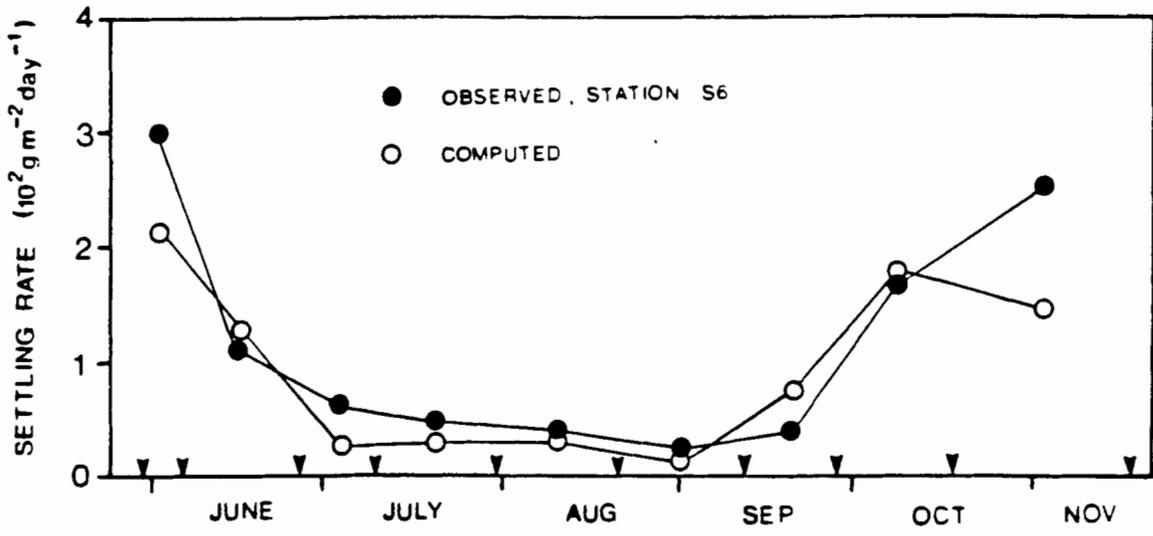


FIGURE 3 a COMPARISON BETWEEN THE OBSERVED (SHOWN AS SOLID LINES) AND CALCULATED (SHOWN AS DASHED LINES) VALUES FOR THE VERTICAL CURRENT SPEED NEAR THE MAIN TOWER ON SEPT. 17-1985.

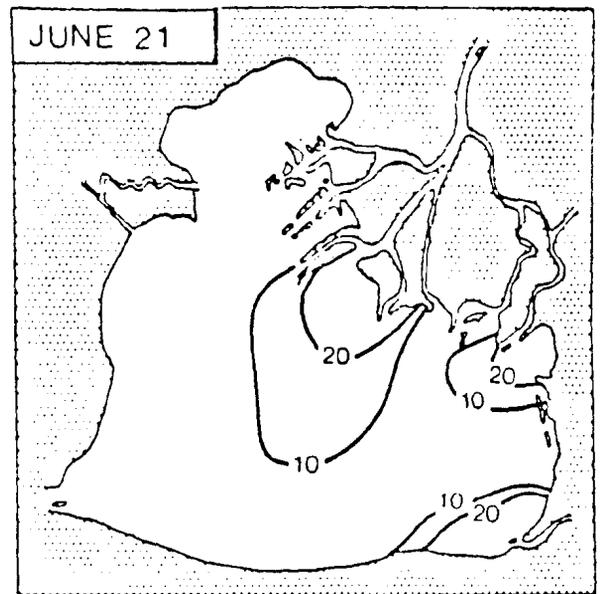
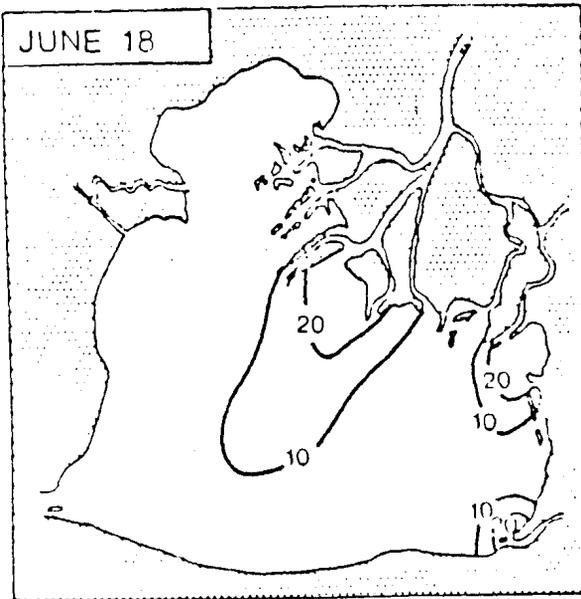
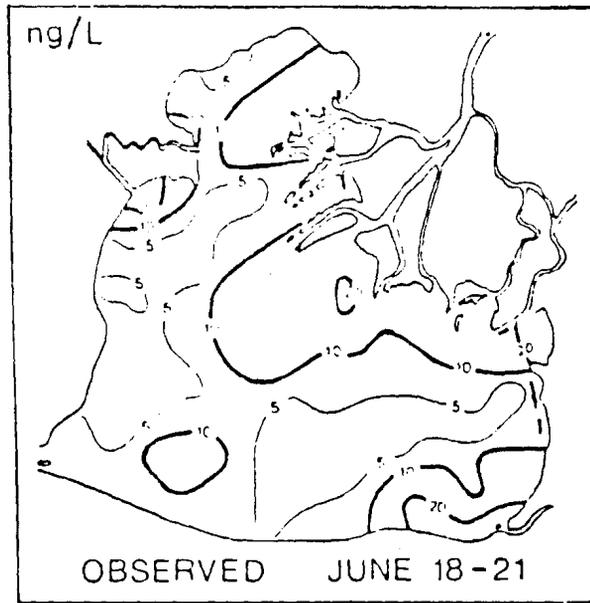
- A model was developed to describe and understand the relationship between waves and sediment settling and resuspension (Simons and Schertzer, CCIW). The importance of these relationships to our ability to predict and understand the transport of contaminants is evident. A dynamic relationship between suspended matter and wave orbital velocity was computed. Integration of computed resuspension rates provided an estimate of sedimentation in sediment traps. These model generated sedimentation rates compared rather well with the sediment trap data (Fig. 22).

Physical-Chemical-Biological models

- To predict the fate and behavior of contaminants, models that integrate physical, chemical, and biological processes are often needed. Two such synthesis models were developed for predicting contaminant fate in Lake St. Clair. Halfon (CCIW) utilized TOXFATE and Lang, Fontaine and Hull (NOAA-GLERL) utilized the EPA's TOXIWASP model. (TOXFATE) was used to predict the spatial distribution of seven halocarbons in Lake St. Clair, and the fate of perchloroethylene in the St. Clair - Detroit River system. The TOXIWASP model was used to predict and understand the fate of the contaminant surrogate Cs-137, as well as PCB's and OCS. Neither of these models could be fully tested for Lake St. Clair applications due to a limited test data set. However, these models are based on well documented cause and effect relationships, and as such, could be used to forecast the fate and behavior of contaminants introduced to the lake in the future. Representative results of Halfon's Lake St. Clair TOXFATE model are demonstrated in Figures 23-24.

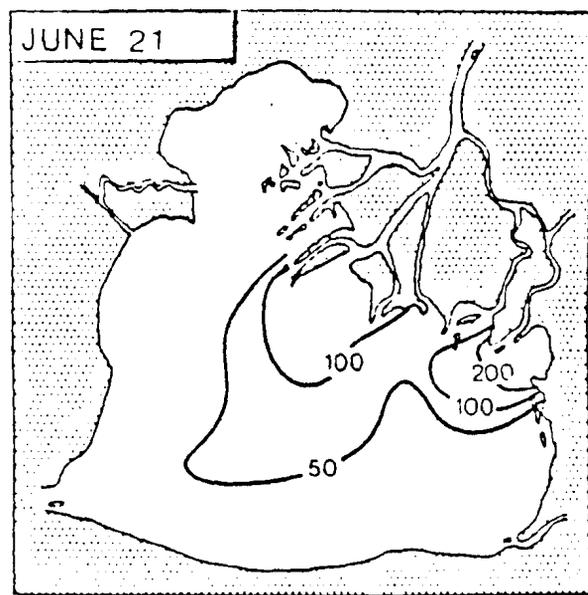
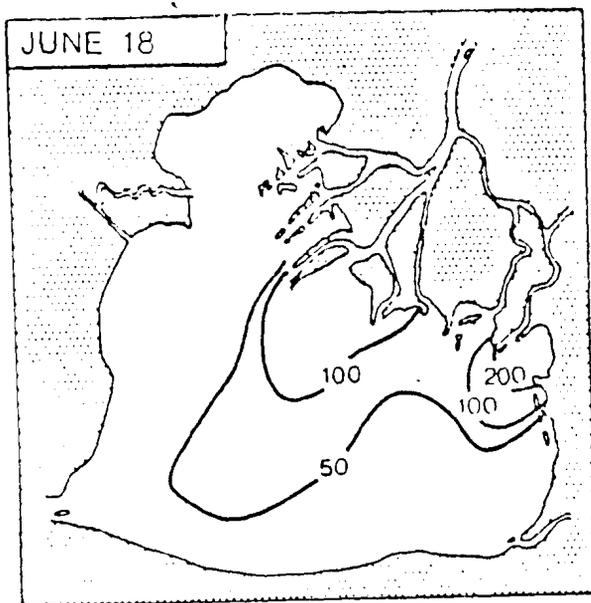
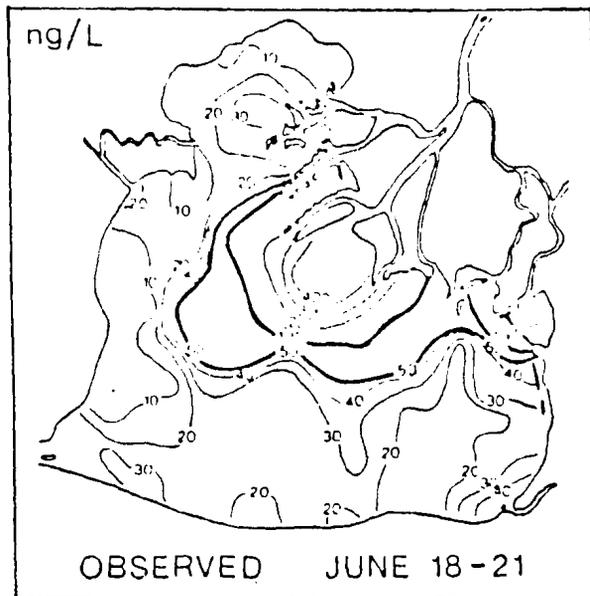


TRICHLOROETHYLENE



PREDICTED

TETRACHLOROETHYLENE



PREDICTED

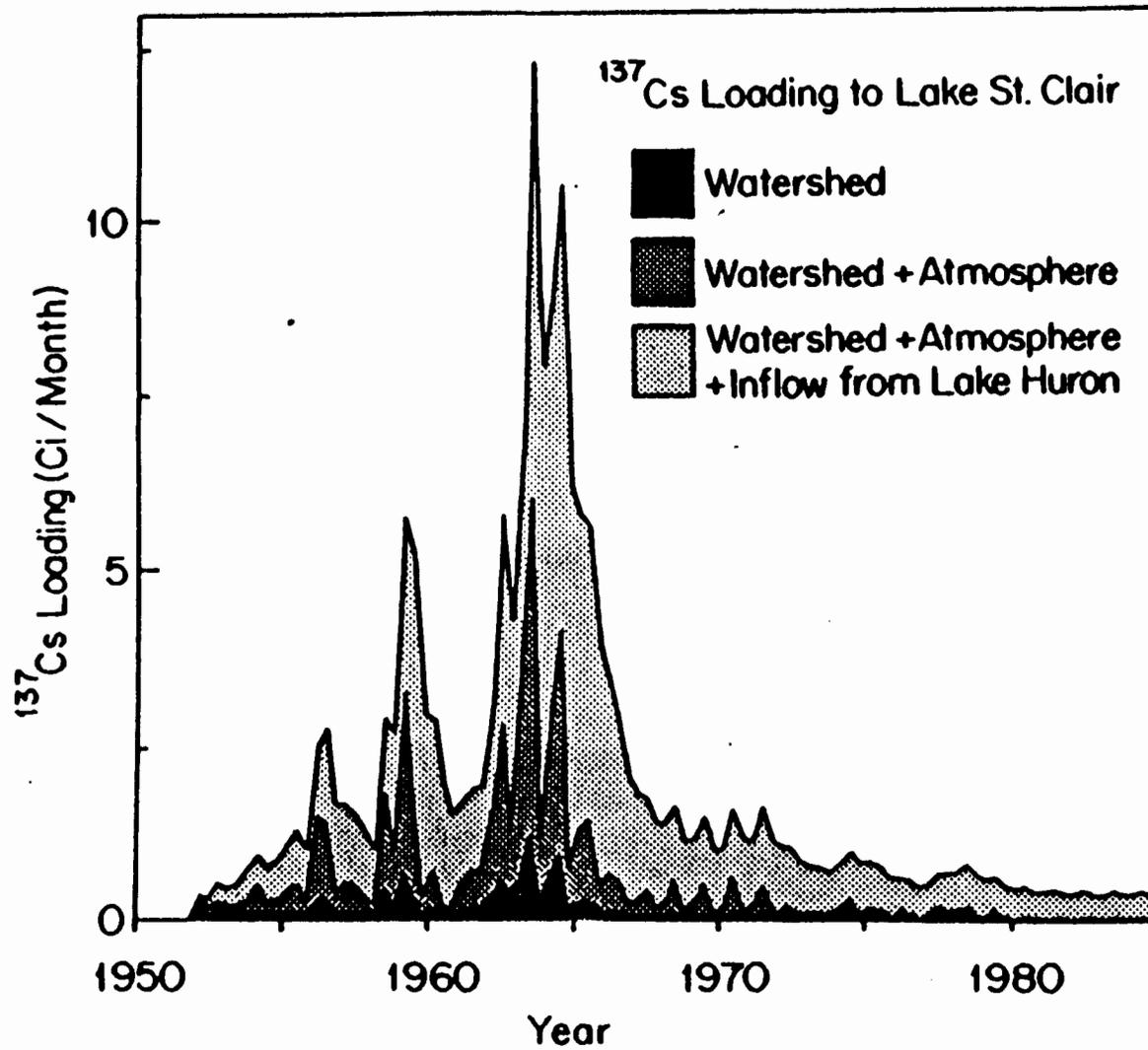
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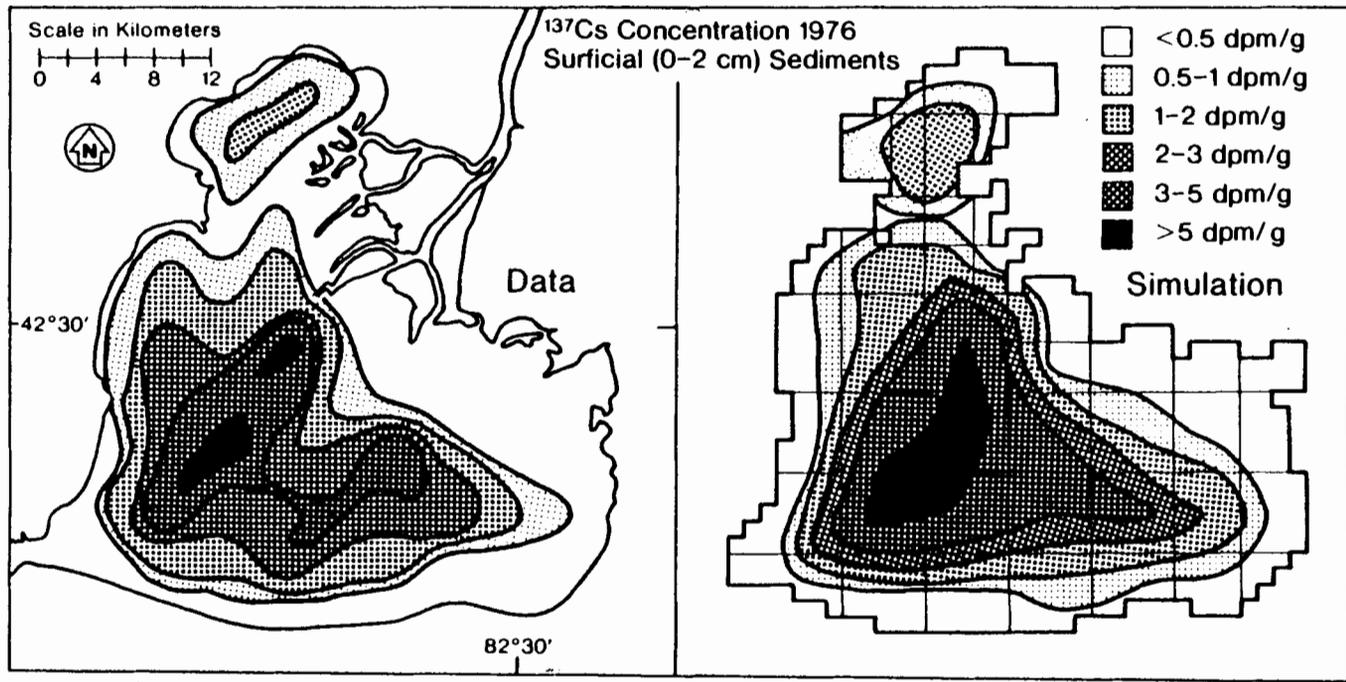
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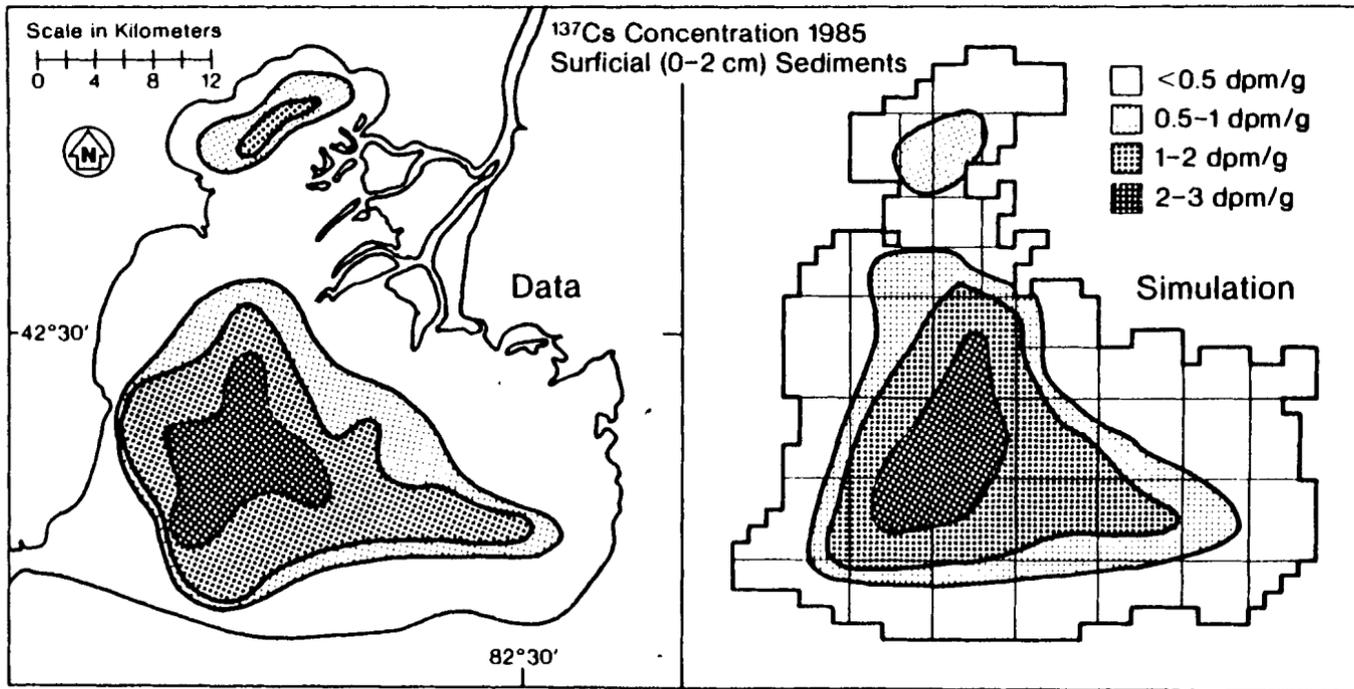
Lang and Fontaine (NOAA-GLERL) developed a multi-segment, generic contaminant fate and transport model for Lake St. Clair. The TOXIWASP code upon which it was based was streamlined to make it more specific to Lake St. Clair. As evidence of biological mixing in Lake St. Clair sediments was extensive this capability was added to the Lake St. Clair version of TOXIWASP. An extremely fast version was created that calculates steady state contaminant concentrations in seconds rather than hours. Numerous programming errors in the original code were found, corrected and passed on to the EPA-Athens modeling group.

Lang and Fontaine (NOAA-GLERL) calibrated the transport mechanisms of TOXIWASP using chloride and meteorological data that were collected during a series of cruises in Lake St. Clair during 1974. After obtaining reasonable agreement with the conservative chloride ion, calibration of contaminant dynamics was carried out using Cesium-137. Cesium-137 was used to calibrate the model's contaminant dynamics since it sorbs to particles in a manner similar to that of many hydrophobic, organic contaminants. Most importantly, the source function of Cesium-137 to the lake is well known (Fig. 25). This information, coupled with knowledge of the spatial and depth distribution of Cesium-137 in the sediments of the lake, provided an excellent calibration and verification data set. Calibration results are shown in Figure 26 and verification results are shown in Figure 27. Both results are quite acceptable.

Having calibrated the TOXIWASP model for Lake St. Clair, it was used to hindcast possible loadings of Octachlorostyrene and PCB's to Lake St.

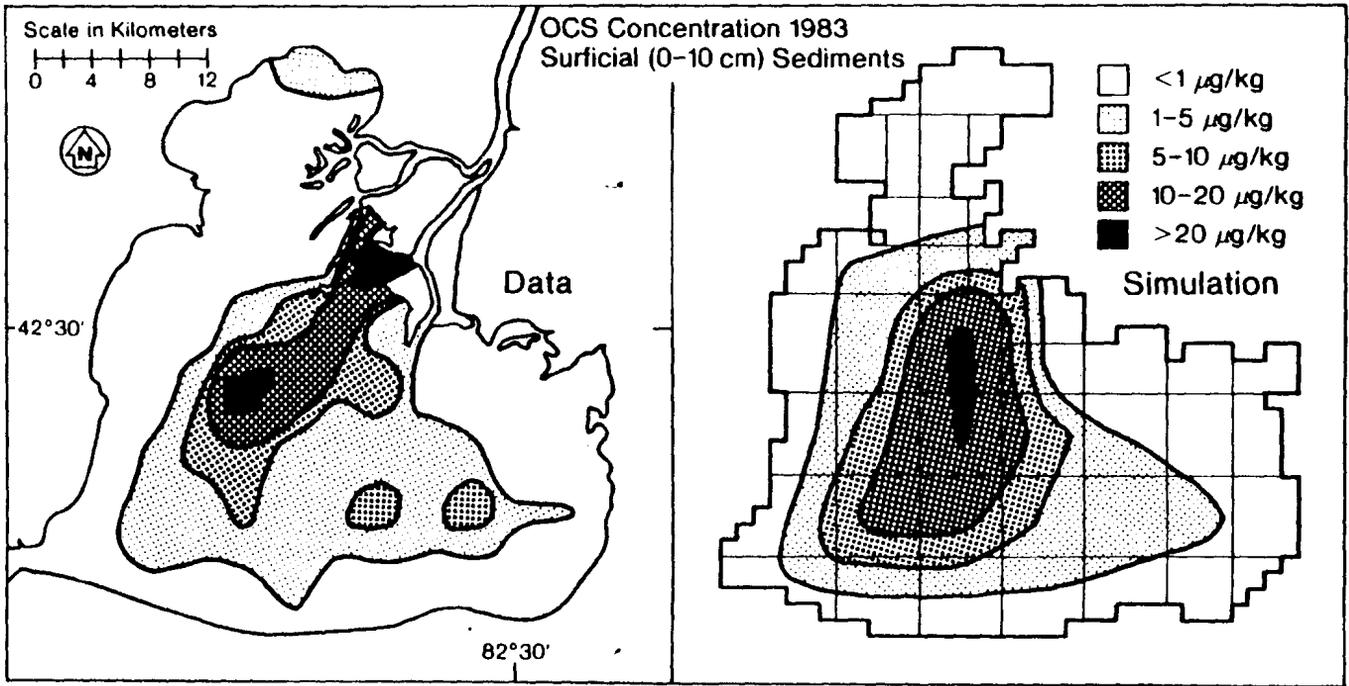


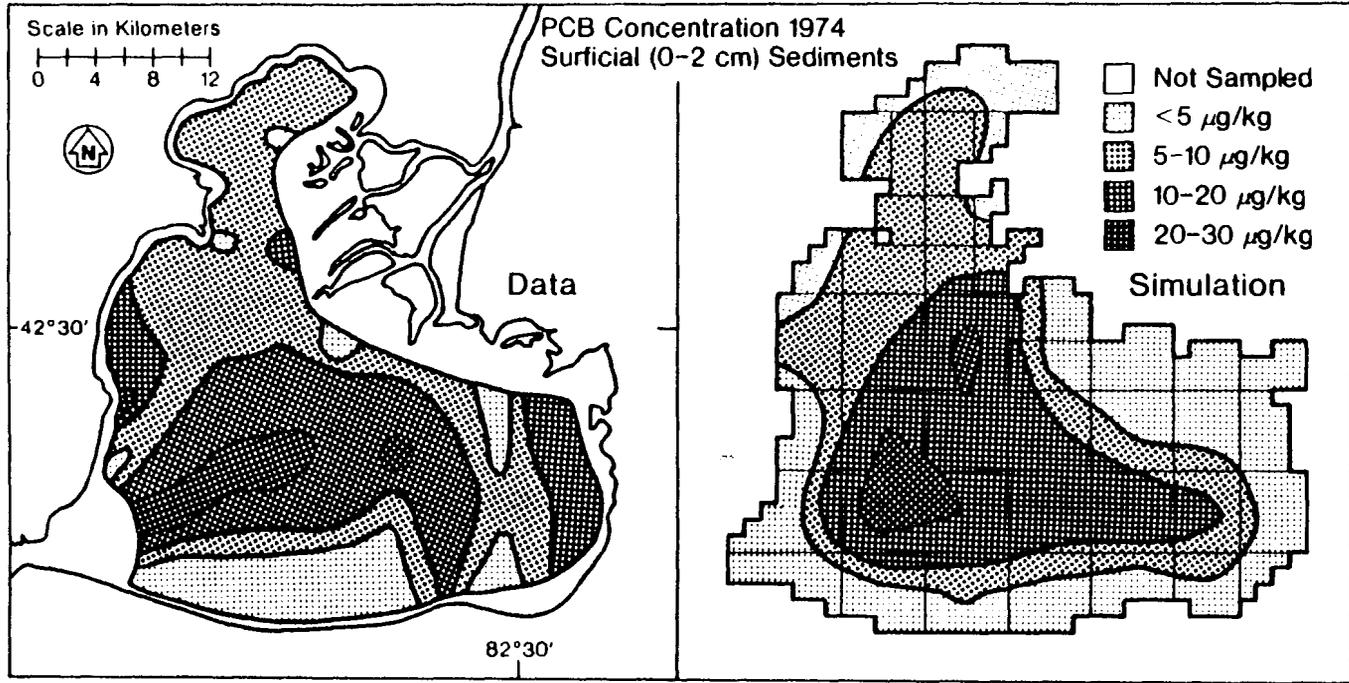




Clair. The model predicted that about 3.9 MT of OCS had to have been loaded to the lake over a period of 12 years to produce measured sediment concentrations (Fig. 28). This finding implies that OCS was first loaded in the latter part of 1970 and is consistent with speculation to that fact. The model also estimated that 3.4 MT of PCB's had to have been loaded to produced measured PCB sediment concentrations (Fig. 29). The model tended to under predict the PCB values along the eastern and western segments of the main lake, which may indicate additional or increased PCB sources in these areas.

-TOXIWASP assumes a local equilibrium between the dissolved, particle-sorbed and bio-sorbed chemical. Hull, Lang, and Fontaine (NOAA-GLERL) modified the TOXIWASP model so that kinetic, instead of equilibrium reactions, were simulated. This was done to determine whether the equilibrium approach was valid in all circumstances. Equilibrium models assume implicitly that incoming contaminant loads are at local equilibrium between dissolved, sorbed, and bioaccumulated phases. When the same load conditions were assumed for the kinetic model, greatest deviations between the two models occurred when predicting the fate of highly hydrophobic contaminants ($K_{ow} > 10^6$). The kinetic model not only required a longer time to reach steady state contaminant concentrations, but also required a longer time to flush out the resident contaminant mass after the input load was shut off. Generally, one would expect problems with an equilibrium approach when the time to equilibrium is longer than the residence time of the water body in question. Work on kinetic models of contaminant fate and behavior continues at NOAA-GLERL.





- Halfon (CCIW) used TOXFATE to predict the fate of perchloroethylene (PERC), i.e., the "blob", in the St. Clair - Detroit River system. The model suggested that about 82 percent of the PERC would be volatilized, and the remainder, less 1 percent that would remain in sediments, would enter Lake Erie. Comparison of simulated and measured PERC concentrations show reasonable agreement (Fig. 30).

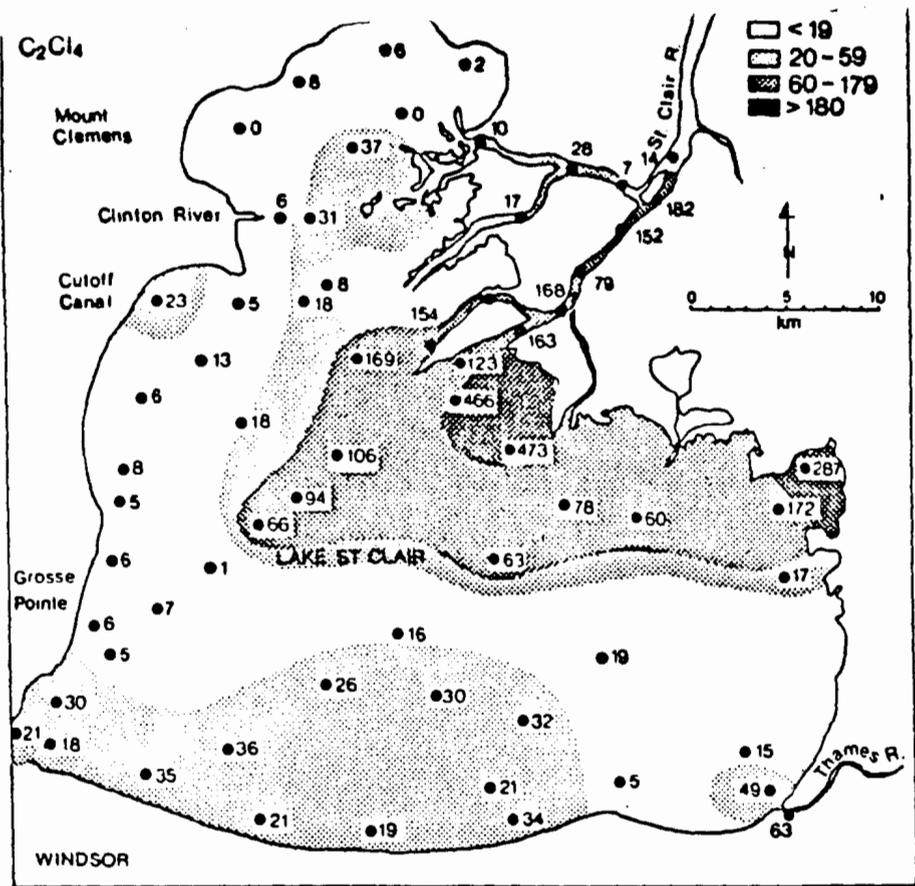


Figure 3. PERC concentrations in Lake St. Clair waters in summer 1984 (ng/L)

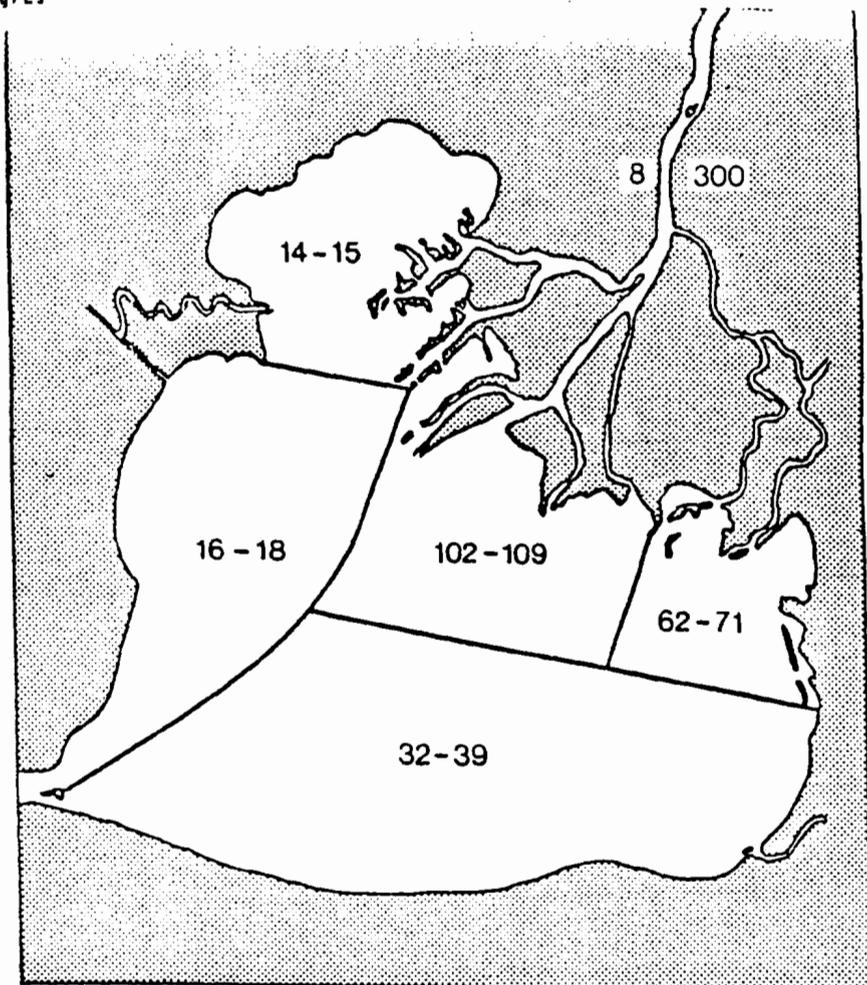


Figure 4. Predicted PERC concentrations in Lake St. Clair waters (ng/L) using the estimated loadings of 64 kg/day over a 40 day period.

DETROIT RIVER

Mass balance calculations

- Mass balance studies were conducted for the Trenton Channel and the Detroit River. These studies were carried out for only a few periods of a year. Therefore, they represent snapshots of contaminant conditions in these systems. The data generated by EPA-LLRS in these studies are summarized graphically in Figures 31-79. Point and non-point source loading estimates are also shown when possible. Aside from the point and non-point source estimates that are marked with an "?" to denote their unavailability, the only data missing from these mass balance diagrams are contaminant fluxes associated with floating aquatic macrophytes. Refer to the introductory section on mass balances to aid in interpretation of the figures. A brief interpretation is, however, provided on each figure.

System Mass Balances (SMB) I and II

These mass balances were conducted on the Detroit River during the periods April 21-29, 1986 and July 25 - August 5, 1986, respectively. The following items are noteworthy:

- During SMB I and II, the Detroit River was a statistically significant source of cadmium. Despite this, some accumulation could also have occurred during SMBI and II if the Detroit Waste Water Treatment Plant (WWTP) loading estimates are reasonable.

- During SMBI and II, the Detroit River was a statistically significant source of copper. If point source loads are reasonable, it appears that there is an unknown source of copper.

- During SMB I and II, the Detroit River was a statistically significant source of lead. Despite this, some accumulation could also have occurred during SMBI and II if the Detroit Waste Water Treatment Plant (WWTP) loading estimates are reasonable.

- During SMB I and II, the Detroit River was a statistically significant source of nickel. Despite this, some accumulation could also have occurred during SMB I if the Detroit Waste Water Treatment Plant (WWTP) loading estimates are reasonable. A nickel loading estimate for the WWTP was not available for SMB II. Undoubtedly, this led to the high apparent surplus load estimate.

- During SMB I and II, the Detroit River was a statistically significant source of PCBs. Despite this, some accumulation could also have occurred during SMB I if the Detroit Waste Water Treatment Plant (WWTP) loading estimates are reasonable. The apparent surplus PCB loads leaving the area suggest that there may have been an unknown PCB source during SMB II.

- During SMB I and II, the Detroit River was a statistically significant source of total phosphorus.

- During SMB I and II, the Detroit River was a statistically significant source of zinc. During SMB I, the Rouge River and the Detroit WWTP contributed more zinc than was coming from upstream sources.

Trenton Channel Mass Balances

Trenton Channel Mass Balances II and III were conducted during the periods May 6-7, 1986 and August 26-27, 1986, respectively. Letters on the right hand sides of diagrams refer to transects indicated in Figure 55. The following items are noteworthy:

- Although the entire Trenton Channel was not a source of cadmium during either survey, it appears as though the C-A area was a significant cadmium source during survey III.

- Although the entire Trenton Channel was not a source of copper during either survey, it appears as though significant accumulation of copper in area D-C occurred during survey III.

- Although the entire Trenton Channel was not a source of lead during either survey, it appears as though the C-A area was a significant lead source during both surveys.

- Although the entire Trenton Channel was not a source of zinc during either survey, it appears as though the C-A area was a significant zinc

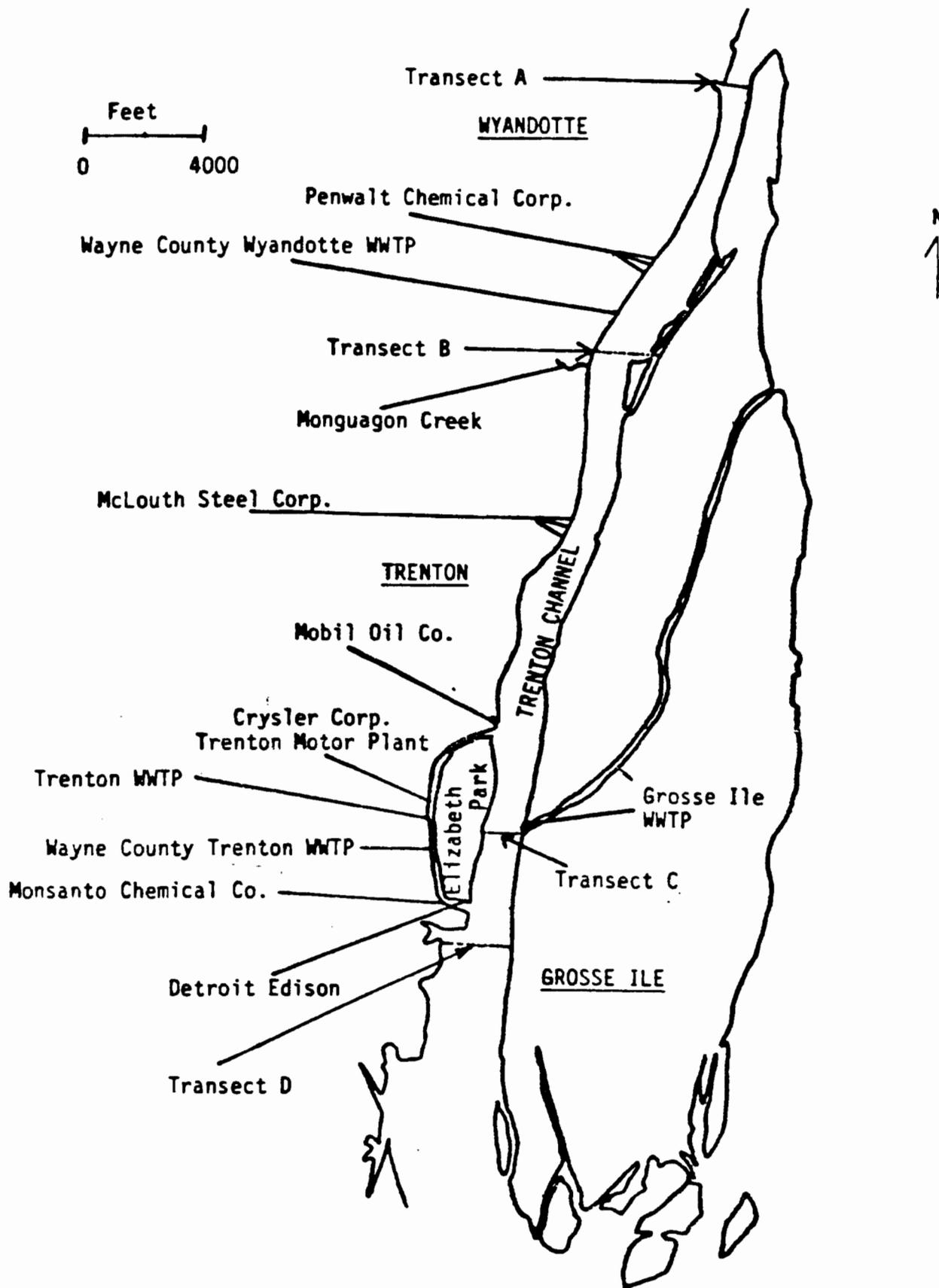


Figure 2.2. Major Point Source Dischargers and 1985-1986 Sample Transects in the Trenton Channel.

source during both surveys and that the D-C area was a significant sink during survey II.

Process-oriented models

- Plume models for the City of Detroit's sewage treatment plant have been developed by Limno Tech, Inc. An executive summary of their work is reproduced below with no modification.

MODELING

MODEL CONSTRUCTION--This chapter describes the development, validation, and application of a 2-dimensional finite element model (NELEUS™) of the DWSD effluent plume in the Detroit River. This hydrodynamic and water quality model of the Detroit River simulates impacts of the effluent plume to help assess appropriate effluent levels to protect Detroit River water quality. The model is comprised of two independent finite element models:

1. A hydrodynamic model that predicts the 2-dimensional flow field and water surface elevations of the river, and
2. A finite element contaminant transport and kinetic model.

A 2-dimensional model was utilized because the Detroit River is not laterally mixed, has rapidly changing bottom geometries, and flow is divided by islands. A 1-dimensional model would yield an inaccurate description of the fate of contaminants. A preliminary model less complex than NELEUS™ was also developed for the Detroit River and was presented in a previous report to DWSD [ESE, LTI, and RRA (1985)]. This preliminary model is easy to run and was used as a screening model for approximate estimates of near-field impacts.

The NELEUS™ model of the DWSD discharge into the Detroit River enables simulation and assessment of environmental impacts under varied ambient and effluent conditions. The hydrodynamic component of NELEUS™ provides a description of the physical characteristics of the river, including: (1) 2-dimensional velocity flow-field, (2) free surface elevations, and (3) flow distribution in individual channels and branches. Second, the contaminant transport component of NELEUS™ simulates the temporal and 2-dimensional distribution of contaminant concentrations using the predicted flow-field of the hydrodynamic model.

The NELEUS™ model has been validated with measurements from intensive water quality field surveys. The effect of the discharge of wastewater on water quality can therefore be accurately assessed using the NELEUS™ finite element model of the hydrodynamic and transport (fate) systems. The model results can in turn assist the planning and coordination of future studies, eventually leading to accurate guidelines for NPDES effluent requirements and for proper plant operation and management. The model provides a basis to evaluate water quality issues from upstream of the Detroit discharge to downstream to the Trenton Channel.

NELEUS™ is a 2-dimensional model designed to simulate both hydrodynamic features and the fate of contaminants in the Detroit River. The hydrodynamic model must be run on a mainframe computer due to its large computational requirements. However, the water-quality model which simulates contaminant fate uses the output of the hydrodynamic model, but runs on a PC-compatible microcomputer.

The NELEUS™ contaminant transport model was calibrated and verified using survey data from both dye and water quality surveys. The dye data were used most extensively because the surveys provided more robust data sets and the measurements were easily discernable. The contaminant water quality surveys also provided data for calibration but were more limited because measurements were often at or below detection limits. For model comparison, ESE field data were matched with the nearest NELEUS™ model section.

Model validation was conducted using the steady state output of the hydrodynamic model as input to the contaminant transport model. Longitudinal diffusion was considered negligible (Fischer et al., 1979) and lateral diffusion was assumed to be spatially constant. This provided reasonable comparisons so more detailed schemes were not explored. Model validation studies demonstrate the model's ability to faithfully reproduce both hydraulic and water quality conditions in the Detroit River under a variety of seasonal conditions.

Model coefficients that were developed included inputs for longitudinal and lateral diffusion, partition coefficients describing the distribution of the contaminant between particulate and dissolved fractions, characteristic suspended solids concentrations, settling velocity (vs), and decay rates (K) for each contaminant. The partition coefficients and settling rates used are representative of those reported in EPA's Guidance to Modeling Toxics in Rivers and Streams. The decay rate for chlorine was derived from experimental observation and observed depletion in the Detroit River.

MANAGEMENT SCENARIOS--Eight effluent management scenarios were chosen by DWSD for model evaluation of environmental fate. These scenarios are summarized in Table 2 and were chosen to evaluate the magnitude and fate of the effluent contaminants expected under critical conditions. Various effluent levels were examined to evaluate management alternatives ranging from status quo to stricter levels than the MDNR-stipulated effluent goals. The results indicate the incremental impact of the DWSD effluent on the Detroit River and the water quality response to various management alternatives. This application of NELEUS™ represents the primary intended utility of modeling, which is the ability to predict levels of contaminants during hypothetical (and unmonitored) critical conditions.

The model forecasts indicate that the wastewater impact on the Detroit River would not exceed acute toxicity criteria for cadmium, mercury, and PCBs. Chronic criteria for the protection of aquatic life also would not be exceeded in the river. Chronic criteria related to edible fish would be exceeded in the allowable mixing zone for mercury, but it would be met by the edge of the mixing zone. The primary purpose of forecasted levels of PCBs is to demonstrate the incremental impact on the Detroit River water quality. PCBs from the WWTP forecasted at the Wyandotte water intakes are less than 1 nanogram per liter (ng/L) and do not represent a significant risk from use as drinking water (based on a 10^{-5} risk level). Based on survey observations, the DWSD effluent contributes less than

Table 2. Management Scenarios

Number	Scenario
1	No action--critical conditions Design effluent flow 7Q10 river discharge Typical effluent chlorine, cadmium, mercury, and PCB concentrations (1983 through 1985 averages as reported by DWSO)
2	Chlorine Management--Conservative chlorine Effluent [TRC]: (2a) 1.25 mg/L (2b) 0.50 mg/L (2c) 0.036 mg/L
3	Chlorine Management--Kinetic chlorine Effluent [TRC]: (3a) 1.25 mg/L (3b) 0.50 mg/L (3c) 0.036 mg/L
4	Loading alternatives for cadmium, mercury, and PCBs (4a) NPDES Goals (4b) Maximum (1983 through 1985) (4c) Minimum (DWSO detection limit) (4d) 50 percent of minimum (DWSO detection limit)
5	Alternate diffuser location using no-action scenario conditions
6	Maximum river flow, WWTP at 805 MGD, no-action scenario concentrations
7	Maximum WWTP = 1200 MGD, no-action scenario concentrations
8	Elevated coliform/reduced chlorine: Cl = 0.5 mg/L, 5,000 counts/100 mL

Source: ESE, 1986.

*loaded
to or
presently*

2 percent of the PCBs in the Detroit River. Therefore, questions regarding incremental impact as well as incremental benefit of proposed abatement appear relevant. Observations of chlorine in the field surveys and in the modeling forecasts reveal measurable chlorine levels near the outfall. These chlorine levels dissipate rapidly and the values never exceed 0.036 mg/L outside the mixing zone.

A complicating factor in assessing whether chronic criteria have been exceeded is identifying the edge of the allowable mixing zone. Within this mixing zone, chronic criteria may be exceeded as long as acute values are not. The mixing zone is defined computationally as 25 percent of the critical flow of the receiving waters. LTI analysis has shown that the physical limits of the DWSD mixing zone extend into the Trenton Channel. Therefore, it is unclear what quantitative measure of regulatory compliance should be used in a model analysis.

Hydraulic conditions of interest in management applications are critical flow conditions for the maximum and minimum (7Q10) river discharge conditions. In addition to the typical low flow (7Q10) critical condition, a high-flow condition was examined because higher stream velocities could mean narrower plumes and higher concentrations at a given transect. Examination of the historical data revealed that the maximum Detroit River flow condition is well represented by flow conditions for the September 10, 1985, field survey which had a discharge of 246,670 cubic feet per second (cfs). Model performance for this flow regime was examined in detail within the report. The MDNR reported a 7Q10 flow for the Detroit River of 119,000 cfs. This low flow condition is well represented by river conditions on April 11, 1984, where $Q = 118,742$ cfs and $Z_d = 572.87$ ft at Amherstburg. The water quality model input data used in simulating the management scenarios are presented in Table 3. The lower portion of Table 3 presents a summary of corresponding

Table 3. Model Input Data and Predictions for Management Scenarios

Input Data Parameter	Management Scenario				
	(1)	(2a)	(3a)	(2b)(3b)	(2c)(3c)
<u>DWSD WWTP effluent</u>					
Discharge (MGD)	805	805	805	805	805
Chlorine (mg/L)	2.5	1.25	0.50	0.036	0.036
Cadmium (µg/L)	4.3	--	--	--	--
Mercury (µg/L)	0.25	--	--	--	--
Total PCB (µg/L)	0.345	--	--	--	--
<u>Detroit River</u>					
Discharge (cfs)	118,740	118,740	118,740	118,740	118,740
<u>Predictions</u>					
<u>First Potable Water Intake--Node 561 between Grassy and Fighting Islands</u>					
Conservative chlorine (mg/L)--		0.0008	0.0003	0.000	0.000
Kinetic chlorine (mg/L)	0.0007	0.0003	0.0001	0.000	0.000
Cadmium (µg/L)	0.0029	--	--	--	--
Mercury (µg/L)	0.0002	--	--	--	--
Total PCB (µg/L)	0.0002	--	--	--	--
<u>Second Potable Water Intake--Node 685, Wyandotte</u>					
Conservative chlorine (mg/L) --		0.0290	0.0116	0.0008	0.0008
Kinetic chlorine (mg/L)	0.0102	0.0051	0.0020	0.0001	0.0001
Cadmium (µg/L)	0.0978	--	--	--	--
Mercury (µg/L)	0.0057	--	--	--	--
Total PCB (µg/L)	0.0078	--	--	--	--

Table 3. Model Input Data and Predictions for Management Scenarios
(Continued, Page 2 of 3)

Input Data Parameter	Management Scenario			
	(4a)	(4b)	(4c)	(4d)
<u>DWSD WWTP effluent</u>				
Discharge (mgd)	805	805	805	805
Chlorine (mg/L)	--	--	--	--
Cadmium (µg/L)	7.0	0.042	0.002	0.001
Mercury (µg/L)	1.1	0.0023	0.0002	0.0001
Total PCB (µg/L)	3x10 ⁻⁴	0.00177	0.000092	0.000046
Detroit River				
Discharge (cfs)	118,740	118,740	118,740	118,740
Predictions				
<u>First Potable Water Intake--Node 561 between Grassy and Fighting Islands</u>				
Cadmium (µg/L)	0.0047	0.0283	0.0013	0.0007
Mercury (µg/L)	0.0007	0.0015	0.0001	0.0001
Total PCB (µg/L)	0.0000	0.0007	0.0001	0.0000
<u>Second Potable Water Intake--Node 685, Wyandotte</u>				
Cadmium (µg/L)	0.1592	0.9589	0.0457	0.0228
Mercury (µg/L)	0.0250	0.0526	0.0046	0.0023
Total PCB (µg/L)	0.0000	0.0231	0.0025	0.0013

05/22/87

Table 3. Model Input Data and Predictions for Management Scenarios
(Continued, Page 3 of 3)

Input Data Parameter	Management Scenario			
	(5)	(6)	(7)	(8)
<u>DWSD WWTP effluent</u>				
Discharge (MGD)	2x402.5	805	1,200	805
Chlorine (mg/L)	2.5	2.5	2.5	0.5
Cadmium (µg/L)	4.3	4.3	4.3	--
Mercury (µg/L)	0.25	0.25	0.25	--
Total PCB (µg/L)	0.345	0.345	0.345	--
Fecal Coliform (#/100 mL)	--	--	--	5,000
Detroit River				
Discharge (cfs)	118,740	118,740	118,740	118,740
Predictions				
<u>First Potable Water Intake--Node 561 between Grassy and Fighting Islands</u>				
Residual chlorine (mg/L)	0.0018	0.0000	0.0010	--
Cadmium (µg/L)	0.0080	0.0001	0.0043	--
Mercury (µg/L)	0.0005	0.0000	0.0003	--
Total PCB (µg/L)	0.0006	0.0000	0.0003	--
Fecal Coliform (#/100 mL)	--	--	--	3
<u>Second Potable Water Intake--Node 685, Wyandotte</u>				
Residual chlorine (mg/L)	0.0141	0.0130	0.0151	--
Cadmium (µg/L)	0.1374	0.0561	0.1458	--
Mercury (µg/L)	0.0080	0.0033	0.0085	--
Total PCB (µg/L)	0.0110	0.0045	0.0117	--
Fecal Coliform (#/100 mL)	--	--	--	82

Source: ESE, 1986.

predictions at two potable water intakes near Wyandotte. These water intakes may be considered important in assessing human impact corresponding to each of the management scenarios. Each of the eight management scenarios is discussed in the report with specific emphasis on incremental impact and the environmental response.

RISK ASSESSMENT

AQUATIC TOXICITY--Water quality criteria are numerical guidelines developed by EPA that indicate appropriate levels of toxicants in ambient waters so as to protect sensitive biotic species. Besides indicating numerical values (or equations) these criteria sometimes indicate duration or frequency of the cited level appropriate for protection. Separate criteria are sometimes cited for protection of aquatic biota and then, if applicable, for protection of human health. Four water quality criteria are relevant to the deliberations of appropriate toxics wasteload allocation in the Detroit River, namely: 1) Chlorine; 2) Cadmium; 3) Mercury; and 4) PCBs. Each of these criteria will be discussed below, along with relevant site-specific observations from this study.

Chlorine was observed to have measurable toxicity on all test species during the bioassay studies. Dechlorinated effluent samples demonstrated less toxicity than the original chlorinated samples. All test species were chosen as sensitive species from different genres and were not indigenous species. Since the plume of DWSD effluent comprises less than 10 percent of the Detroit River's width, it is not expected that chlorine exerts much of a direct impact on indigenous fish species. This hypothesis is supported by: 1) the observed rapid dilution and dissipation (decay) of chlorine in the Detroit River; and 2) a fish avoidance behavior in the presence of chlorine and turbulent, high-flow outfalls.

Chlorine is apparently not affecting the benthic community downstream of the outfall, as indicated by the presence of chlorine sensitive organisms (Gammarus sp.). The minimal impact on the benthic community is probably due to the rapid dissipation of chlorine in combination with a poor benthic substrate which prevents natural habitation by a more highly diverse population. In fact, stations within the plume displayed a similar number of taxa as the control and generally had a larger density of organisms.

Field observations of chlorine confirmed previous observations by MDNR that chlorine rapidly dissipates to low or non-detectable levels. Only 45 measurements out of 434 samples produced measurable values (detection limit = 0.05 mg/L). Most of these observations were just downstream of the discharge and were the result of the effluent.

The environmental fate of chlorine under critical low-flow conditions is best illustrated through the modeling effort which examines various effluent management scenarios. The most informative model evaluations of chlorine are projections of the 0.5 mg/L effluent concentration compared to other possible effluent conditions. The maximum ambient concentration predicted for an effluent concentration of 0.5 mg/L (the NPDES goal) is 0.087 compared to a peak value of 0.218 for an effluent value of 1.25 mg/L. These peak values are representative of only the narrow center line of the plume. Evident in both simulations is the rapid dissipation of chlorine both in the longitudinal and lateral directions in the receiving waters. An aerial view of the effluent plume for predicted chlorine concentrations greater than 0.02 mg/L indicates a very limited zone having values in excess of the chronic criteria (see Figure 5). The simulations generally indicate a "zone of initial dilution," where substantial dilution of the effluent occurs very near the outfall, followed by a rapid dissipation directly downstream. To summarize, the relevant site-specific observations made previously are

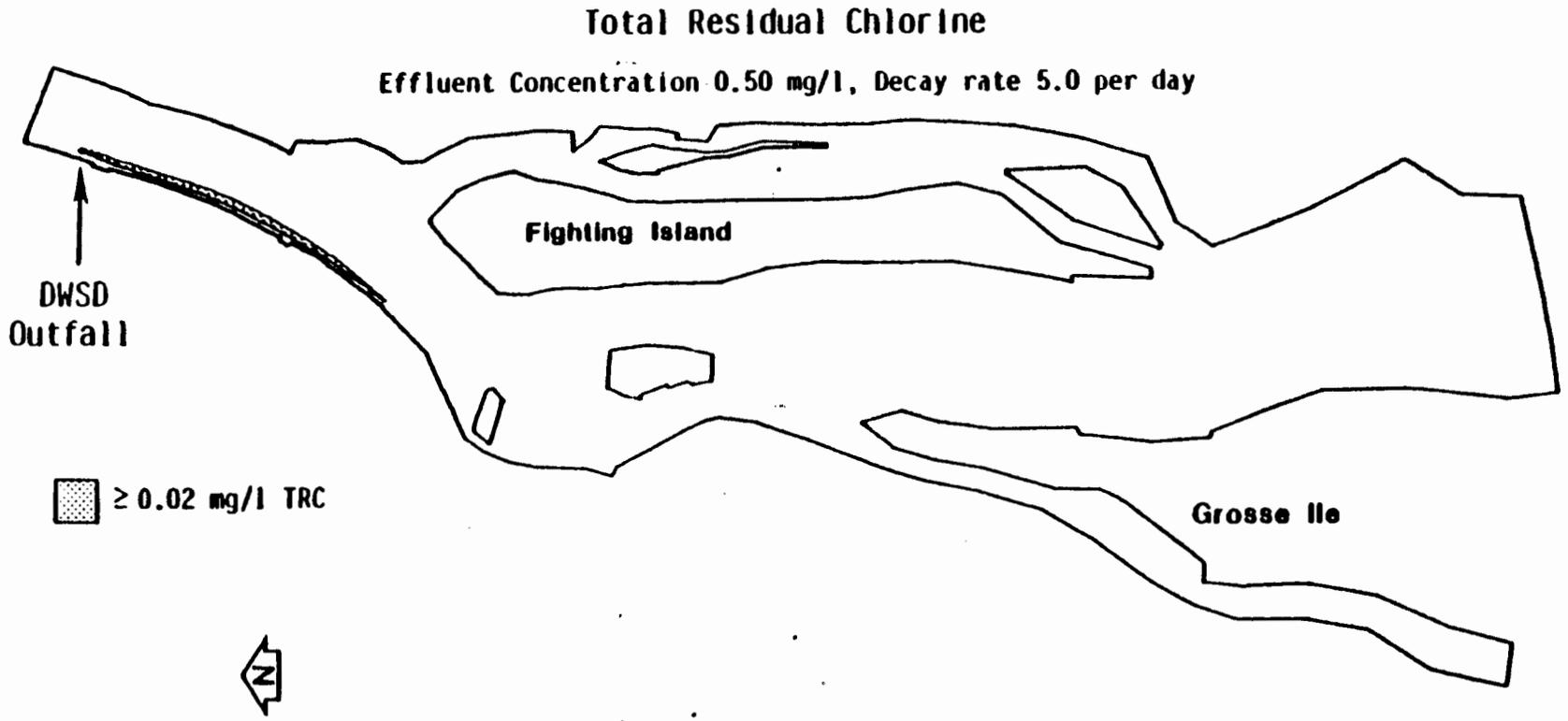


Figure 5
CHLORINE MANAGEMENT: MIXING ZONE FOR 0.50 mg/L
TRC EFFLUENT

DETROIT WATER AND
SEWERAGE DEPARTMENT

05/21/87

that: (1) the final chlorinated effluent in laboratory tests proved toxic, (2) instream concentrations are dissipated rapidly, (3) the plume above chronic values is narrow and within the mixing zone, and (4) benthic organisms apparently are not impacted.

CADMIUM--The detection limit for cadmium in this study was 1 µg/L which is below the chronic criteria. Only 5 out of 479 samples collected were above detection and these samples were below the chronic criteria of 1.6 µg/L. These results include the final effluent samples taken during the study.

Model analyses at critical low-flow conditions indicate that neither acute nor chronic criteria are projected to be exceeded in the Detroit River under all management scenarios. Thus, the DWSO effluent currently meets water-quality-based effluent levels for cadmium.

MERCURY--The NPDES permit for the DWSO outfall requested an evaluation of what measures can be taken to minimize the discharge of mercury. Here, water-quality-based information is examined to establish what effluent values might be appropriate to ensure protection of aquatic health. These values are then compared to DWSO effluent levels for mercury. The 1-hour average (acute) value is 2.4 µg/L. The levels found by EPA (1984) to be protective of aquatic biota as a result of chronic exposure are approximately 1.2 µg/L. The acute value was not exceeded in the DWSO effluent during 1984 and 1985. The chronic value is infrequently exceeded in the mixing zone which is allowable by State of Michigan wasteload allocation methodologies. In fact, the modeling analysis indicates that under critical low-flow conditions the critical criteria are met well within the mixing zone.

PCBs--Although the primary concern regarding PCBs is their impact on human health, PCBs may also impact aquatic biota. Water quality criteria for PCBs were published by EPA in 1980. The acute value to protect sensitive aquatic species is 2000 ng/L, while the chronic value is

14 ng/L. The acute value is not exceeded in the DWSD effluent. Background upstream concentrations measured in this study were 5 to 8 ng/L. Based on effluent concentrations measured during the study of about 30 ng/L, the maximum incremental impact due to the DWSD effluent would be less than 10 ng/L. Therefore, the chronic criteria would be exceeded only in a small portion of the mixing zone, which is allowable under State law. In fact, the average incremental impact of the DWSD effluent on PCB levels in the mixing zone would only be about 2 ng/L. Outside the immediate mixing zone the effluent has virtually no effect on the ambient water concentrations. A mass balance of PCBs being transported downstream in the Detroit River reveals that the DWSD effluent is responsible for less than 2 percent of the total mass of PCBs at typical flow conditions.

HUMAN HEALTH—All data collected in this study support the hypothesis that PCBs in the Detroit River system are principally present as a result of past discharges that have contaminated the sediments, or sources, other than DWSD, potentially including both point and non-point sources upstream of the outfall. The findings and data supportive of this hypothesis are summarized here:

1. The median PCBs concentration in the Detroit River is <0.005 µg/L, both upstream and downstream of the DWSD outfall;
2. Water quality modeling results indicate that the plume of the DWSD effluent would exhibit undetectable incremental increases in PCBs in the river water, with the exception of a limited area near the outfall (within 1,000 - 2,000 ft.); the incremental effect of the discharge on PCBs is small (<2 percent);
3. Contamination of Detroit River sediment by PCBs is widespread, with highest concentrations in the study area observed in a depositional area just upstream of Fighting Island. Sediment contamination has also been observed in Canadian waters along this reach, clearly outside the influence of the DWSD outfall. The sediment PCBs level are apparently roughly one order of

05/21/87

magnitude higher than would result from equilibration with the water column, suggesting that the sediments may be a source of PCBs to the water column, rather than the sediment PCBs resulting from settling of suspended PCBs;

4. Fish tissue contamination was associated with bottom feeders (carp) and top predators (muskellunge that fed on carp and other bottom feeders). Fishes that feed in the water column and those most prized by sportsmen, including walleye and coho salmon, were contaminated to much lower levels and were within the guidelines for edible fish recommended by FDA; and
5. Bioaccumulation studies conducted with channel catfish indicated levels of bioaccumulation from 50-percent effluent that were much lower than the levels found in fish tissue in the river.

Considering these facts, it is concluded that the City of Detroit outfall is not a significant contributor to PCB levels in the Detroit River. It is well known that, as a result of stringent limitation on the use of PCBs during the 1970s, current discharges of PCBs to the nation's surface water are much less than the loadings of the late 1960s and that most residual PCBs contamination result from persistent sediment contamination as a result of historical discharges (EPA, 1980a). This generally recognized condition also applies to the Detroit River.

Cadmium and Mercury—Measurements taken during the study demonstrated that cadmium concentrations are within the drinking water standards in the final effluent as well as all areas of the DWSM mixing zone suggesting that cadmium is not a major human health concern.

To protect human health from the toxic effects of organic mercury, drinking water supplies should not exceed 10 µg/L over a long-term "chronic" exposure period. If individuals ingest water and consume fish from surface water, concentrations below 144 ng/L are considered to be protective of human health with an adequate margin of safety. During

05/21/87

water-quality monitoring conducted in the Detroit River, approximately 478 samples were taken. Ninety-eight percent of these samples contained less than 200 ng/L, the analytical detection limit of the negative cold vapor method. The maximum concentration observed was 1,000 ng/L. There was no pattern indicating higher concentrations in the area affected by the DWSD outfall plume. The DWSD effluent was also consistently below the analytical detection limit of 200 ng/L. There is no evidence to suggest that the DWSD outfall has any effect on mercury levels in the Detroit River, nor that it could be contributing to health effects associated with exposure to mercury.

Fish tissue data for mercury consistently indicated levels below the FDA guidelines of 1 mg/kg. In its updated evaluation of ambient water quality criteria for mercury, the EPA (1985) concluded: "...for mercury, monitoring for unacceptable environmental effects should be relatively straightforward. The most sensitive adverse effect will probably be exceedence of the FDA action level. Therefore, existing discharges should be acceptable if the concentration of methylmercury in the edible portion of exposed, consumed species does not exceed the FDA action level." Since all fish tissue samples indicated levels less than the FDA action level it is concluded that the DWSP effluent is of limited risk to human health because of potential mercury bioconcentration in fish tissue.

- A Trenton Channel transport model was developed and calibrated using specific conductance as a tracer. The transport model was then used as the basis for a toxic unit transport model. This model calculates the probability distribution of the concentration of toxicity in the overlaying water due to a random sequence of sediment-associated contaminant resuspension fluxes. This work is still underway (DiToro et al., Manhattan College), but a hypothetical example of how the modeling approach would be applied in the Trenton Channel is reproduced below without modification from an interim report.

SECTION V

Trenton Channel Toxicity Distribution

Section IV presented the probabilistic toxicity analysis framework. To apply this framework to the Trenton Channel requires specification of the locations of toxic sediments (i.e., in what segments of the water quality model), the time between resuspension events, the magnitude of sediment resuspended and the toxicity associated with the resuspended material. At this stage in the project, the data needed to make these determinations are unavailable. However, a hypothetical application of the framework has been completed. This illustration of the modeling procedure provides useful insights into the type of information generated by the analysis as well the potential significance of in-place pollution within the channel.

V.1 Hypothetical Application

The hypothetical application predicts water column toxicity resulting from the resuspension of Trenton Channel sediment in the vicinity of Mongaugan Creek (i.e., segment 12 in the water quality model). Toxicity introduced to the water column is assumed to remain in the water column. No settling of resuspended toxicity occurs. It is not necessary to make this assumption but it is useful in that it simplifies the analysis and provides a conservative estimate of downstream toxicity resulting from a resuspension event.

V.1.1 Resuspension

In the probabilistic calculation resuspension is defined by the joint probability of time between resuspension events and magnitude of resuspension. The time between events is assumed to follow a Poisson process. In problems where the time between events is a random variable it is common to use this distribution. An advantage of the Poisson distribution is that it is completely specified by a single parameter equal to both the

mean and the variance of the distribution. For the illustrative calculation the mean time between resuspension events is assumed to be either 10 days or 30 days. The probability distribution of time between events is shown for both cases in Figure V-1.

In a resuspension event a volume of bed, including both pore water and solids, is scoured into the water column. Because the toxic chemical is present both in the pore water and on the solids, the magnitude of resuspension must be specified in terms of total volume resuspended. Resuspension magnitude is assumed to be a random variable that is described by a log-normal distribution. For the illustrative calculation the distribution shown in Figure V-2 is used. The median resuspension volume is 4300 cubic meters of bed. This is equivalent to resuspending the top 3 cm of bed over the area of segment 12 of the model (0.14 km^2). The distribution has an arithmetic coefficient of variation of 2.

V.1.2 Toxicity

For the illustrative calculation a toxic unit concentration is assigned to the resuspension volume. The equivalent mass input of toxicity to the water column is the product of the toxic unit concentration and the resuspension volume. A single concentration is used to describe the sediment site. This concentration is determined from the dose-response analysis of the bioassay tests conducted on samples from the site.

Toxic unit concentrations of 1000 and 10000 are used in the example.

V.1.3 Results

The data and model calibration for conductivity (Section II) indicate that resuspension occurring below Mongaugan Creek (i.e., in segment 12 of the model) will result in an increase in water column toxicity along the western shore of the channel with some lateral migration to the east. Therefore results are presented only for the segment at Mongaugan Creek and the most downstream transect of segments. Probability distributions of computed water column toxicity are presented to provide a visual representation of the range of impacts.

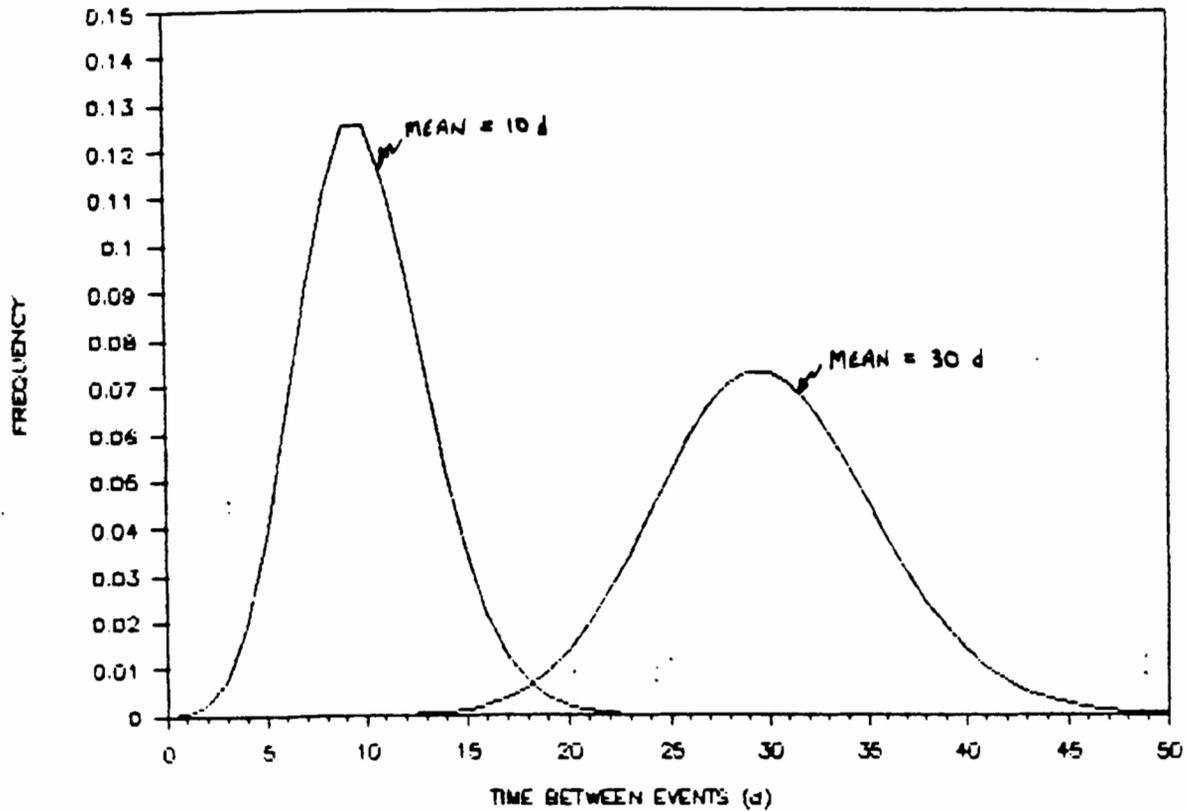


Figure V-1. Time between resuspension events frequency density functions for means of 10 days and 30 days.

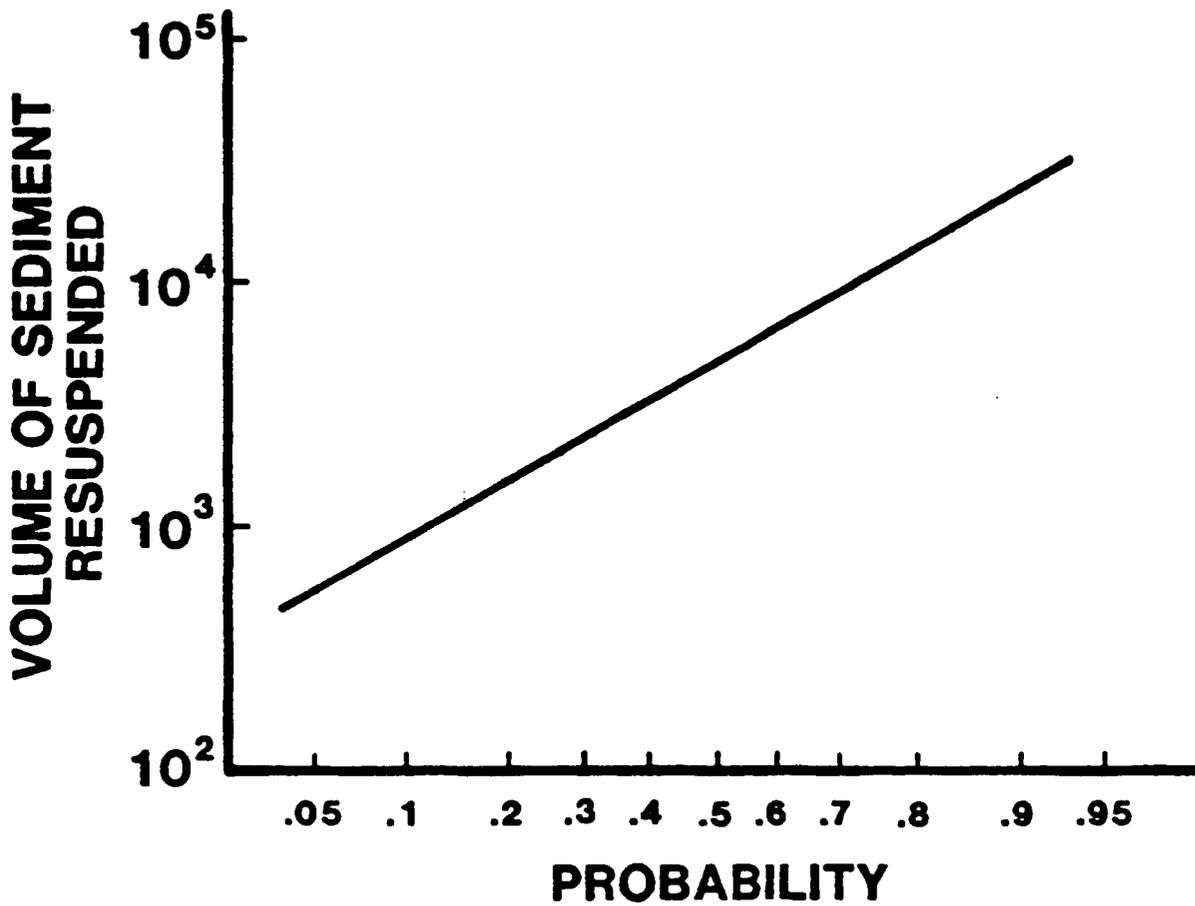


Figure V-2. Probability distribution of sediment volume resuspended during an event.

Figure V-3 shows the toxic unit distributions in the Mongaugan Creek area for the four cases considered. Toxicity is seen to increase as the time between events decreases or the toxicity of the sediment increases. The mean time between events appears to be particularly significant. A factor of 3 change (10 days to 30 days) alters the toxicity by about a factor of 5. An approximately one-to-one relationship exists between sediment toxicity and water column toxicity. The variability of toxicity for any case is large, ranging over several orders of magnitude. This variability is a consequence of the large variability assigned to resuspension magnitude.

At the most downstream transect of stations most of the toxicity remains along the western shore (Figure V-4). A slight decline in toxicity occurs from between Mongaugan Creek and the bottom of the channel (segment 36). Toxicity decreases rapidly across the channel from the western shore, declining two orders of magnitude by the center of the channel.

These results indicate that toxic impacts associated with resuspension from the area of Mongaugan Creek are likely to be highly variable and localized to the western shore of the channel. The frequency of resuspension has a large effect on the computed toxicity. An accurate determination of resuspension probability is clearly an important remaining task.

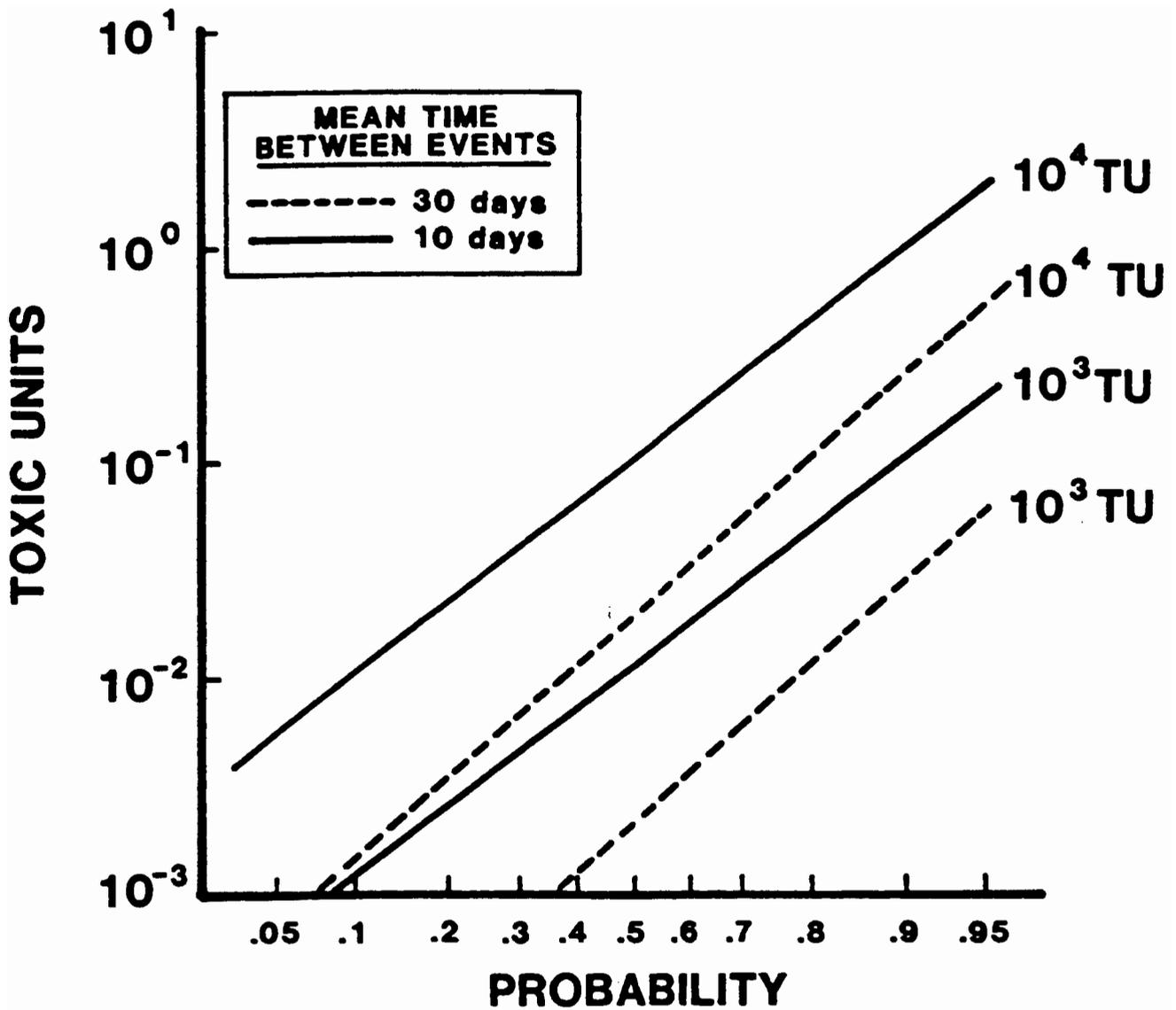


Figure V-3. Computed probability distributions of water column toxicity in the vicinity of Mongaugan Creek.

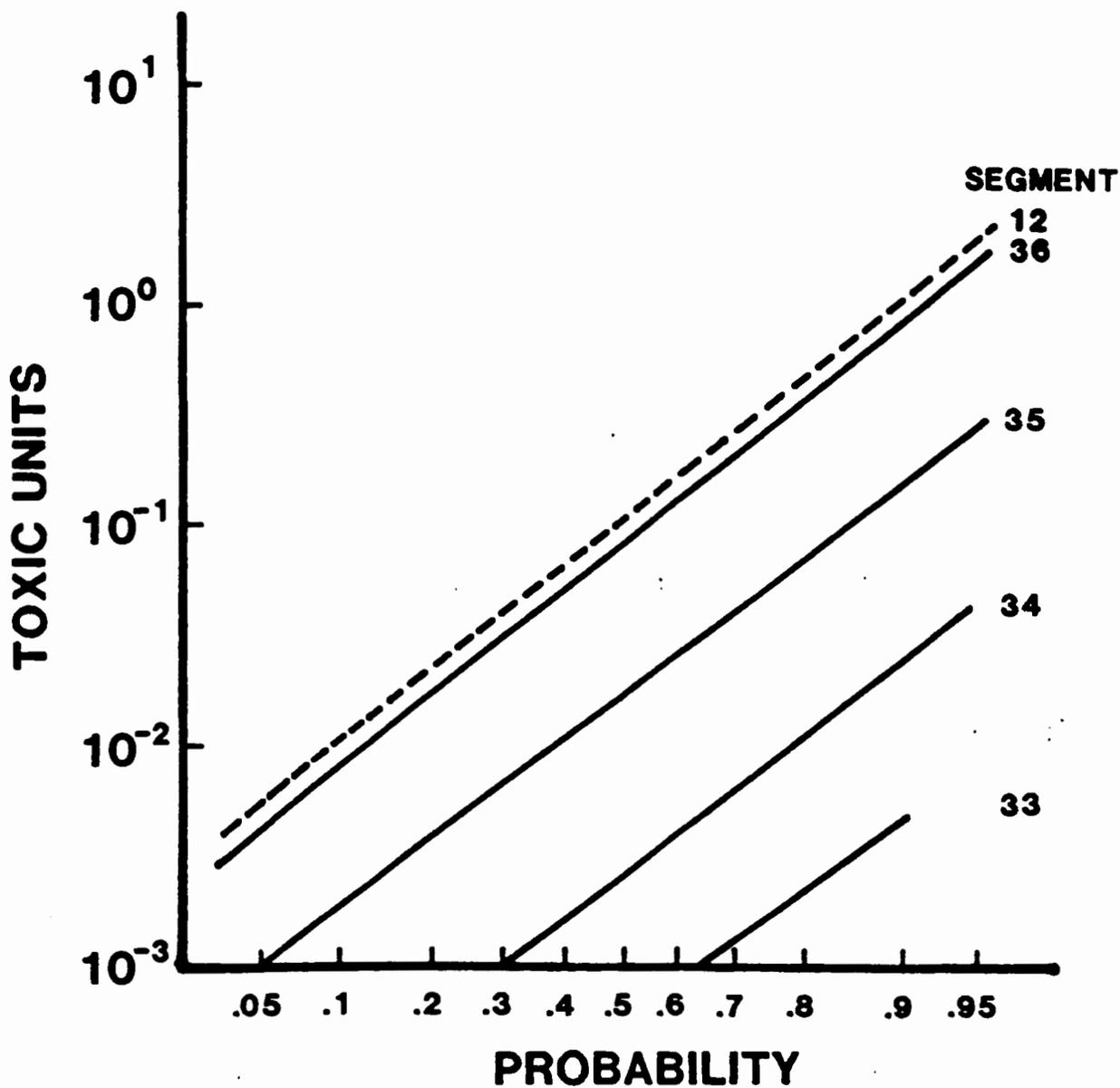


Figure V-4. Computed probability distributions of toxicity in the area of resuspension (seg. 12) and at the most downstream lateral transect of stations (seg. 36, 35, 34, 33).

GENERIC RECOMMENDATIONS FOR FUTURE STUDIES

Coordinating an international, multi-agency study is not a trivial exercise. From experiences in the Upper Great Lakes Connecting Channels Study, a few recommendations are worth mentioning that may make future studies easier. It is encouraging that some of these recommendations have already been implemented in new studies, such as the Green Bay modeling project underway at the Large Lakes Research Station.

1. Most importantly, the goals of the study must be clearly defined. Recommendations for appropriate data collection and model development depend on it. Goals should be agreed to and supported by all major players at the onset of the study. If goals cannot be clearly defined then the study should not proceed until they are.
2. Goals fall into several categories: research, regulatory, remedial and political. The resource priority that each of these categories can expect to receive should be identified early on and be consistent with the goals of the study. For example, if all that can be accomplished is a contaminant mass balance for regulatory purposes (and this is no small or trivial undertaking), the study should not be described as having an ecosystem approach. Doing so tends to foster unrealistic expectations by the public and the study participants. Processes leading to attainment of one goal should be carefully examined to ensure that they aid the attainment of other goals. If they do not, then resources may be spread too thinly.

3. Goals must be realistic, given time, personnel, financial, and laboratory capacity constraints. Realistic goals may not equate with ideal goals, but realistic goals promulgate realistic expectations. How are realistic goals set - by using PERT diagrams, spread sheet programs, and timeline diagrams to determine the resources needed to accomplish goals. This must be done early on.
4. Modelers are often asked to give direction to a study since models include the physical, chemical and biological processes of a system that are important for understanding it's functioning and the behavior of contaminants in it. By understanding the sensitivity of the system's behavior to these processes, areas can be identified where data collection is most important. Modelers should be encouraged to develop "speculative" models as quickly as possible in order to perform these sensitivity analyses. Doing so is not always possible, however, as was primarily the case with the UGLCCS.
5. If modelers are given the responsibility of identifying monitoring and research that is needed to accomplish the study's goals, then that monitoring and research should be given top funding priority. If said monitoring and research cannot be accomplished for whatever reason, then (a) the study's goals must be redefined or (b), the models developed must be viewed as preliminary only.
6. A criterion for selection of those persons who will shoulder a considerable amount of committee work, major report writing, etc.,

should be that their agency will recognize the importance of and have the capability to reward such work. Without such a reward system, these persons will be spread too thin trying to accomplish the mutually exclusive goals of the study and their agency.



INTERNATIONAL JOINT COMMISSION

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December 10, 1987

File No. 1300

Mr. William Richardson, Chief
U.S. EPA
Large Lakes Research Station
9311 Groh Road
Grosse Ile, Michigan 48138

Dear Bill:

Enclosed are example applications of the Maximum Likelihood Estimate (MLE) method that I propose to use to obtain estimates of differential loadings in the Detroit River Systems Mass Balance (SMB) Study. The two examples chosen are phosphorus and cadmium from SMB1. Note that each upstream data set contained at least one value reported as below detection limit. This method maximizes information gained by these measurements without altering the probability distribution or biasing the result.

I have worked out these two examples by hand, but I intend to program the method in SAS and use it for all SMB data. It is general enough so that it can be applied to normal or log-normal data with or without censoring. I will notify you when I have completed the program.

Very truly yours,

David M. Dolan

David M. Dolan
Data Analyst
Great Lakes Regional Office

DMD/sk

ENCLOSURES

cc: D.J. Williams
T. Fontaine
A. El-Shaarawi

APPENDIX I

EXAMPLE APPLICATIONS OF THE METHOD OF MAXIMUM LIKELIHOOD
WITH SINGLY CENSORED DATA FROM THE DETROIT RIVER

The Modeling Committee of the Upper Great Lakes Connecting Channels Study is attempting to perform a mass balance on the Detroit River using samples taken at the head (at Windmill Point) and the mouth (at Grosse Ile). Samples were taken for many conservative, nutrient, metals and organic parameters twice a day for a one week period during the spring and summer. Samples were taken by integrating each transect according to the horizontal flow distribution in the river at that point. Upstream and downstream sampling times were 'lagged' by 18 hours to account for time of travel in the river.

Because many of the chemicals were measured in trace amounts, large percentages of the data were sometimes reported as ND (non-detectable or below the detection limit). Without a consistent and unbiased way of handling these measurements, the task of estimating loadings for these chemicals and associated confidence intervals would be extremely difficult.

The method of maximum likelihood (Cohen 1959, David 1981, El-Shaarawi 1987) can be applied to this type of data (log-transformed if appropriate) and used to produce theoretically sound estimates and confidence intervals. Two examples are chosen from the 1986 spring surveys to illustrate the method. One data set, total phosphorus contains only one non-detectable value, while the other data set contains eleven out of fourteen non-detects.

Application of the method is complicated by the fact that it is iterative and requires convergence of three parameters. However, tables in David (1981) greatly simplify the procedure.

EXAMPLE 1

Phosphorus in Detroit River

Data Upstream: .0146, .0116, .0113, .0109, .0107, .0097, .0083,
(mg/L) .0083, .0069, .0069, .0064, .0064, .0063, ND

Detection limit = .0023 mg/l

$$h = \frac{\# \text{ non-detects}}{\text{sample size}} = \frac{1}{14} = .07143$$

Take natural logs of all concentration data including detection limit and find, in log space,:

$$\begin{aligned} \bar{x} &= -4.736 \\ s^2 &= 0.0714 \\ x_0 &= -6.075 \\ s^2 / (\bar{x} - x_0)^2 &= 0.03983 \end{aligned}$$

Need $\hat{\lambda}$ from David's (1981) tables. Use linear interpolation in two dimensions to find value (see Appendix for method used (Carnahan et al.)). We are interested in this section of David's table:

$\frac{s^2}{(\bar{x} - x_0)^2}$	h	.07	.08
.00		.074953	.086488
.05		.077909	.089834

Interpolation gives: $\hat{\lambda} = 0.079$

$$\begin{aligned} \hat{\sigma}^2 &= s^2 + \hat{\lambda}(\bar{x} - x_0)^2 \\ &= .0714 + .079(-4.736 - -6.075)^2 \\ &= 0.2130 \end{aligned}$$

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2} = .4616$$

$$\begin{aligned} \hat{\mu} &= \bar{x} - \hat{\lambda}(\bar{x} - x_0) \\ &= -4.736 - .079(-4.736 - -6.075) \\ &= -4.842 \end{aligned}$$

$$\hat{\xi}_0 = \frac{(x_0 - \hat{\mu})}{\hat{\sigma}} = \frac{(-6.075 - -4.842)}{.4616} = -2.672$$

Can now calculate large sample variance covariance matrix for $\hat{\mu}$ and $\hat{\sigma}$. Follow equations in El-Shaarawi (1987) with corrections as noted.

$$V = \begin{bmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{bmatrix} = \frac{\hat{\sigma}^2}{N(1-F(\hat{\xi}_0))(\zeta_{11}\zeta_{22} - \zeta_{12}^2)} \begin{bmatrix} \zeta_{22} & -\zeta_{12} \\ -\zeta_{12} & \zeta_{11} \end{bmatrix}$$

Where $\zeta_{11}^* = 1 + \frac{n_1}{N-n_1} Z(-\hat{\xi}_0)\{Z(-\hat{\xi}_0)+\hat{\xi}_0\}$

$$\zeta_{12}^* = \frac{n_1}{N-n_1} Z(-\hat{\xi}_0)\{1+\hat{\xi}_0(Z(-\hat{\xi}_0)+\hat{\xi}_0)\}$$

$$\zeta_{22} = 2 + \hat{\xi}_0 \zeta_{12}$$

* derivation in Cohen (1959) incorrect; correction provided by David (1981).

$F(\hat{\xi}_0)$ is the value of the standard normal distribution function at $\hat{\xi}_0$ (tabulated)

$$F(\hat{\xi}_0) = .0038 \quad F(-\hat{\xi}_0) = .9962 = 1 - F(\hat{\xi}_0)$$

$$Z(-\hat{\xi}_0) = \frac{e^{-\hat{\xi}_0^2/2}}{\sqrt{2\pi(1-F(-\hat{\xi}_0))}} = \frac{e^{-(2.672)^2/2}}{\sqrt{2\pi(.0038)}} = 2.959$$

So,

$$\zeta_{11} = 1 + \left(\frac{1}{13}\right) 2.959 (2.959 + (-2.672)) = 1.0654$$

$$\zeta_{12} = \left(\frac{1}{13}\right) 2.959 \{ -2.672 (2.959 - 2.672) \} = .0531$$

$$\zeta_{22} = 2 + (-2.672)(.0531) = +1.8582$$

and: $V = \frac{0.2130}{(14)(.9962)((1.0654)(1.8582)-(.0531)^2)} \begin{bmatrix} 1.8582 & - .0531 \\ - .0531 & 1.0654 \end{bmatrix}$

$$V = \begin{bmatrix} 0.0144 & -.00041 \\ -.00041 & 0.00823 \end{bmatrix}$$

so $V_{11} = .0144$, $V_{12} = V_{21} = -.00041$ and $V_{22} = .00823$
Transforming back to observation space,

$$\begin{aligned} \hat{a} \text{ (biased)} &= e^{(\hat{\mu} + \hat{\sigma}^2/2)} \\ &= e^{(-4.842 + .213/2)} \\ &= 0.00878 \end{aligned}$$

$$\begin{aligned}
\tilde{a} \text{ (bias corrected)} &= \hat{a} e^{-(V_{11} - 2 \hat{\sigma} V_{12} + \hat{\sigma}^2 V_{22})/2} \\
&= .00878 e^{-(.0144 + 2(.4616)(-.00041) + (.213)(.00823))/2} \\
&= .00878 (.984) \\
&= .00864
\end{aligned}$$

To test if the downstream and upstream concentrations are the same, the confidence interval for the ratio, $\rho = \frac{\tilde{a}_2}{\tilde{a}_1}$ is estimated and if it includes 1,

then there is no significant difference between upstream and downstream. The limits of the 95% confidence interval are:

$$\frac{\tilde{a}_2}{\tilde{a}_1} \exp \left\{ \pm 1.96 \sqrt{Q_2 + Q_1} \right\}$$

where $Q = V_{11} + 2V_{12} \hat{\sigma} + V_{22} \hat{\sigma}^2$ for downstream or upstream.

For phosphorus, $\tilde{a}_1 = .00864$ and $Q_1 = .0158$ from previous page. For the downstream estimate, no non-detects were found and $\tilde{a}_2 = .0158$ mg/l and $Q_2 = .0029$

$$\begin{aligned}
\text{so limits} &= \frac{.0158}{.00864} \exp \left\{ \pm 1.96 \sqrt{.0029 + .0158} \right\} \\
&= (1.3965, 2.3870)
\end{aligned}$$

EXAMPLE 2

Cadmium in Detroit River

Data Upstream: .0349, .0272, .0220, ND, ND, ND, ND,
 (µg/L) ND, ND, ND, ND, ND, ND, ND

Detection limit = 0.0212 µg/l

$$h = \frac{\# \text{ non-detects}}{\text{sample size}} = \frac{11}{14} = .7857$$

Take natural logs of all concentration data including detection limit and find, in log space,:

$$\begin{aligned} \bar{x} &= -3.592 \\ s^2 &= 0.03556 \\ x_0 &= -3.854 \\ s^2 / (x - x_0)^2 &= 0.518 \end{aligned}$$

Need $\hat{\lambda}$ from David's (1981) tables. Use linear interpolation in two dimensions to find value (see Appendix for method used (Carnahan et al.)). We are interested in this section of David's table:

$\frac{s^2}{(\bar{x} - x_0)^2}$	h	
	.7	.8
.5	1.770	2.421
.55	1.778	2.443

Interpolation gives: $\hat{\lambda} = 2.336$

$$\begin{aligned} \hat{\sigma}^2 &= s^2 + \hat{\lambda}(\bar{x} - x_0)^2 \\ &= .03556 + 2.3363(-3.592 - (-3.854))^2 \\ &= .19544 \end{aligned}$$

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2} = .4421$$

$$\begin{aligned} \hat{\mu} &= \bar{x} - \hat{\lambda}(\bar{x} - x_0) \\ &= -3.592 - 2.336(-3.592 - (-3.854)) \\ &= -4.203 \end{aligned}$$

$$\begin{aligned} \hat{\xi}_0 &= \frac{(x_0 - \hat{\mu})}{\hat{\sigma}} = \frac{(-3.854 - (-4.203))}{.4421} \\ &= 0.791 \end{aligned}$$

Can now calculate large sample variance covariance matrix for $\hat{\mu}$ and $\hat{\sigma}$. Use equations in Example 1.

$$F(\hat{\xi}_0) = .7854 \quad F(-\hat{\xi}_0) = .2146 = 1 - F(\hat{\xi}_0)$$

$$Z(-\hat{\xi}_0) = \frac{e^{-\hat{\xi}_0^2/2}}{\sqrt{2\pi(1-F(-\hat{\xi}_0))}} = \frac{e^{-(.791)^2/2}}{\sqrt{2\pi(.7854)}} = .3715$$

So,

$$\zeta_{11} = 1 + \frac{(11)}{3} .3715 (.3715 + .791)$$

$$= 2.5835$$

$$\zeta_{12} = \frac{(11)}{3} .3715 \{ 1 + .791 (.3715 + .791) \}$$

$$= 2.6417$$

$$\zeta_{22} = 2 + .791(2.6417)$$

$$= 4.0683$$

$$\text{and: } V = \frac{.19544}{(14)(.2146)((2.5835)(4.0683) - (2.6417)^2)} \begin{bmatrix} 4.0683 & -2.6417 \\ -2.6417 & 2.5835 \end{bmatrix}$$

$$V = \begin{bmatrix} .0720 & -.0468 \\ -.0468 & .0457 \end{bmatrix}$$

so $V_{11} = .0720$, $V_{12} = V_{21} = -.0468$, $V_{22} = .0457$

Transforming back to observation space,

$$\hat{a} \text{ (biased)} = e^{+(\hat{\mu} + \hat{\sigma}^2/2)}$$

$$= e^{+(-4.203 + .19544/2)}$$

$$= 0.0165$$

$$\tilde{a} \text{ (bias corrected)} = \hat{a} e^{-(V_{11} - 2\hat{\sigma}V_{12} + \hat{\sigma}^2 V_{22})/2}$$

$$= \hat{a} e^{-(.0165 + 2(.4616)(-.00041) + (.213)(.00823))/2}$$

$$= .0165(.9804)$$

$$= .0162$$

For cadmium, the same equations for the confidence interval are used as in Example 1.

$$\tilde{a}_1 = .0162 \quad \text{and} \quad Q_1 = .03955$$

from the previous page. For the downstream estimate, no non-detects were found and $\tilde{a}_2 = .03509$ and $Q_2 = .00652$.

$$\text{so limits} = \frac{.0351}{.0162} \exp \{ \pm 1.96 \sqrt{.00652 + .03955} \}$$

$$= (1.4226, 3.2999)$$

These examples were run through El-Shaarawi's modified MLE program. The estimates made for the various parameters are compared.

Parameter	Phosphorus		Cadmium	
	Example 1	El-Shaarawi	Example 2	El-Shaarawi
$\hat{\sigma}$.4616	.4619	.4421	.4468
$\hat{\mu}$	-4.842	-4.8417	-4.203	-4.219
V_{11}	0.0144	0.0154	.0720	.0796
V_{12}, V_{21}	-0.00041	-0.000407	-.0468	-.0505
V_{22}	0.00823	0.008797	.0457	.0481
\tilde{a}	0.00864	0.00878	.0162	.0163
Q	0.0158	0.0169	.03955	.04408

Conclusion

The maximum likelihood method with singly censored (Type I) data has been applied to two example data sets from the UGLCC study. Estimates for the mean concentration and 95% confidence intervals of the ratio of downstream to upstream mean concentrations were made with the help of tables provided in David (1981). Since these tables require interpolation, the accuracy of the method depends partly on the interpolation scheme used as well as the 'nearness' of the required value to the tabulated values. Overall, the agreement between these examples and output provided by the program of El-Shaarawi is quite good.

References:

- Carnahan, B., H.A. Luther, and J.O. Wilkes. Applied Numerical Methods, John Wiley & Sons, Inc., 1969.
- Cohen, Jr., A.C., Simplified Estimators for the Normal Distribution When Samples Are Singly Censored or Truncated, Technometrics, 1, 217-237, 1959.
- David, Order Statistics, 1981.
- El-Shaarawi, A.H., Inferences About the Mean from Censored Water Quality Data, National Water Research Institute Draft Report, 1987.

Appendix

2-D Linear Interpolation Method

Let $x_1 \leq x \leq x_2$ and $y_1 \leq y \leq y_2$

Where x_1 and x_2 are the values of the quantity corresponding to the row of the table and x is the value for which the interpolation is desired

and y_1 and y_2 are the values of the quantity corresponding to the columns of the table and y is the value for which interpolation is desired

(in this case, $h = y$ and $s/(\bar{x}-x_0)^2 = x$)

The values of the function that are tabulated are:

$$\begin{array}{cc} f(x_1, y_1) & f(x_1, y_2) \\ f(x_2, y_1) & f(x_2, y_2) \end{array}$$

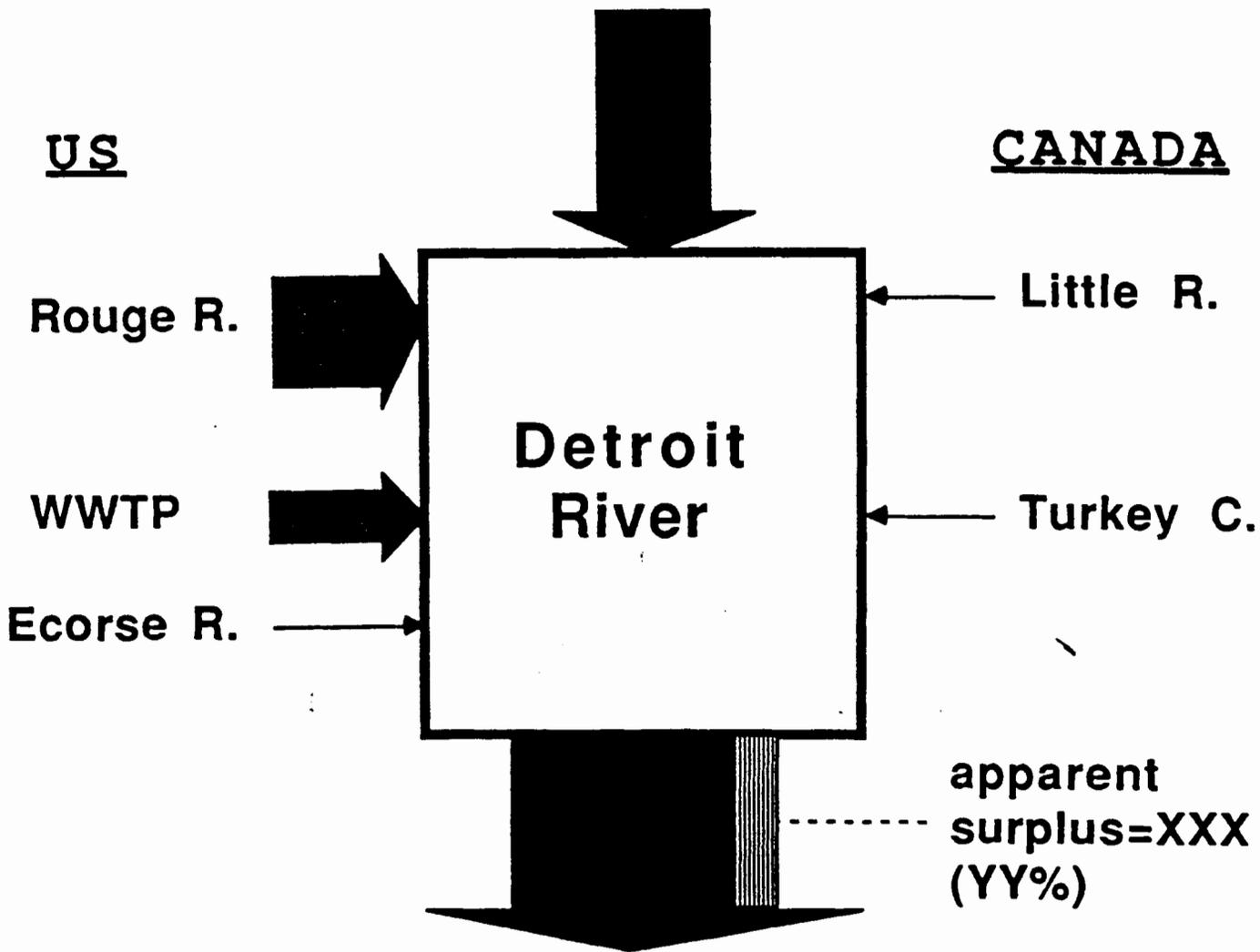
$$\text{Let } A = \frac{x_2 - x}{x_2 - x_1} \quad \text{and} \quad B = \frac{y_2 - y}{y_2 - y_1}$$

then

$$f(x, y) \approx A \cdot B \cdot f(x_1, y_1) + (1-A) \cdot B \cdot f(x_1, y_2) + (1-B) \cdot A \cdot f(x_2, y_1) + (1-A) \cdot (1-B) \cdot f(x_2, y_2)$$

SMB1 CONTAMINANT ABC (Kg/d)

Upstream input

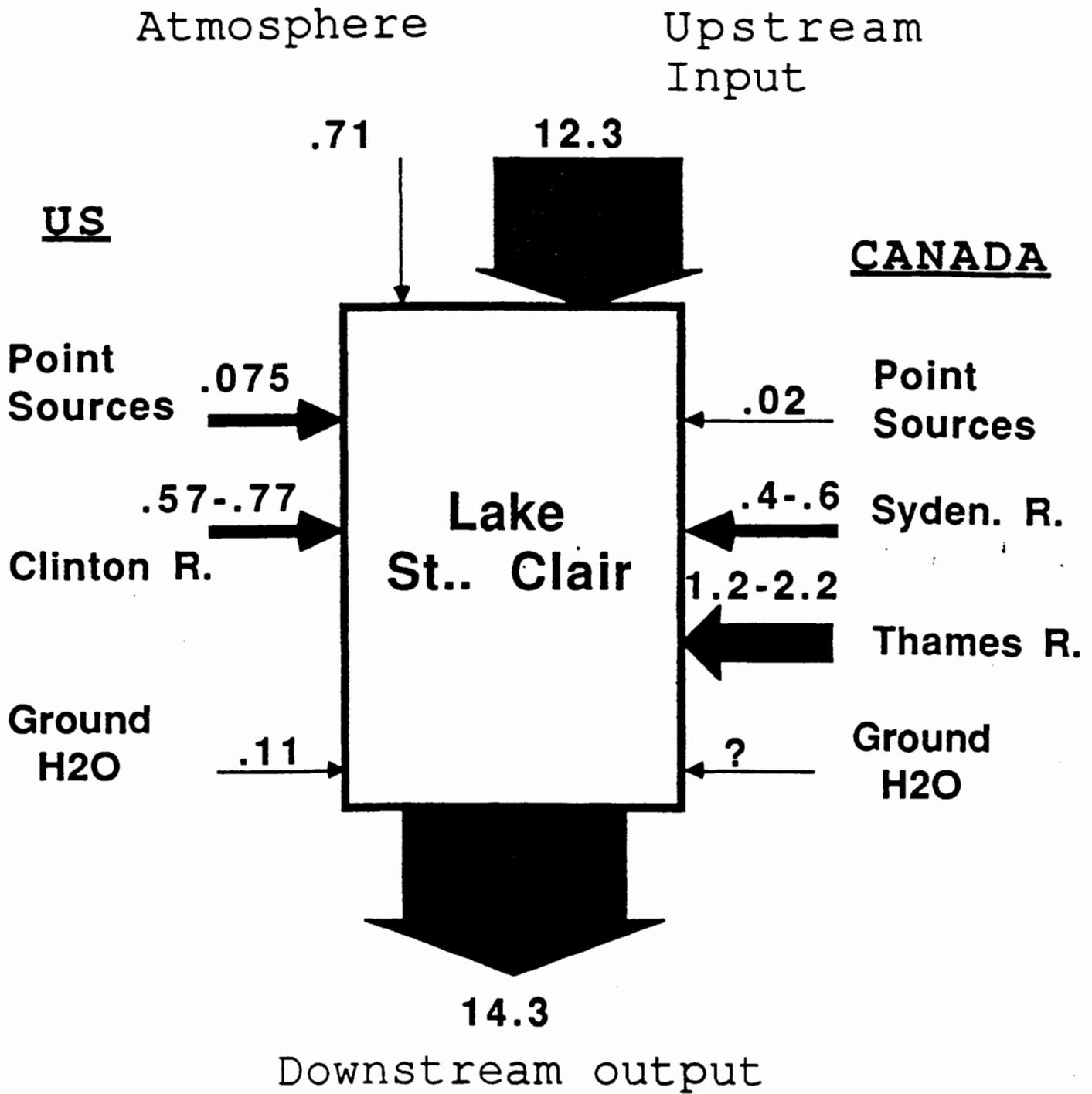


Downstream output

***Note: a surplus suggests an unknown source
and a deficit suggests a sink.***

Interpretation

LAKE ST. CLAIR CADMIUM, TOTAL (Kg/d)

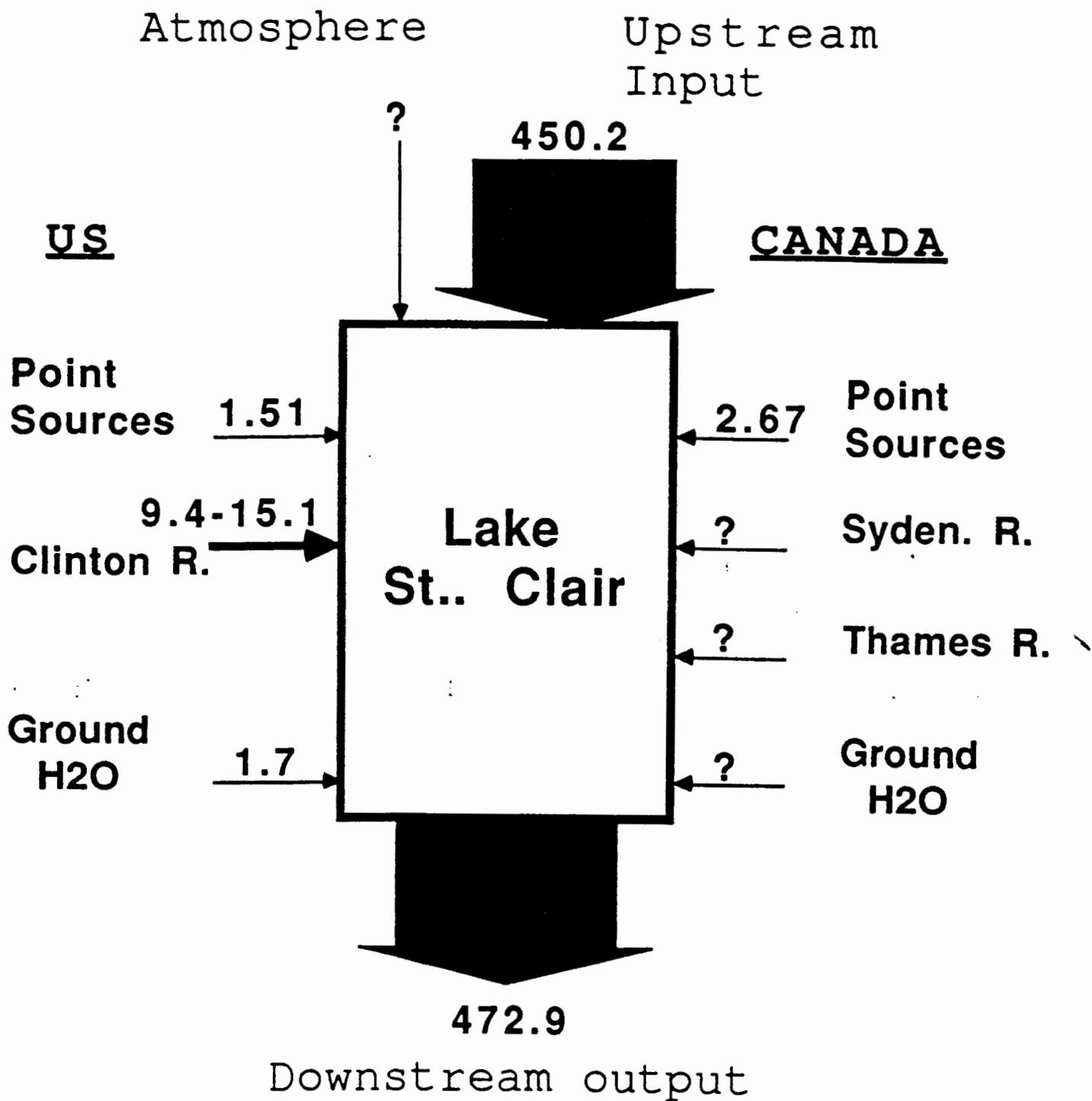


in=15.4-16.8

out=14.3

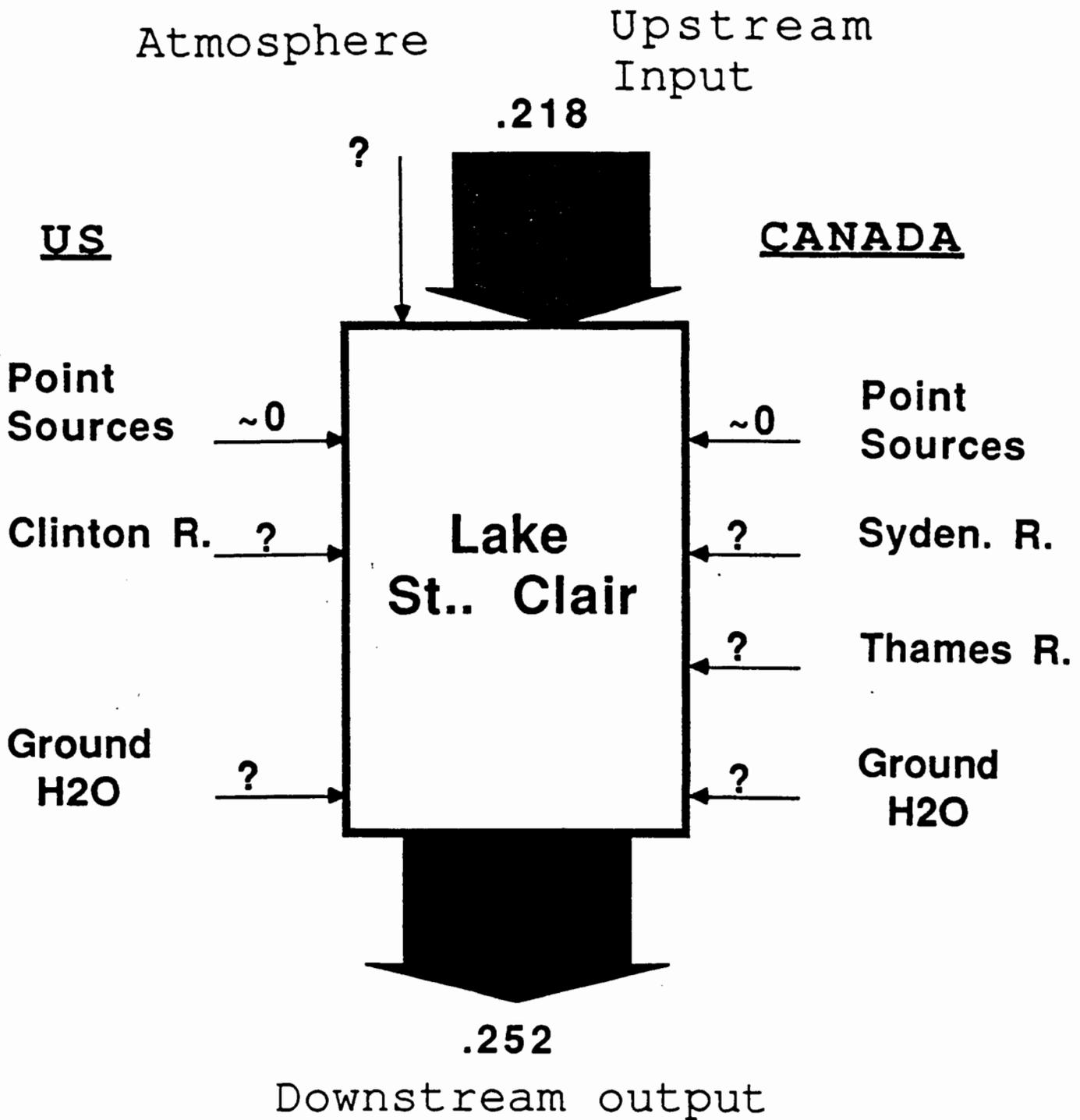
sink=1.1 - 2.5?

LAKE ST. CLAIR COPPER, TOTAL (Kg/d)



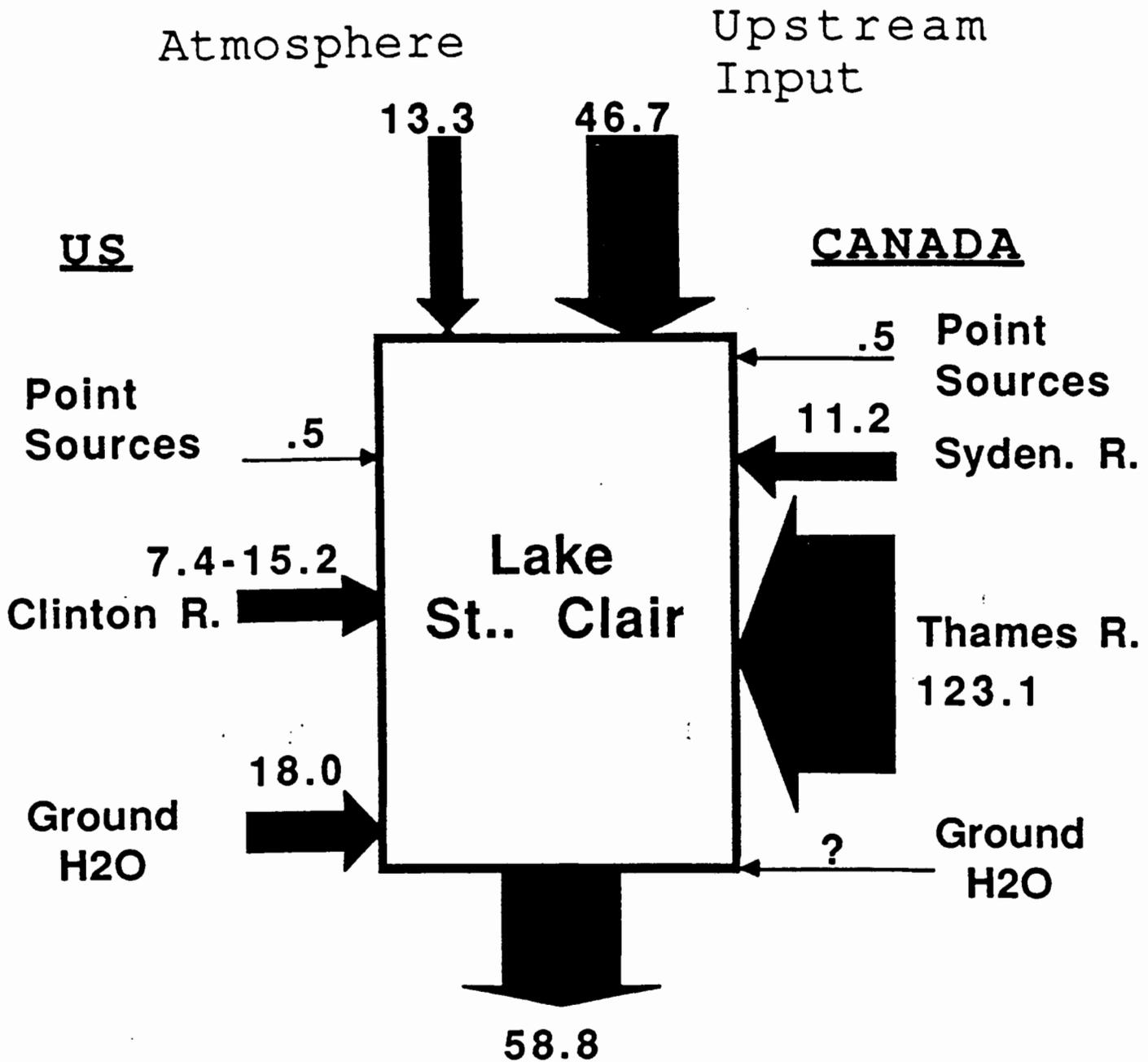
in=465.5-471.2
out=472.9
source=7.4-1.7?

LAKE ST. CLAIR HCB (Kg/d)



in=.218
out=.252
source=.034?

LAKE ST. CLAIR LEAD, TOTAL (Kg/d)

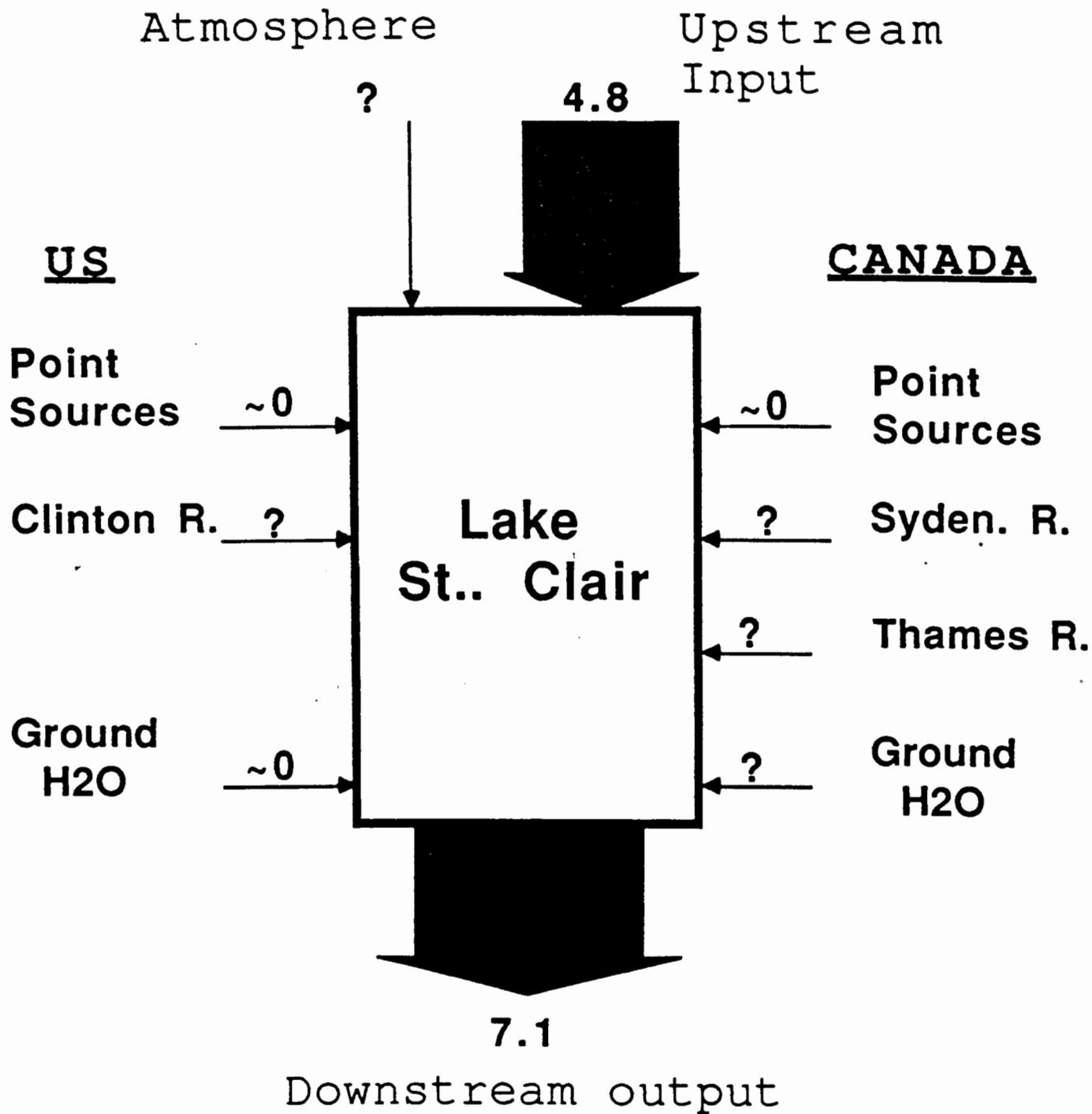


in=220.7-228.5

out=55.8

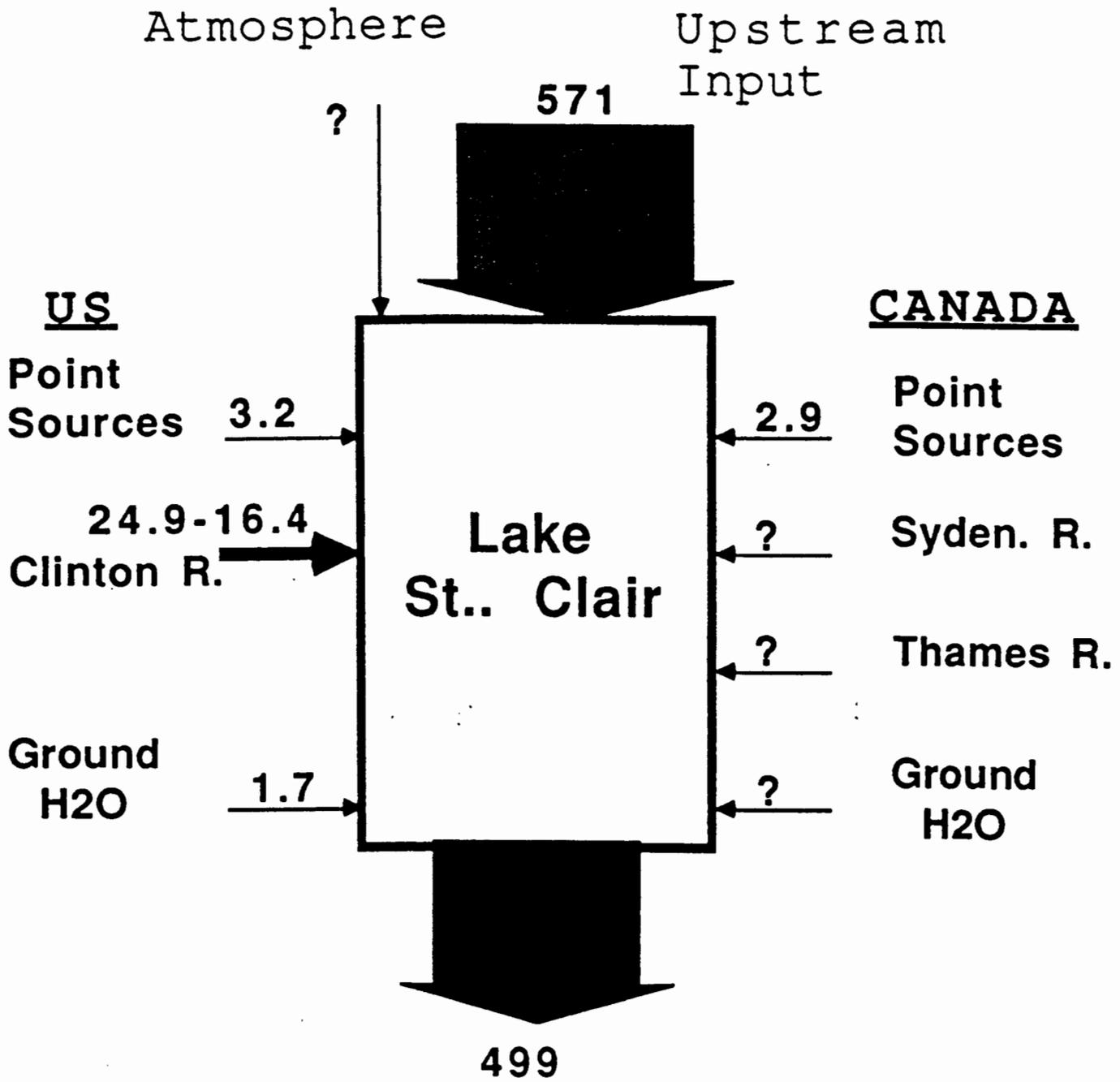
store=161.9-169.7?

LAKE ST. CLAIR MERCURY, TOTAL (Kg/d)



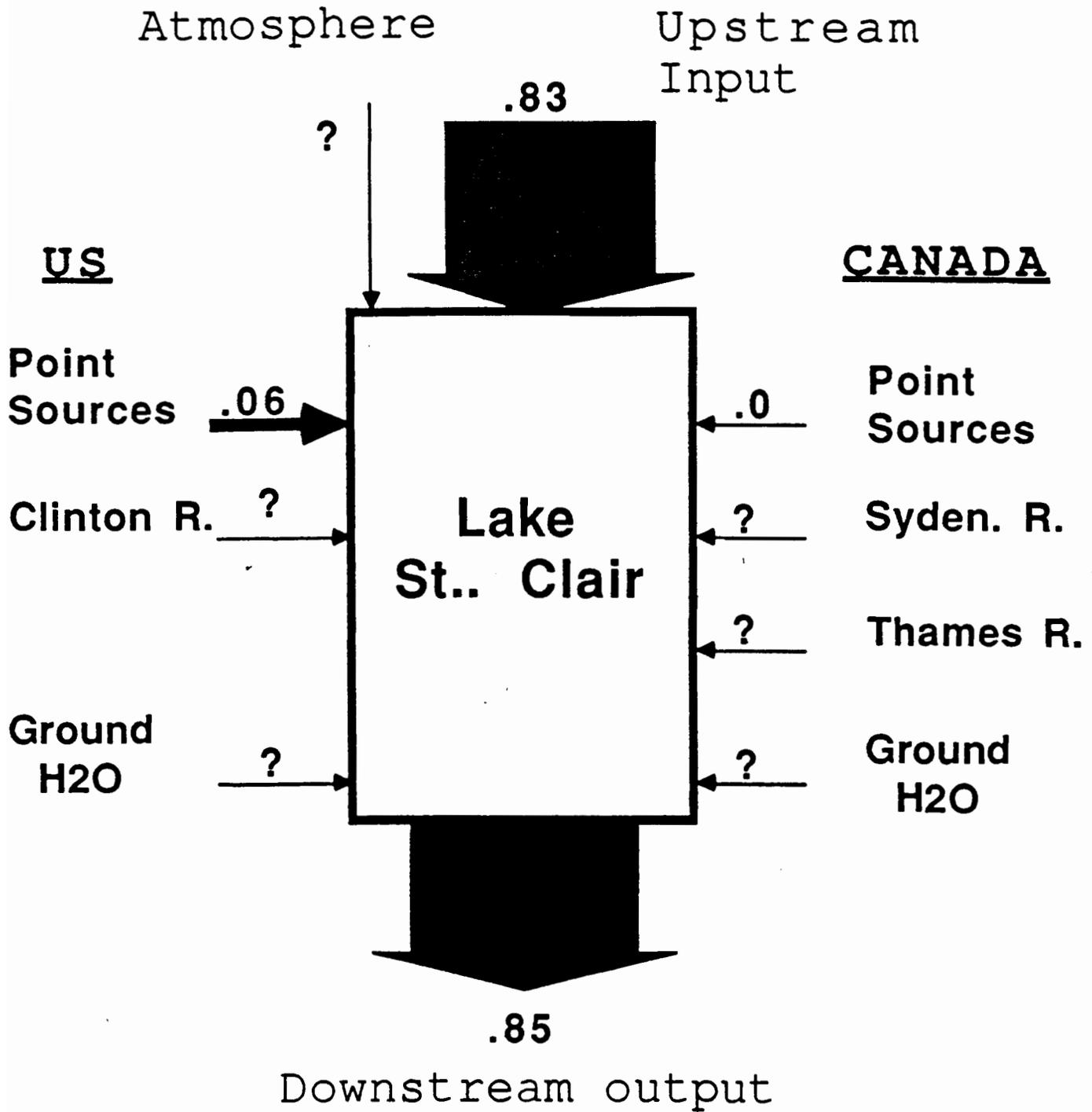
in=4.8
out=7.1
source=2.3?

LAKE ST. CLAIR NICKEL, TOTAL (Kg/d)



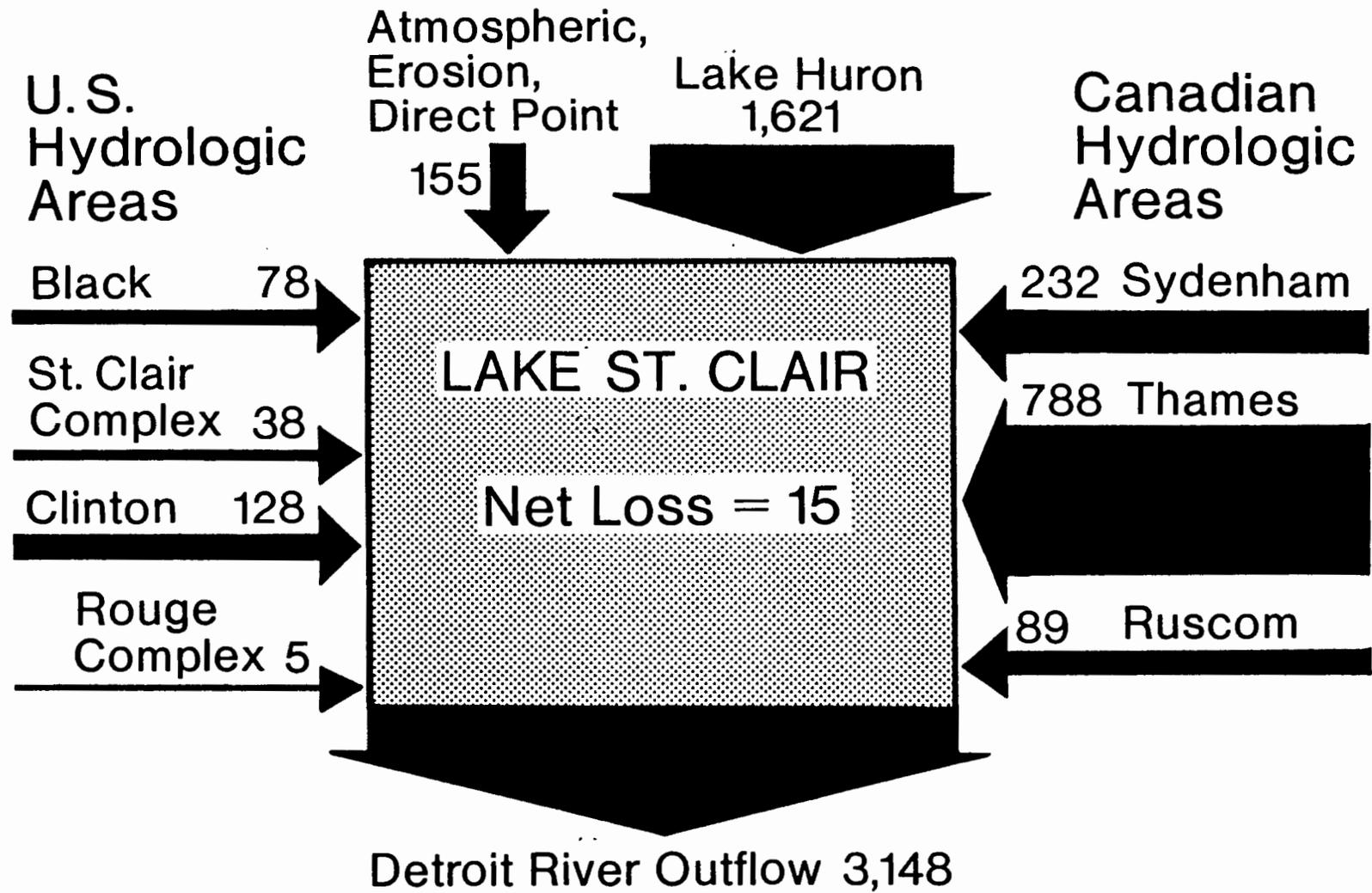
in=595.2-603.7
out=499
sink=96-105?

LAKE ST. CLAIR PCB, TOTAL (Kg/d)



in=.89
out=.85
store=.04?

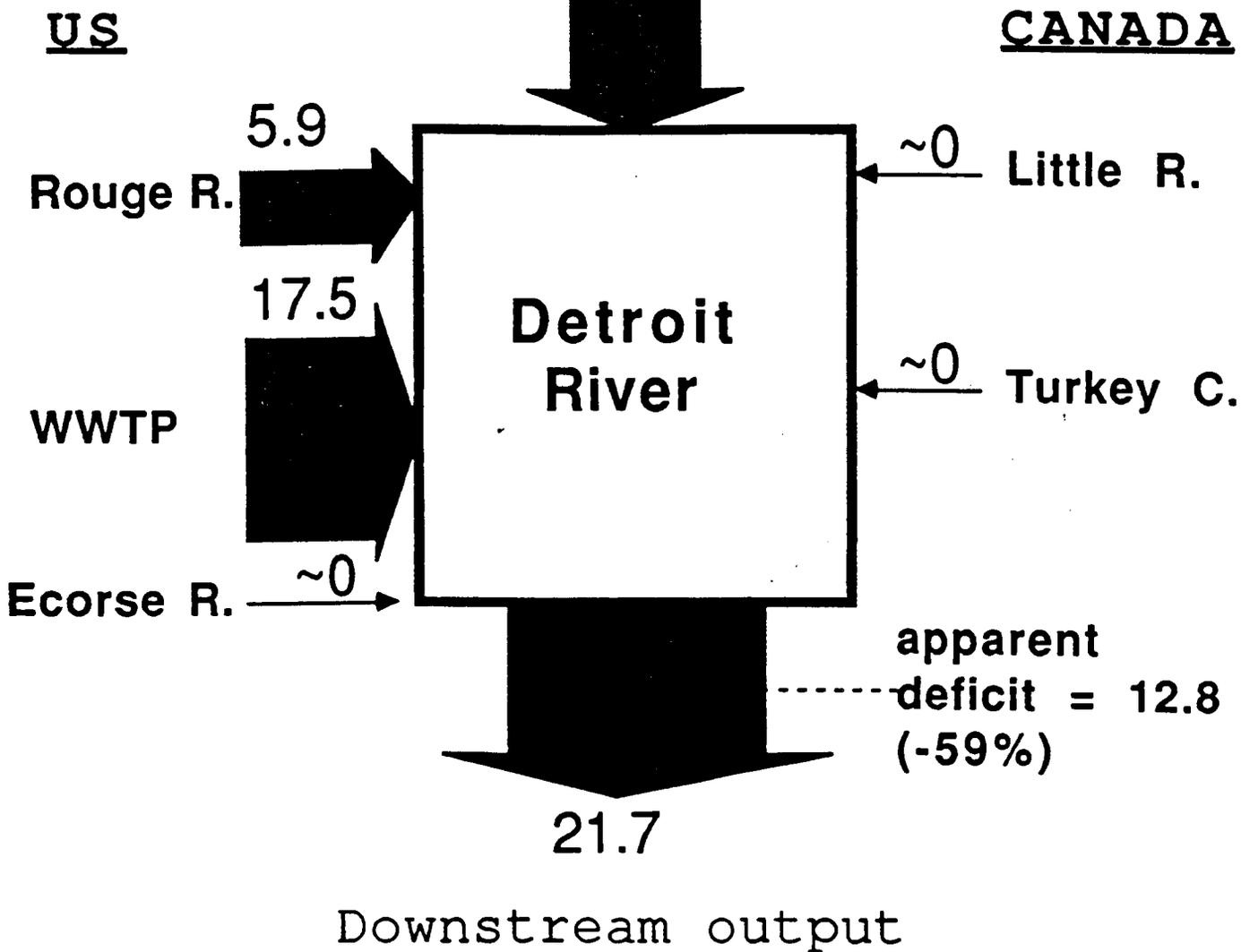
Lake St. Clair average phosphorus loads and losses during the 1975-'80 period (metric tonnes per year)



SMB1 CADMIUM, TOTAL (Kg/d)

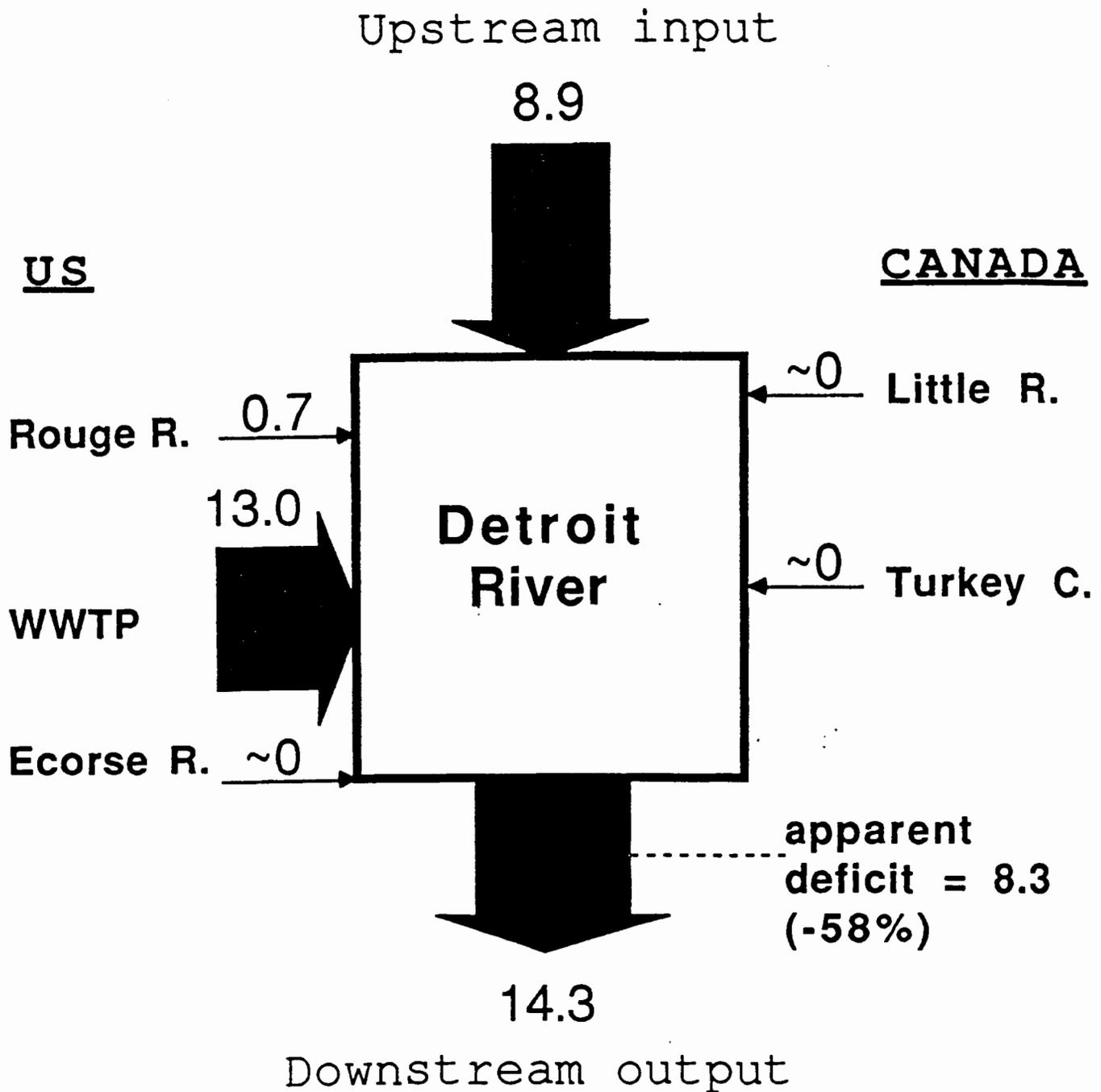
Upstream input

11.1



Area is a statistically significant source of cadmium (10.6 Kg/d), although accumulation may be occurring.

SMB2 CADMIUM, TOTAL (Kg/d)



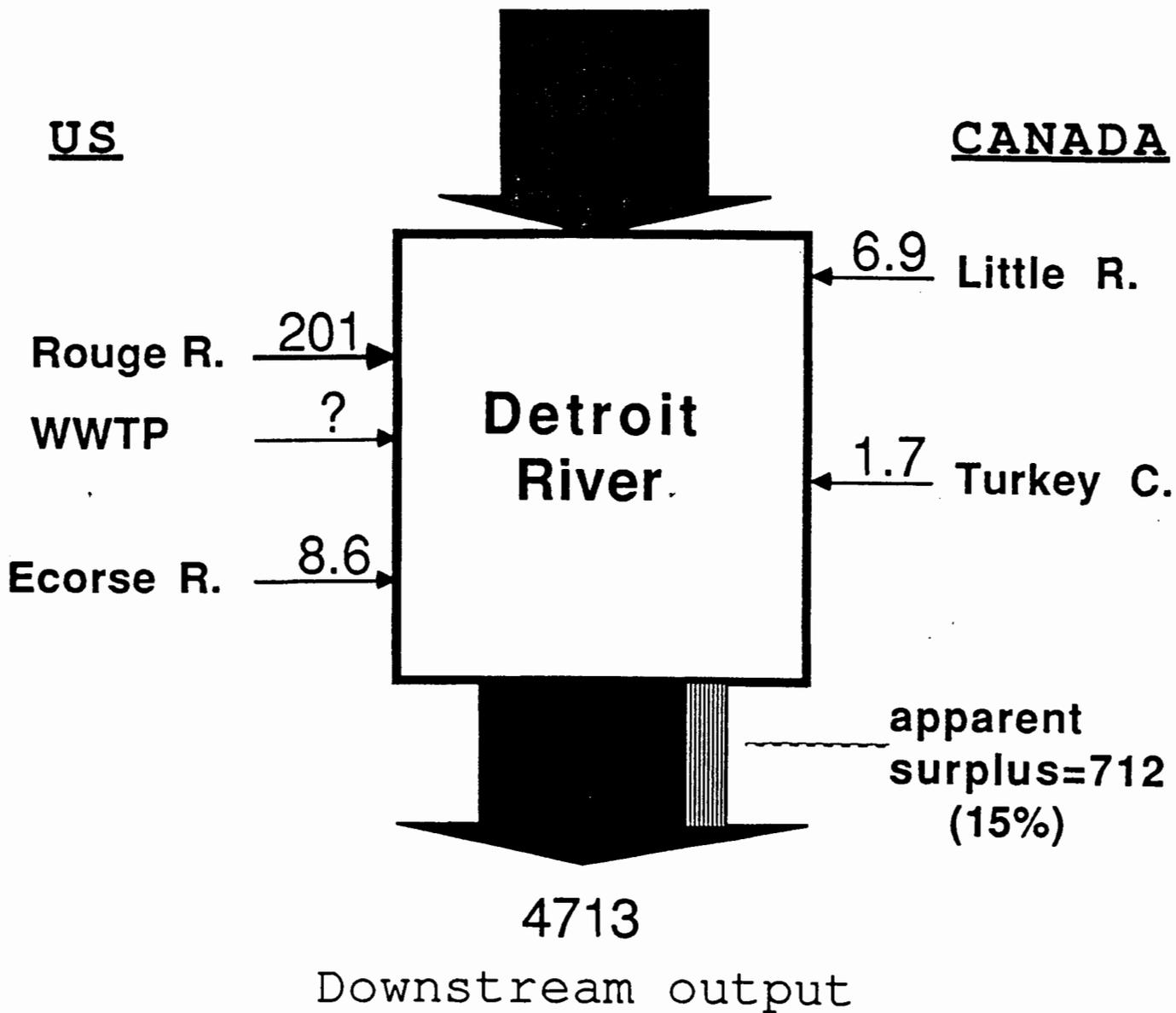
Area is a statistically significant source of cadmium (5.4 Kg/d) although accumulation may be occurring.

SMB1 CHLORIDE, FILTERED (mt/d)

Upstream input
3784

US

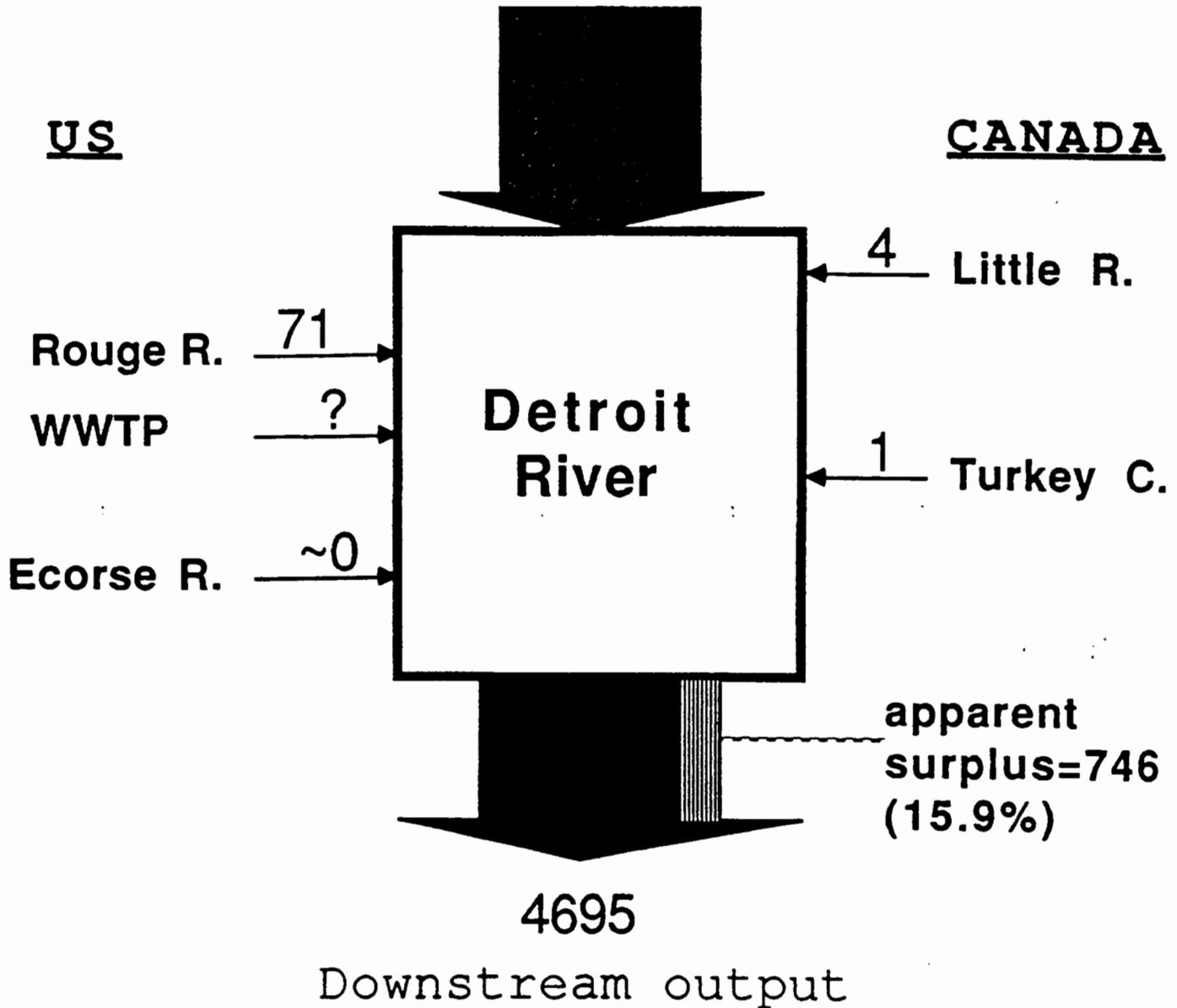
CANADA



Area is a statistically significant source of chloride (929 MT/d).

SMB2 CHLORIDE, FILTERED (mt/d)

Upstream input
3872

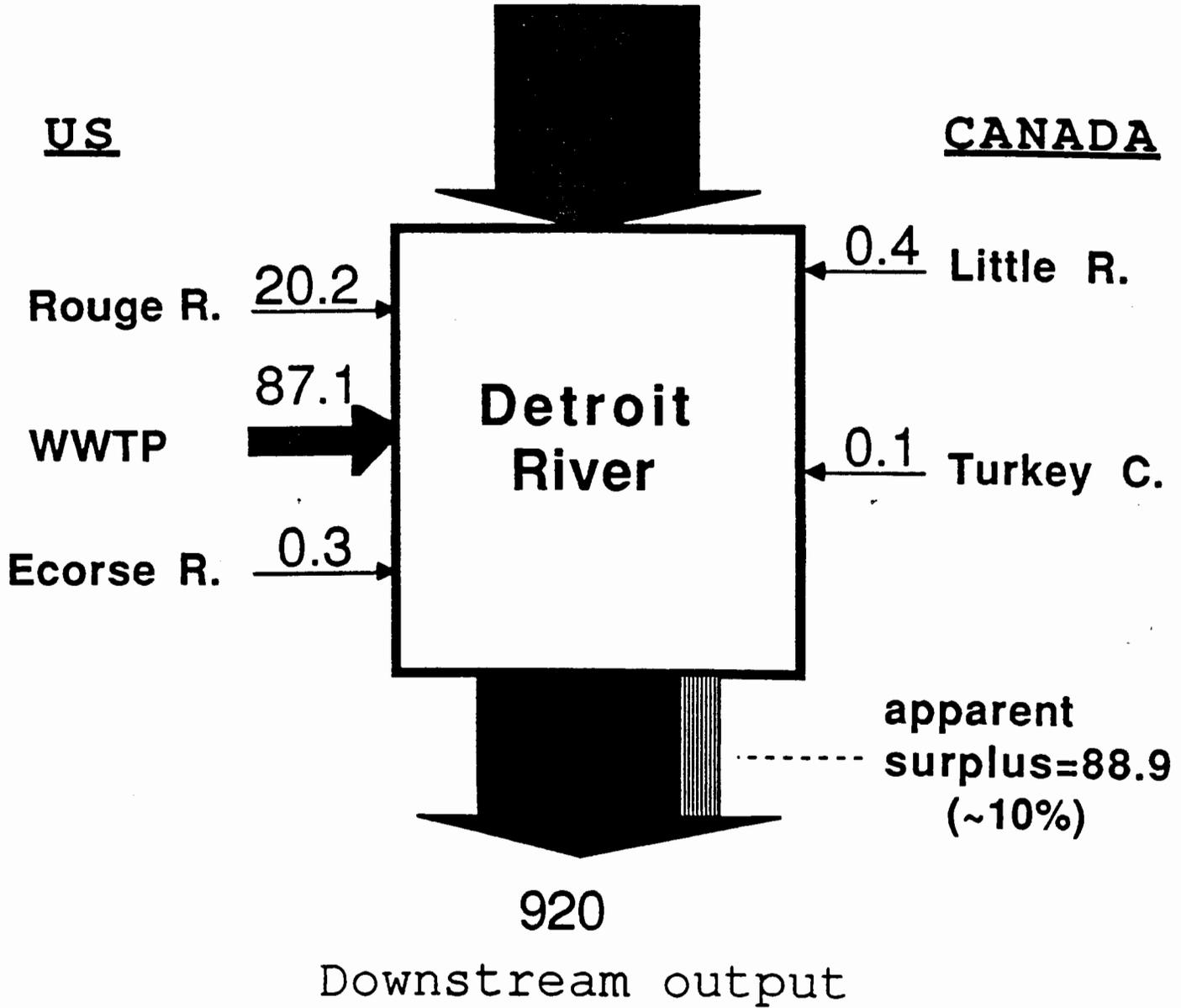


Area is a statistically significant source
(823 MT/d) of chloride.

SMB1 COPPER, TOTAL (Kg/d)

Upstream input

723

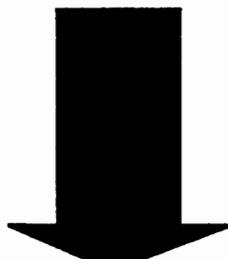


Area is a statistically significant source of copper (197 Kg/d).

SMB1 HCB (Kg/d)

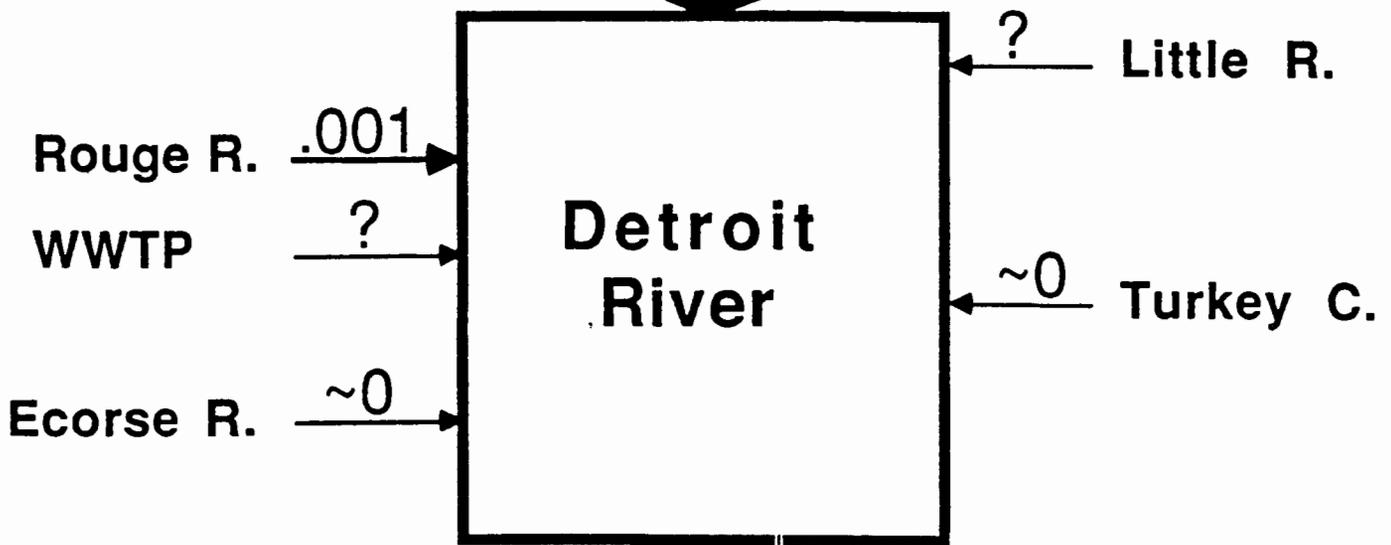
Upstream input

.11



US

CANADA



apparent surplus = $.009$
(7.5%)

.12

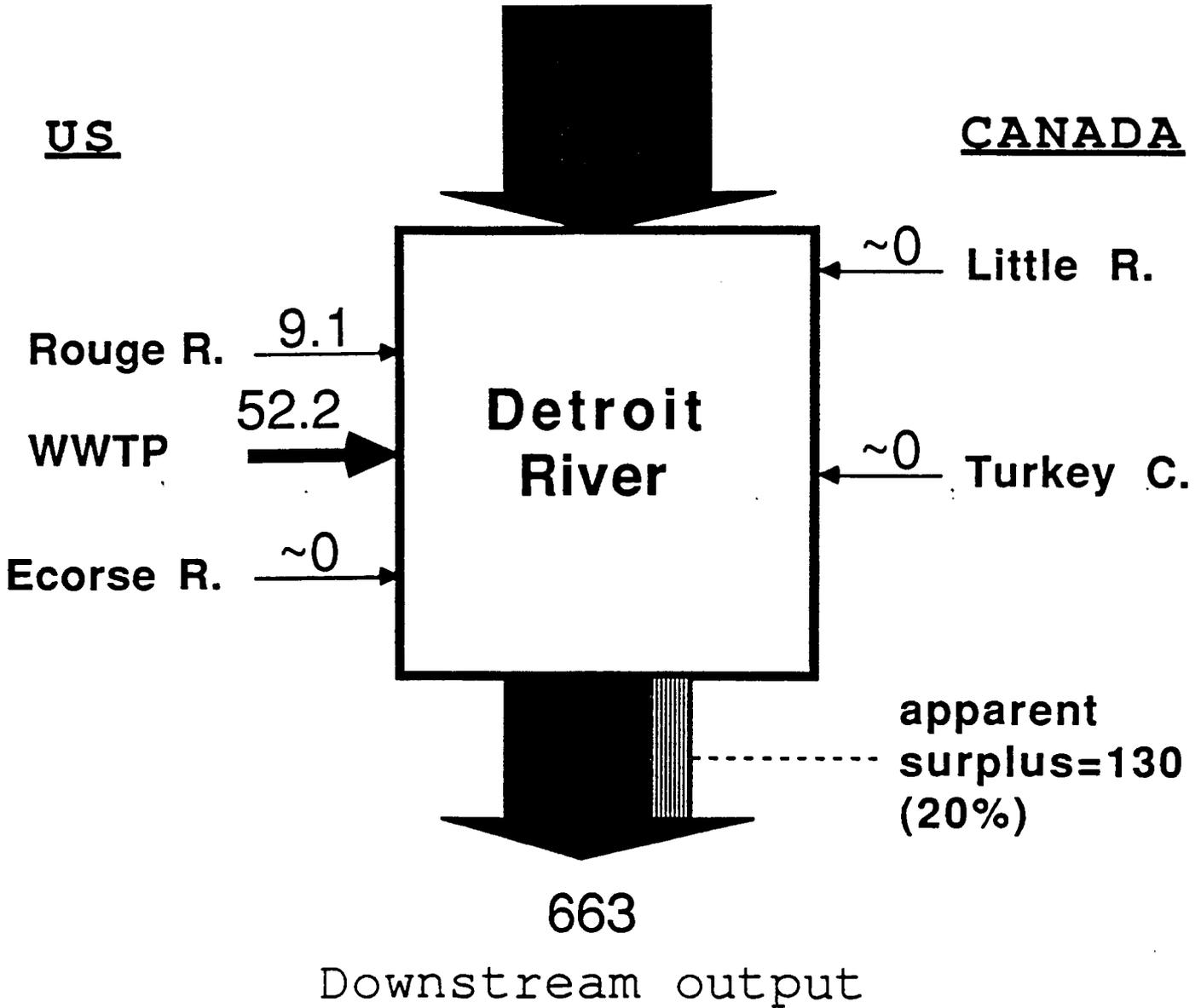
Downstream output

Area is a not a statistically significant source of HCB.

SMB2 COPPER, TOTAL (Kg/d)

Upstream input

472



663

Downstream output

Area is a statistically significant source
(191 Kg/d) of copper.

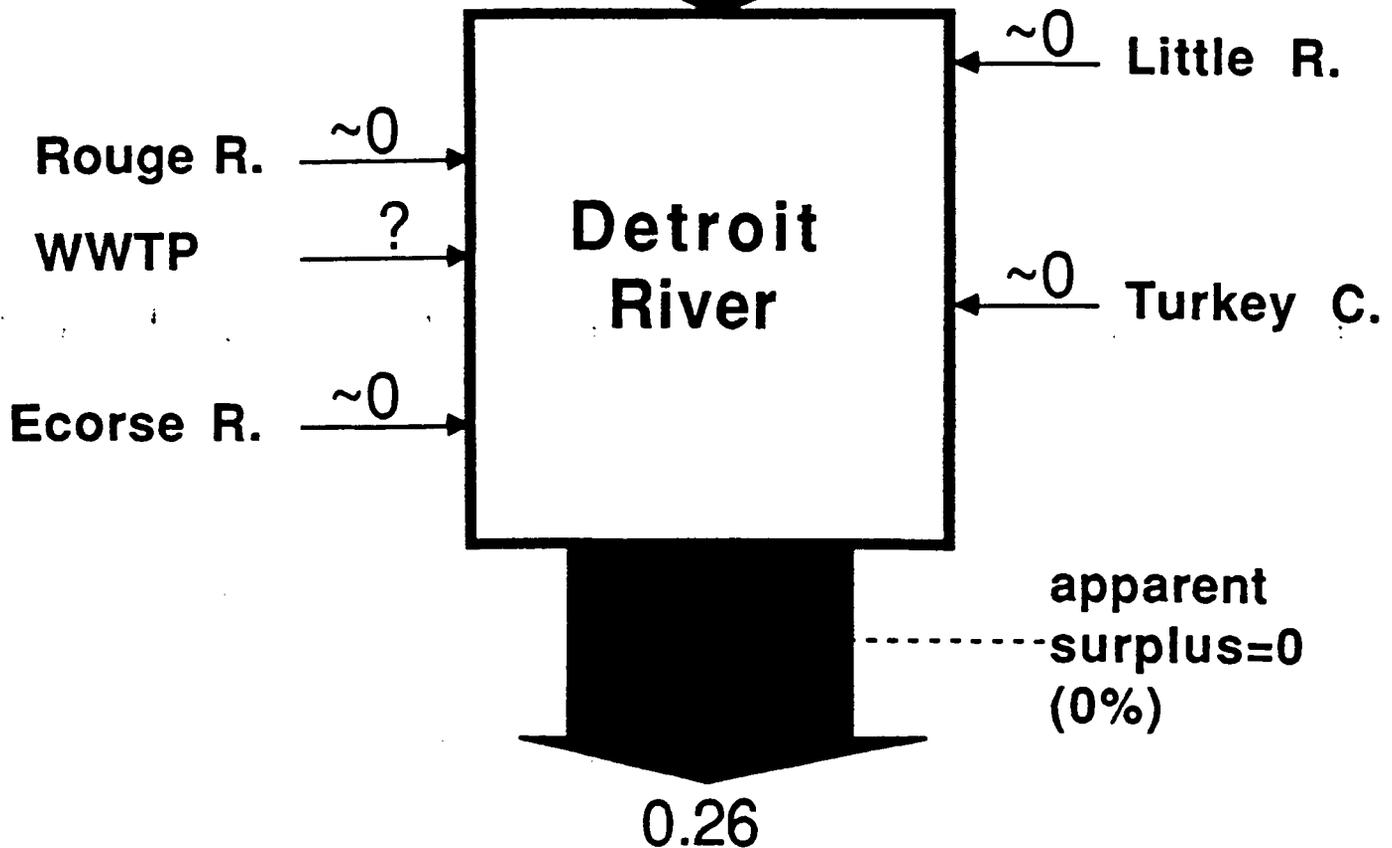
SMB2 HCB (Kg/d)

Upstream input

0.26

US

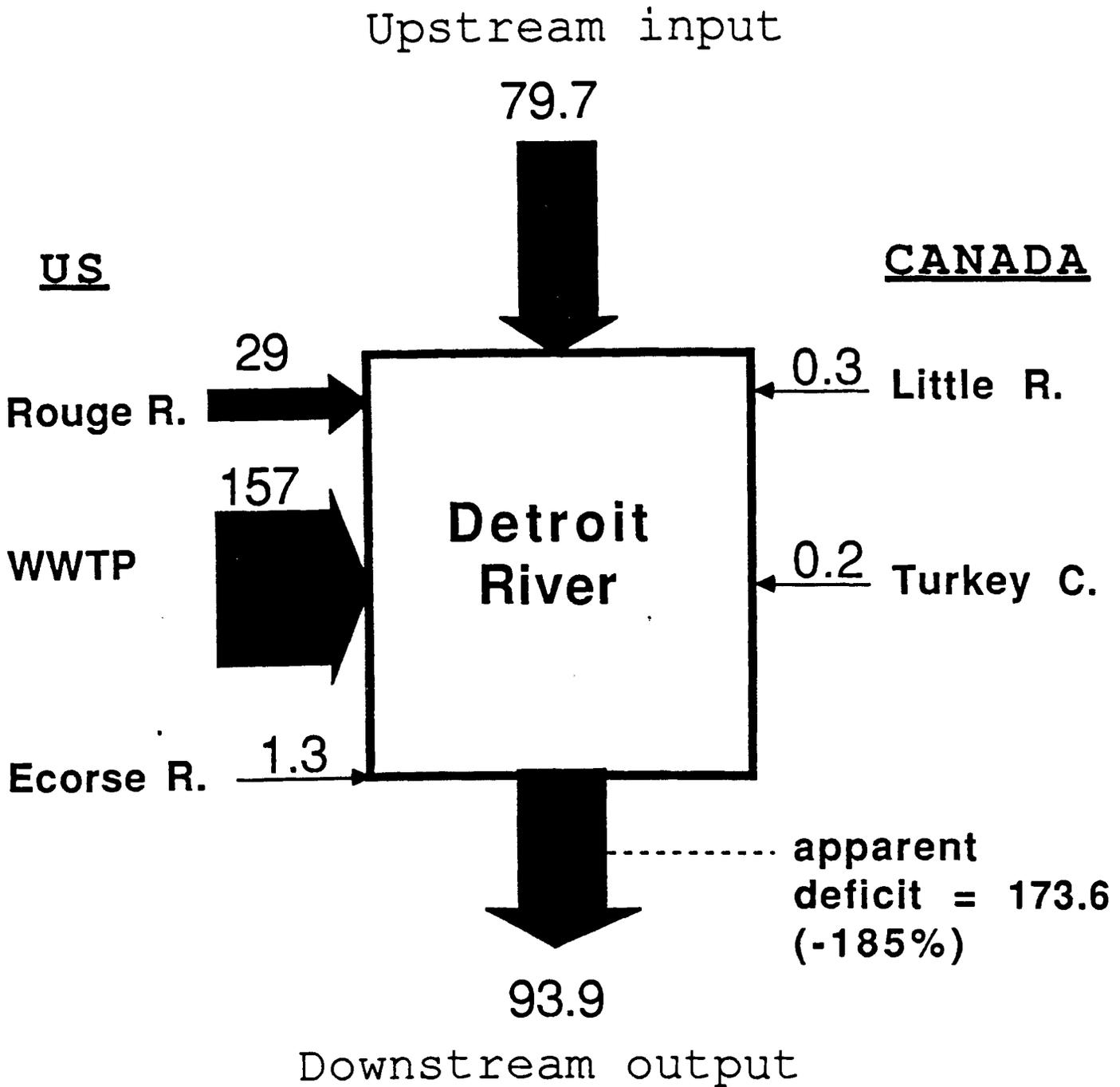
CANADA



Downstream output

Area is a not a statistically significant source of HCB.

SMB1 LEAD, TOTAL (Kg/d)



Area is a statistically significant source of lead (14.2 Kg/d) although accumulation may be occurring.

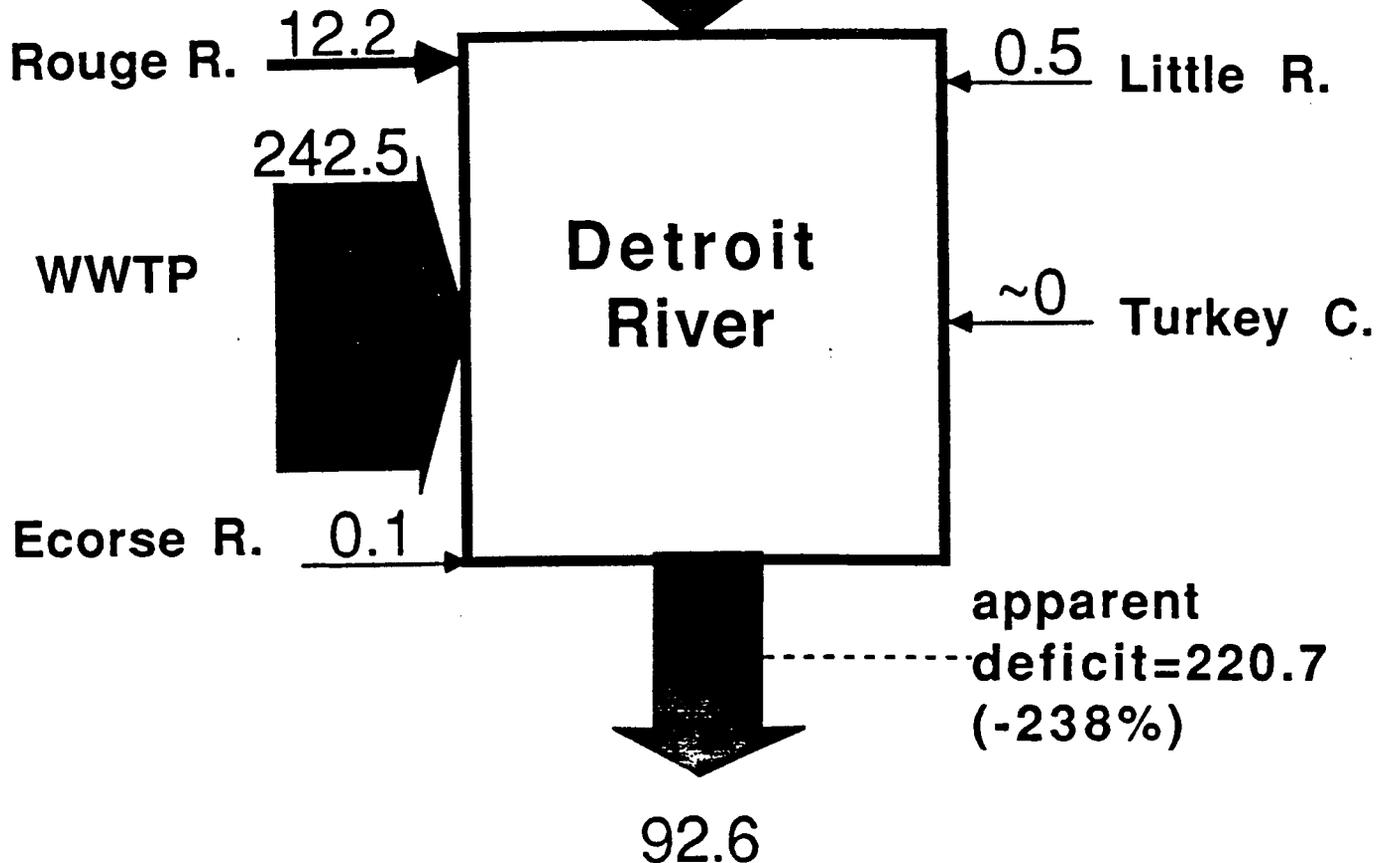
SMB2 LEAD, TOTAL (Kg/d)

Upstream input

58.0

US

CANADA



apparent deficit=220.7 (-238%)

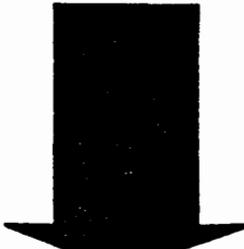
Downstream output

Area is a statistically significant source (34.6 Kg/d) of lead although accumulation may be occurring.

SMB1 MERCURY, TOTAL (Kg/d)

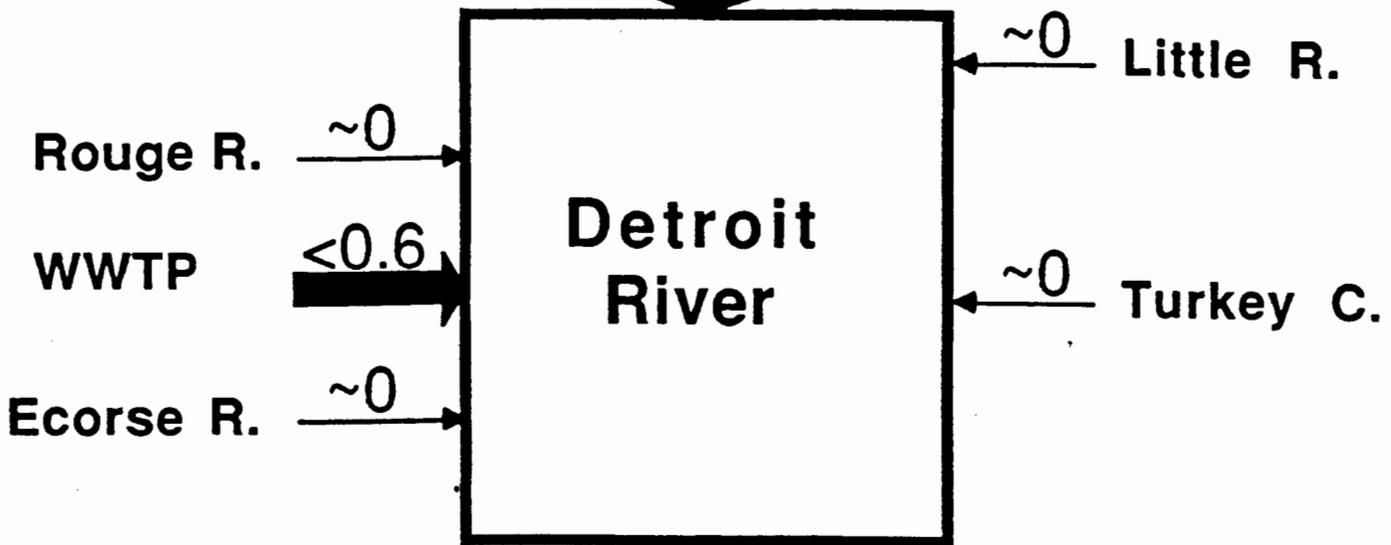
Upstream input

4.7



US

CANADA



apparent deficit = 0.5 (-10%)

4.8

Downstream output

Area is not a statistically significant source of mercury; accumulation may be occurring.

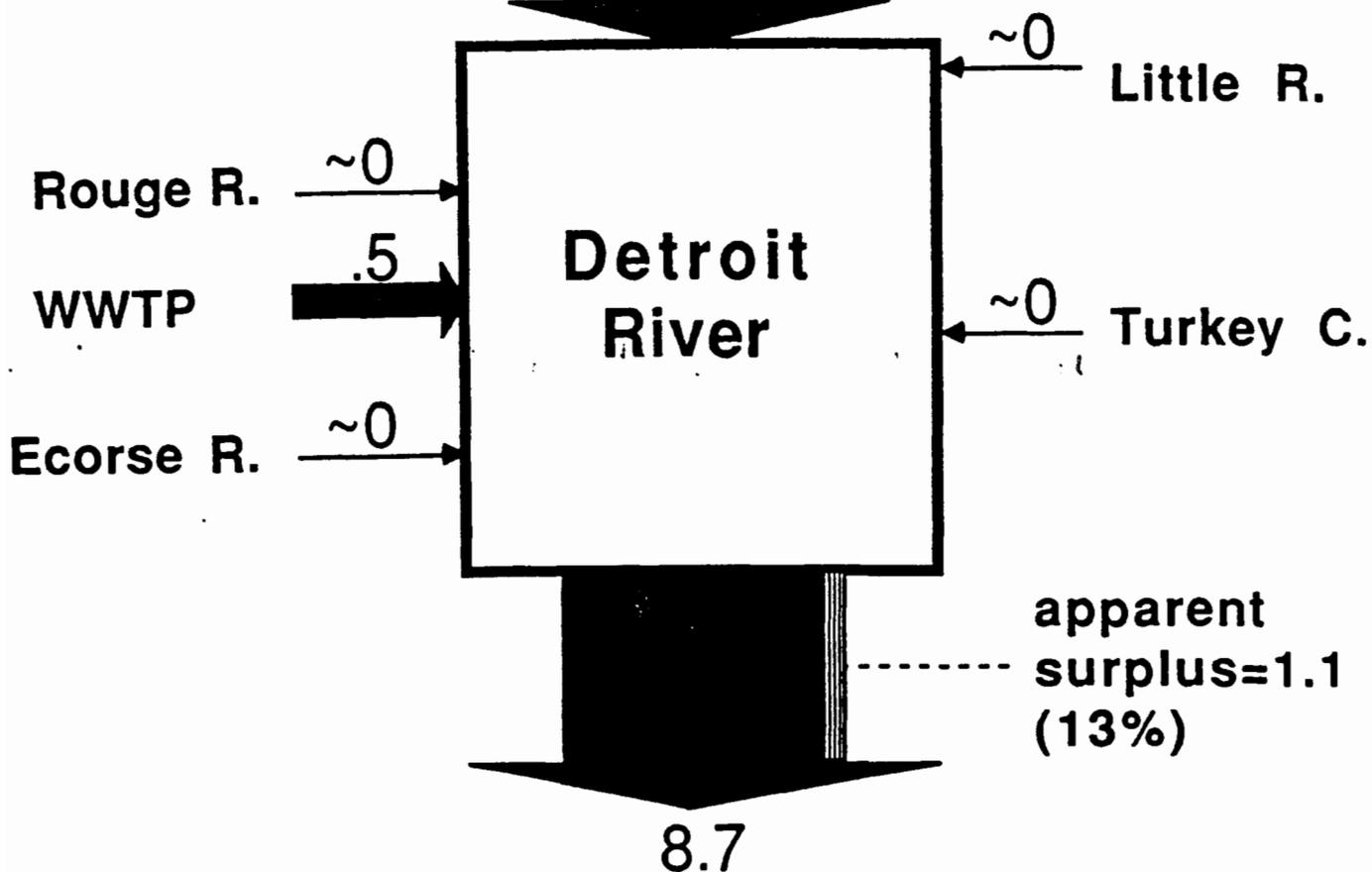
SMB2 MERCURY, TOTAL (Kg/d)

Upstream input

7.1

US

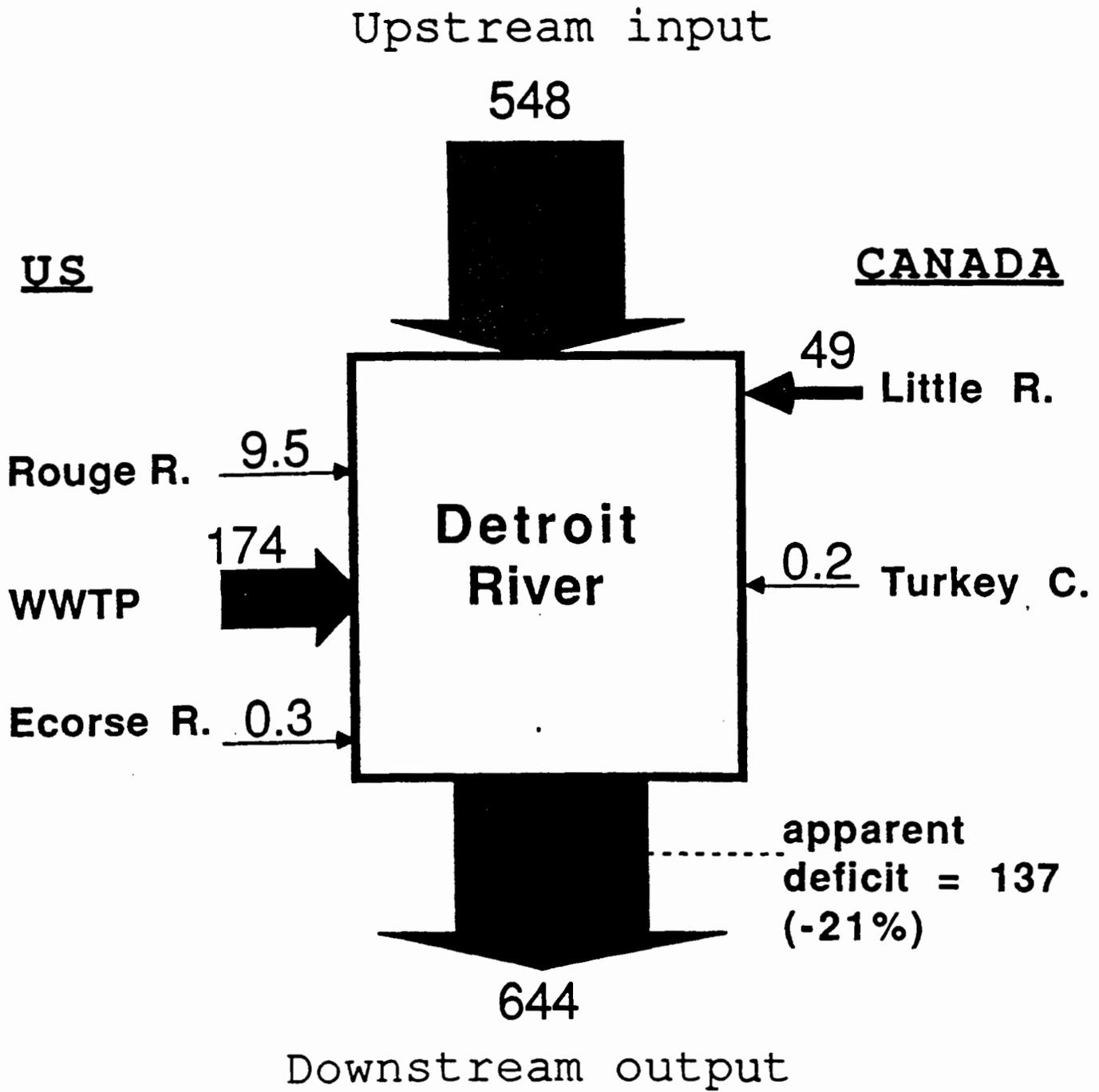
CANADA



Downstream output

Area is a statistically significant source
(1.6 Kg/d) of mercury.

SMB1 NICKEL, TOTAL (Kg/d)



Area is a statistically significant source of nickel (96 Kg/d) although accumulation may be occurring.

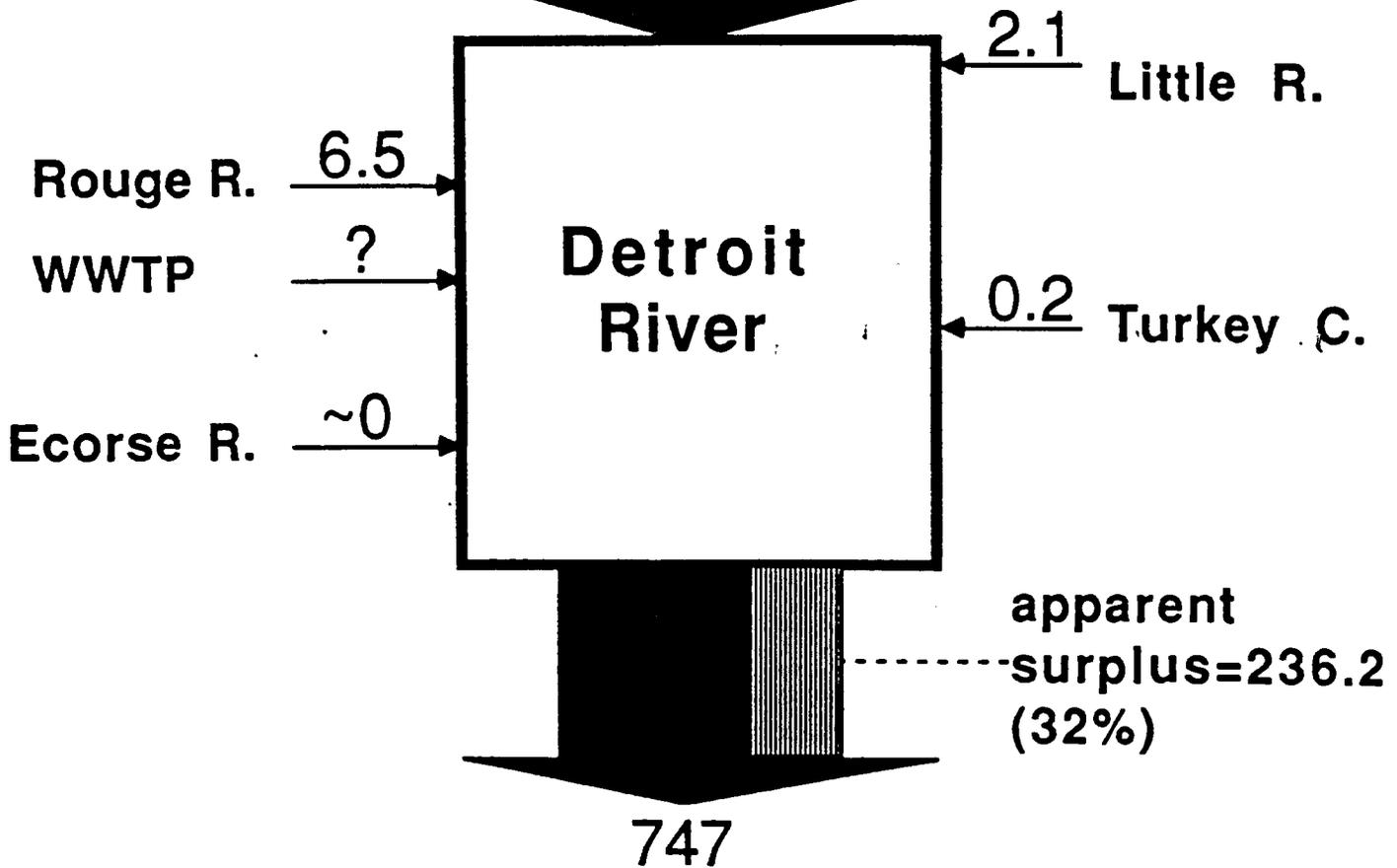
SMB2 NICKEL, TOTAL (Kg/d)

Upstream input

502

US

CANADA



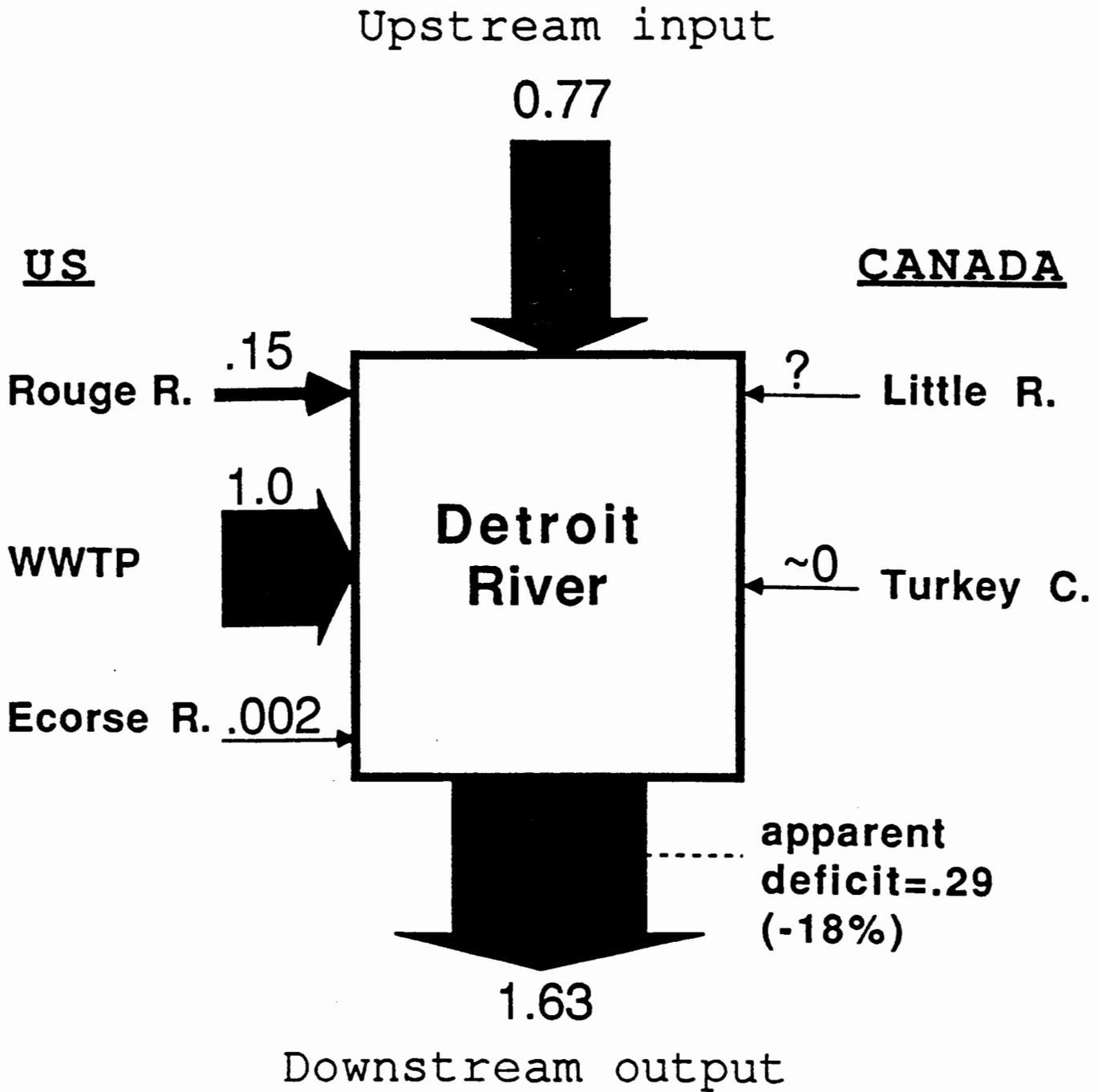
Downstream output

747

apparent
surplus=236.2
(32%)

Area is a statistically significant source
(245 Kg/d) of nickel.

SMB1 PCB, TOTAL (Kg/d)



Area is a statistically significant source of PCB (.86 Kg/d) although accumulation may be occurring.

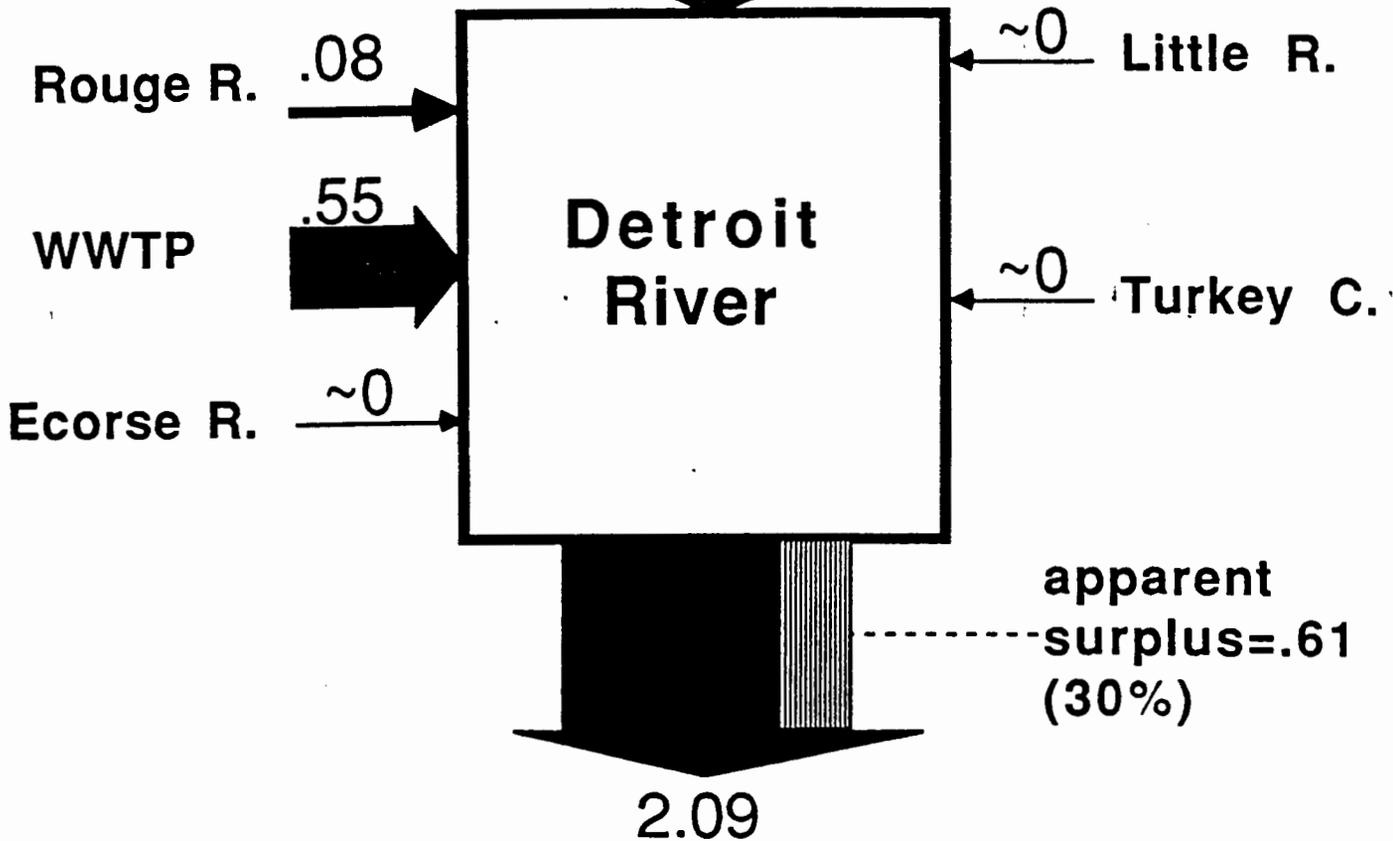
SMB2 PCB, TOTAL (Kg/d)

Upstream input

.85

US

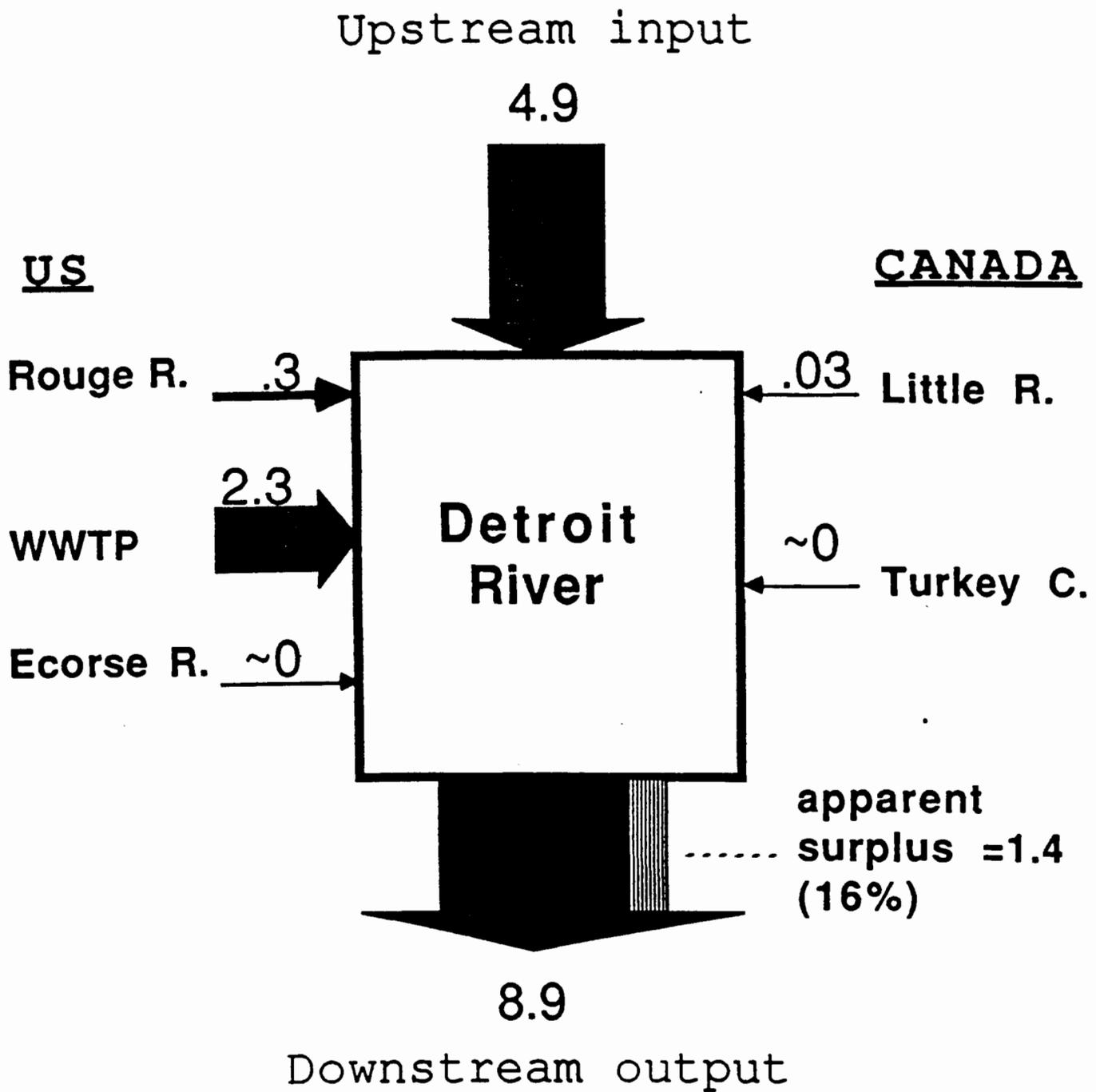
CANADA



Downstream output

Area is a statistically significant source
(1.24 Kg/d) of PCB.

SMB1 PHOSPHORUS, TOTAL (mt/d)

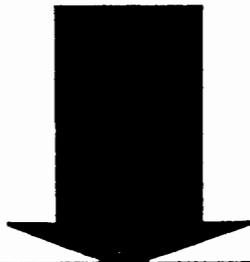


Area is a statistically significant source (4 MT/d) of total phosphorus.

SMB2 PHOSPHORUS, TOTAL (mt/d)

Upstream input

4.4



US

CANADA

Rouge R.

0.2



1.3



WWTP

~0



Ecorse R.

~0



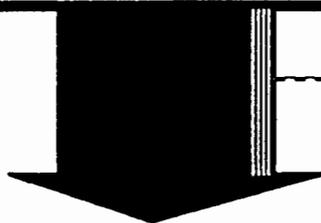
Little R.

~0



Turkey C.

Detroit River



apparent surplus=0.6 (9%)

6.5

Downstream output

Area is a statistically significant source (2.1 MT/d) of total phosphorus.

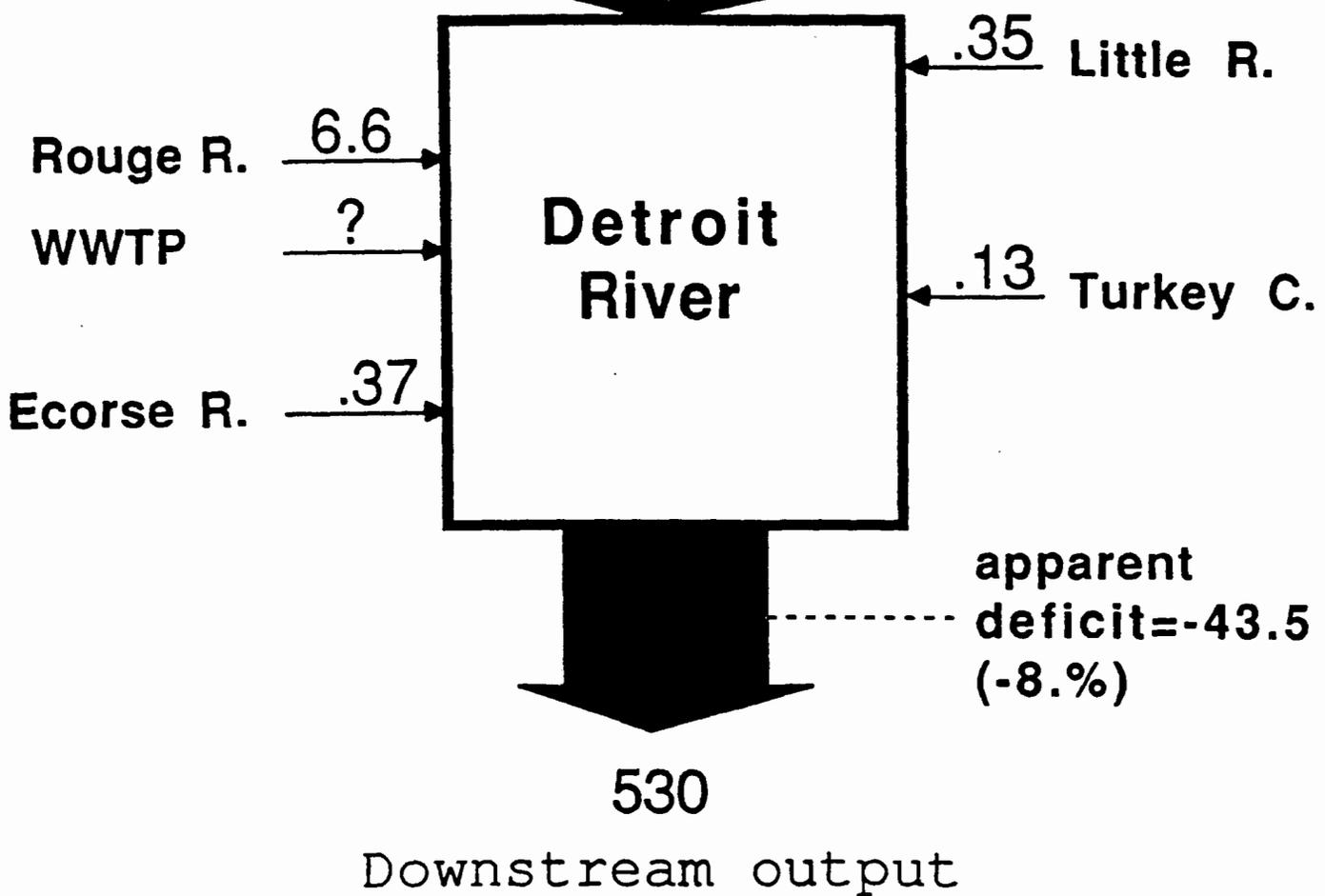
SMB1 SILICA FILTERED (mt/d)

Upstream input

565

US

CANADA

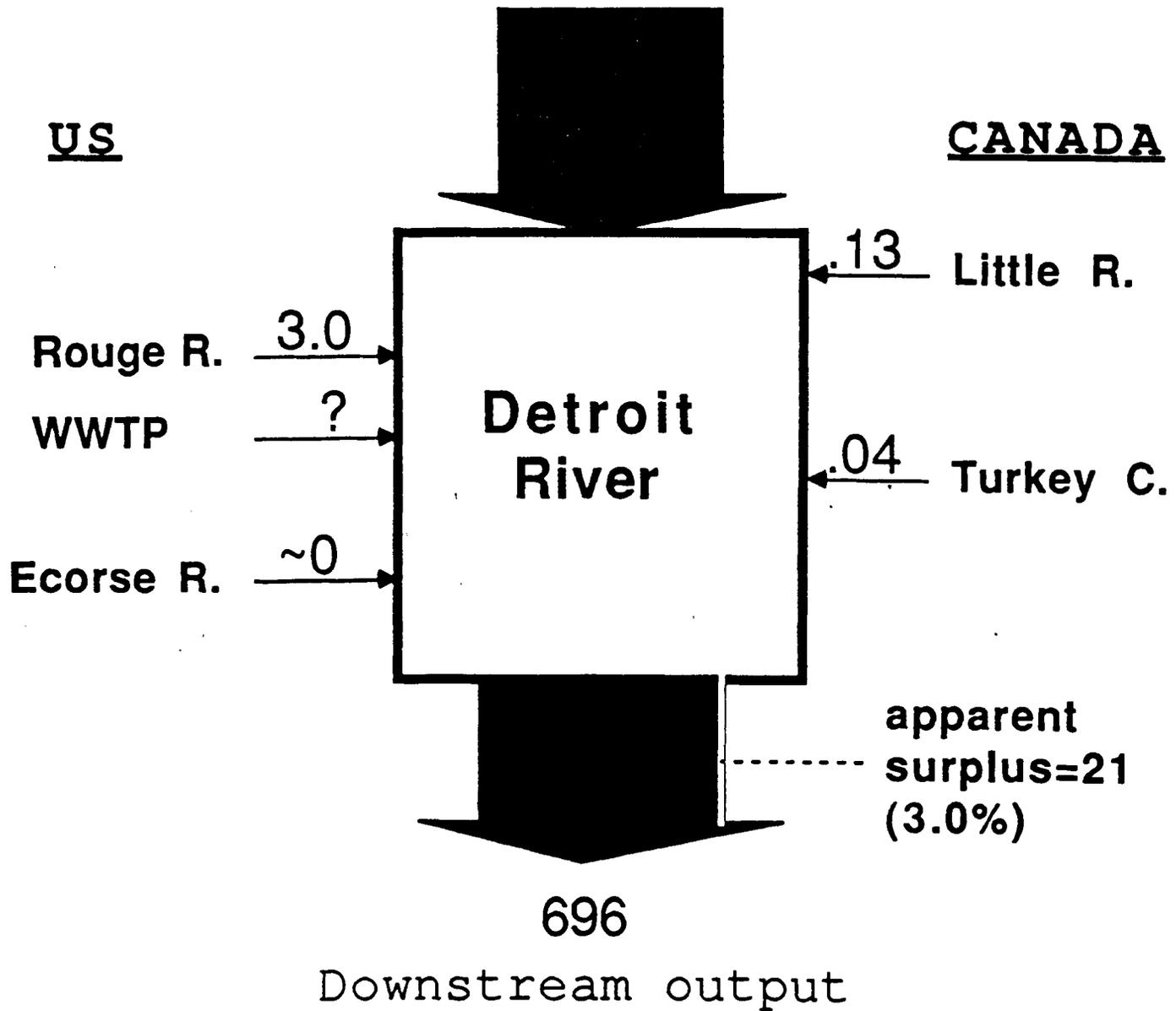


Area is a statistically significant sink
(35 MT/d) of silica.

SMB2 SILICA, FILTERED (mt/d)

Upstream input

672



Area is a statistically significant source (24 MT/d) of silica.

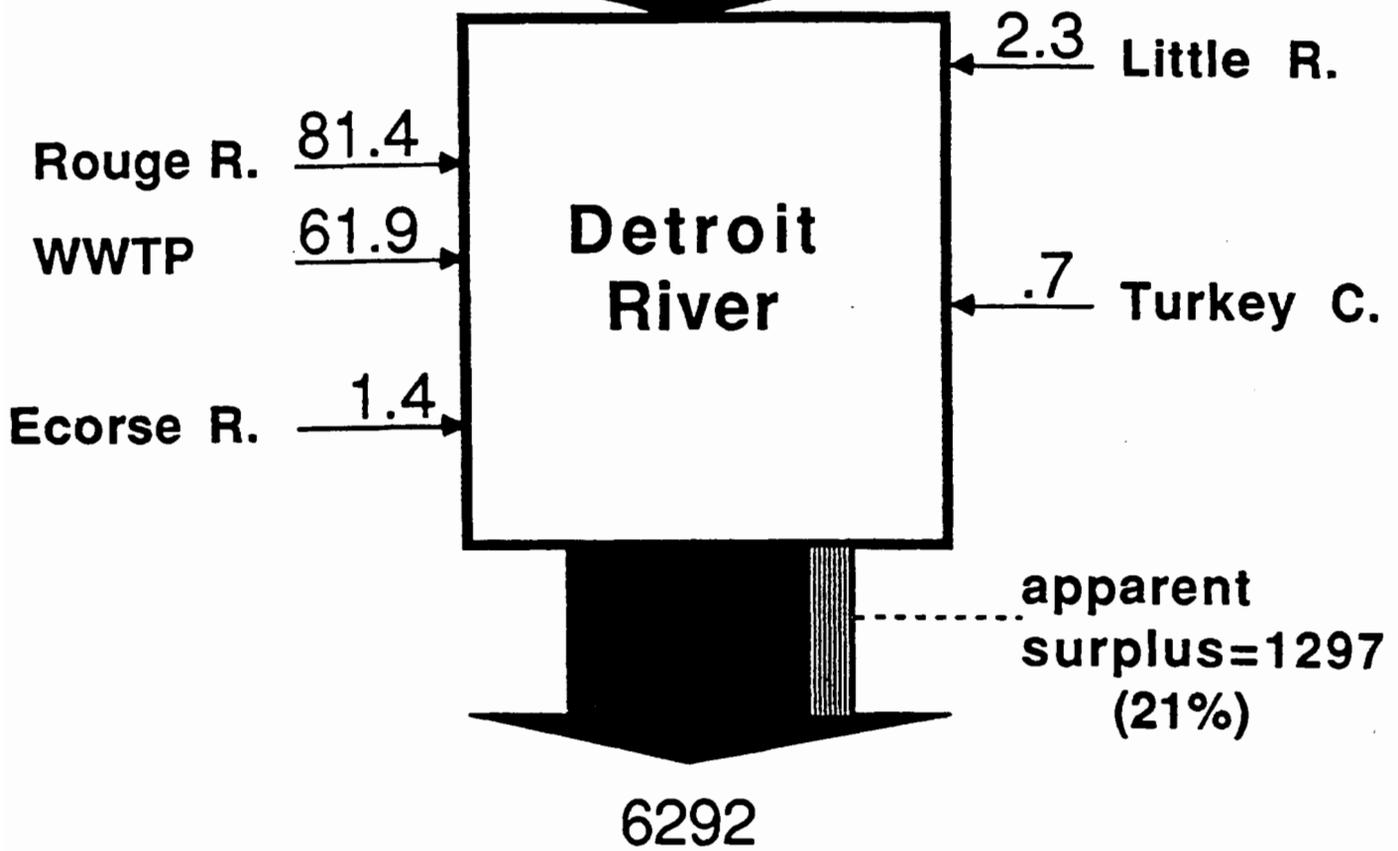
SMB 1 - SUSPENDED SOLIDS (mt/d)

Upstream input

4847

US

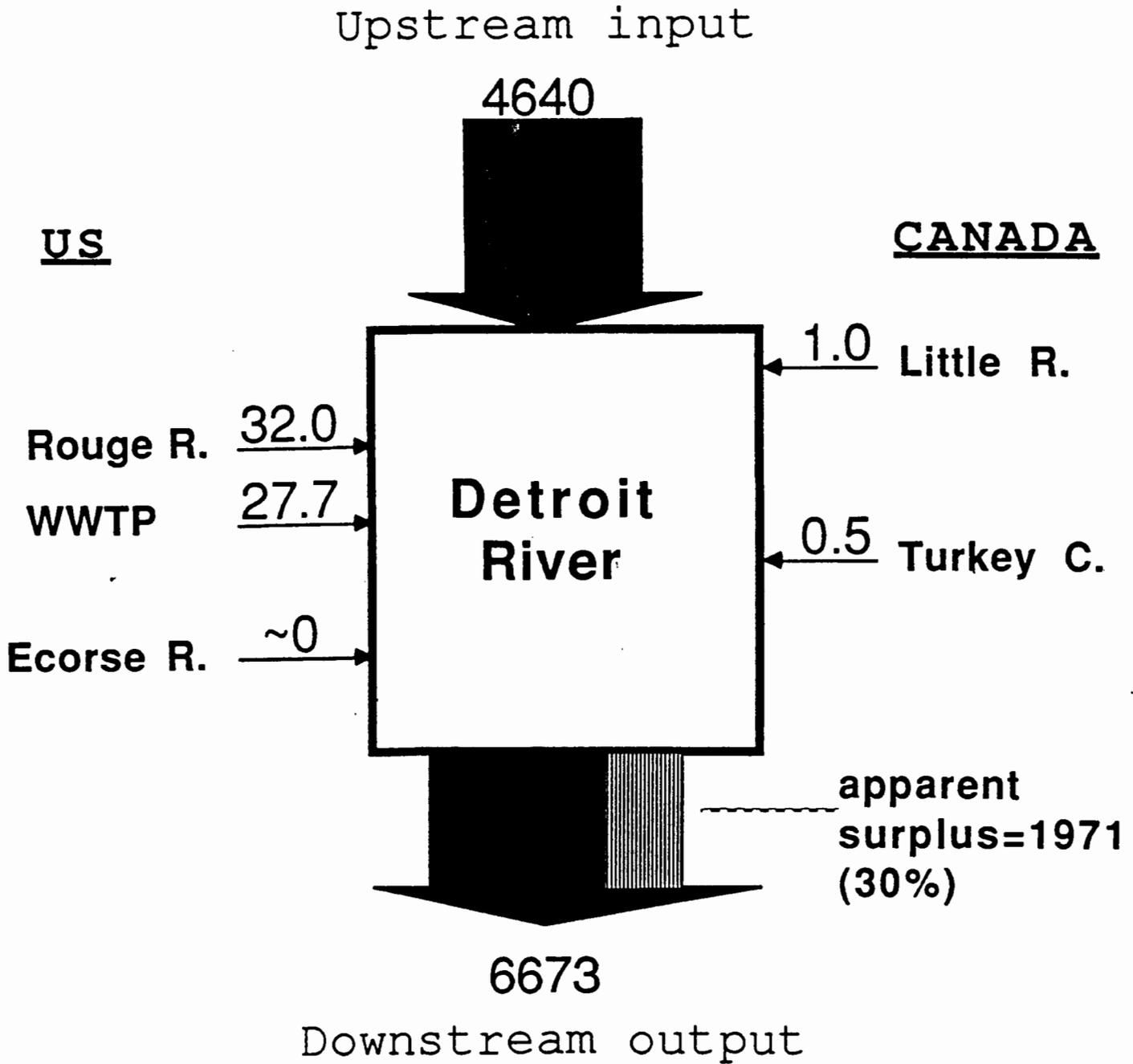
CANADA



Downstream output

Area is a statistically significant source (1445 MT/d) of suspended solids.

SMB 2 - SUSPENDED SOLIDS (mt/d)



Area is a statistically significant source (2033 MT/D) of suspended solids.

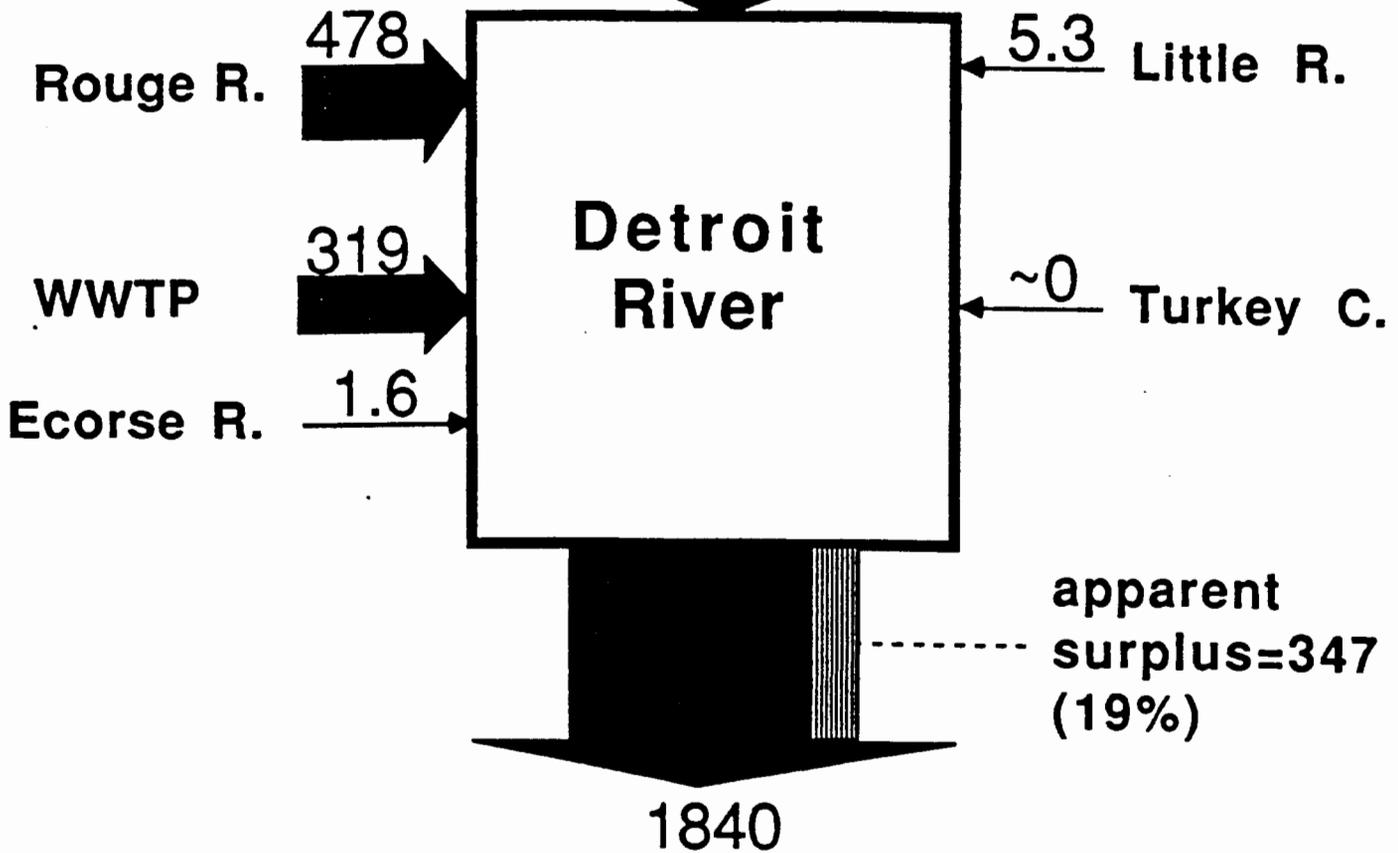
SMB1 ZINC, TOTAL (Kg/d)

Upstream input

689

US

CANADA



apparent
surplus=347
(19%)

Area is a statistically significant source
(1151 Kg/d) of zinc.

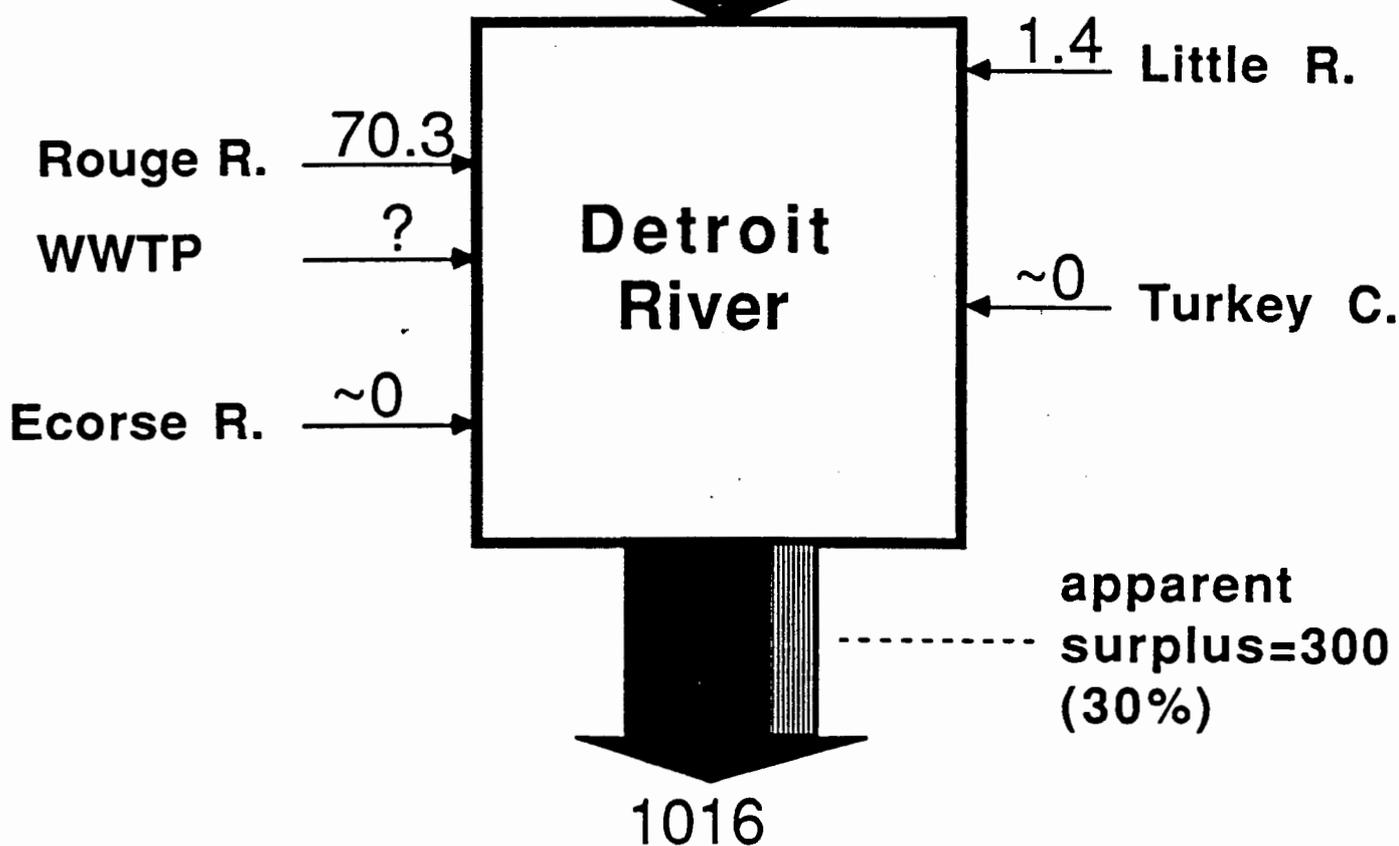
SMB2 ZINC, TOTAL (Kg/d)

Upstream input

644

US

CANADA

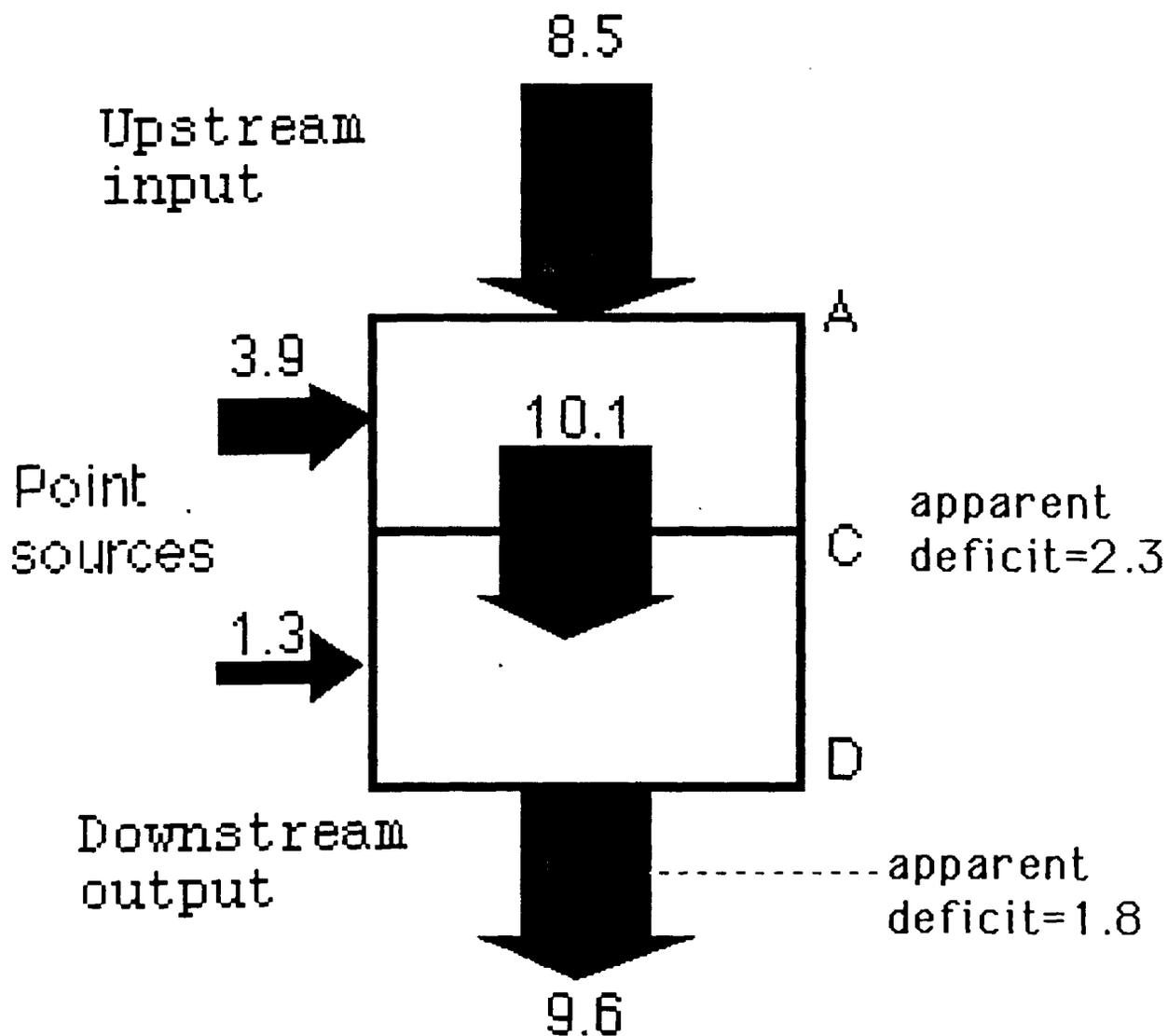


Downstream output

Area is a statistically significant source
(372 Kg/d) of zinc.

TRENTON CHANNEL SURVEY II

Cadmium, Total (Kg/d)

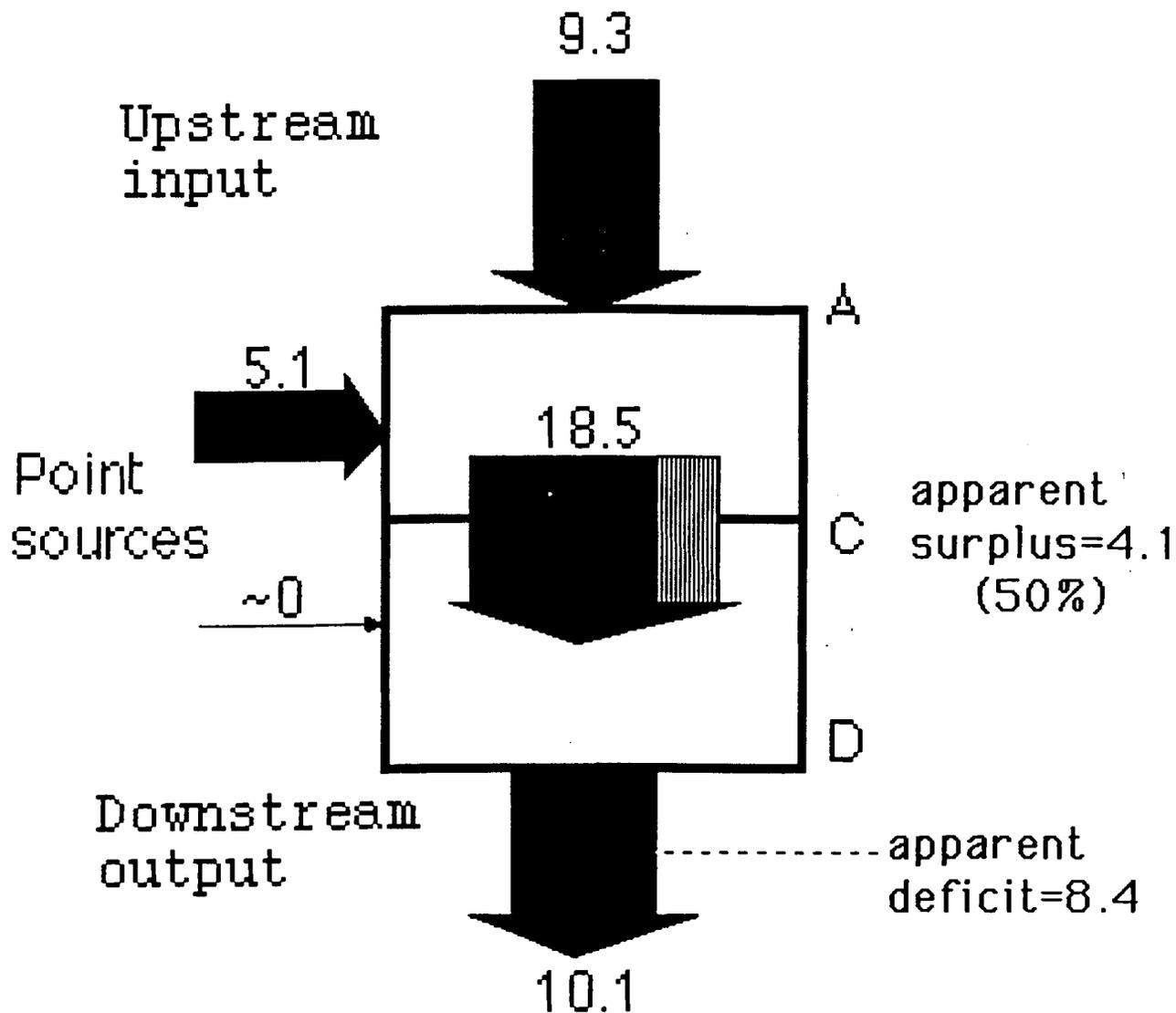


downstream - upstream = 1.1 Kg/d

Entire area is not a statistically significant source of cadmium.

TRENTON CHANNEL SURVEY III

Cadmium, Total (Kg/d)

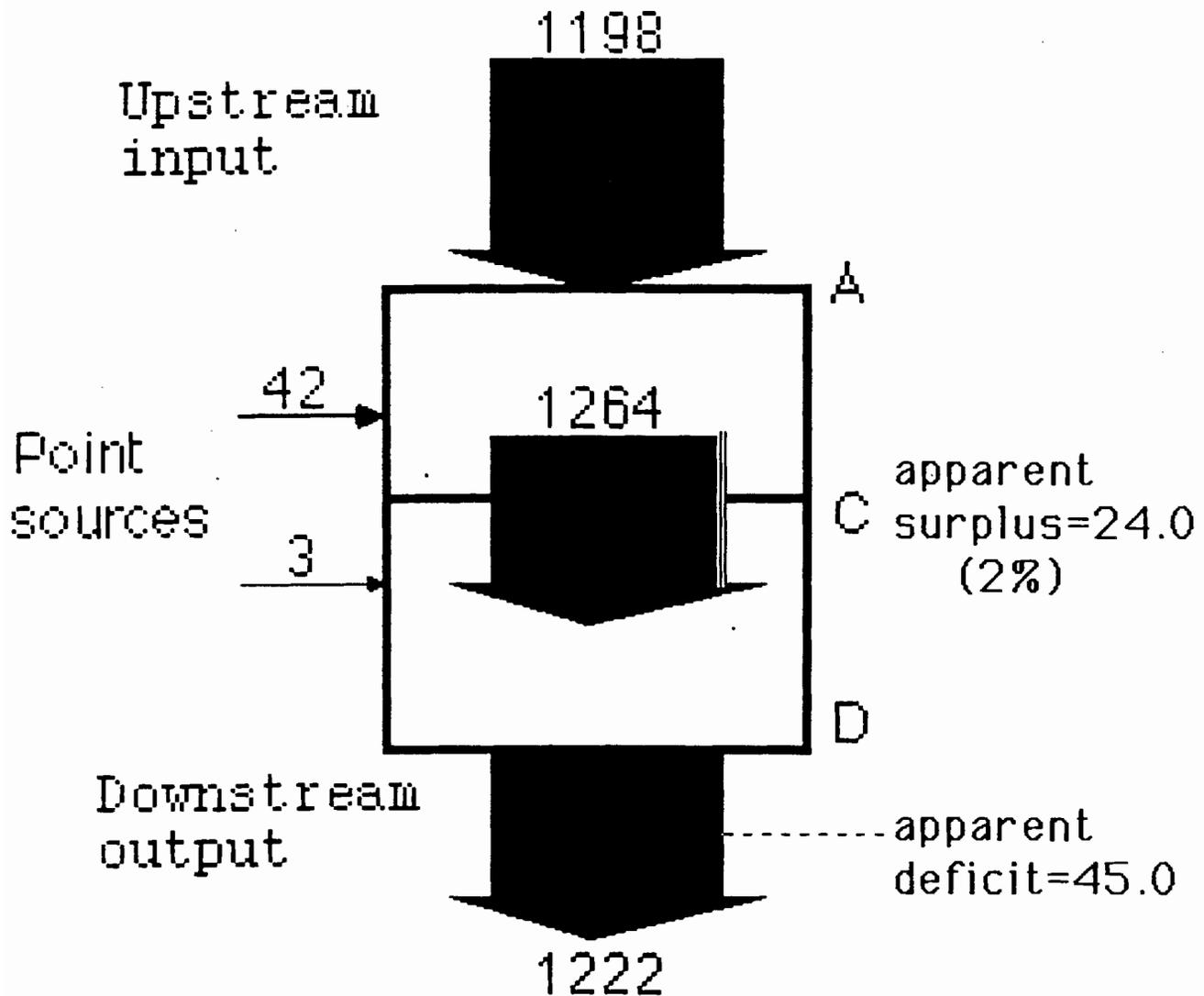


$$\text{downstream} - \text{upstream} = 0.8 \text{ Kg/d}$$

Entire area is not a statistically significant source of cadmium although C-A area is a significant source.

TRENTON CHANNEL SURVEY III

Chloride, Filtered (MT/d)

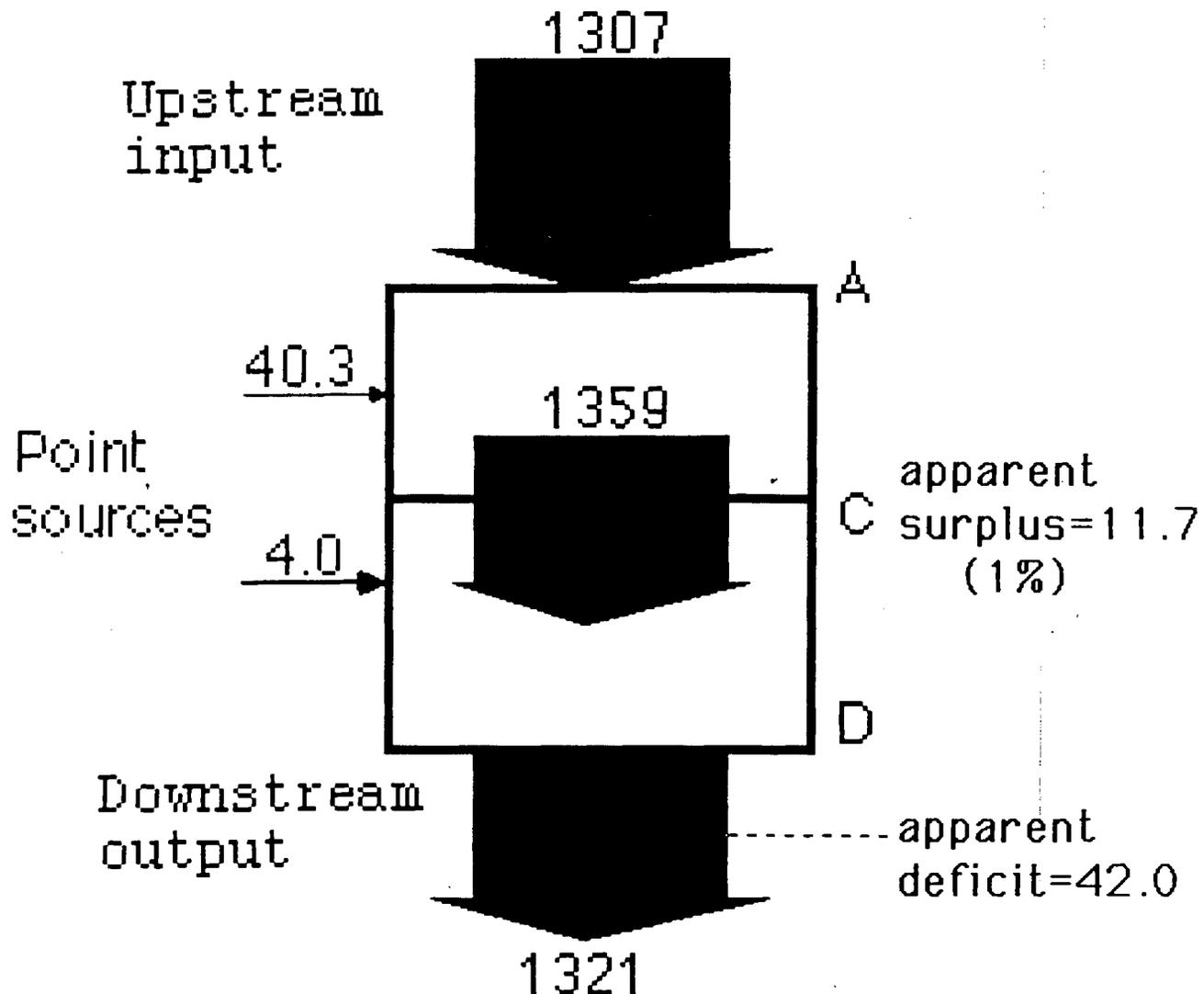


downstream - upstream = 24 MT/d

Entire area is not a statistically significant source of chloride.

TRENTON CHANNEL SURVEY II

Chloride, Filtered (MT/d)

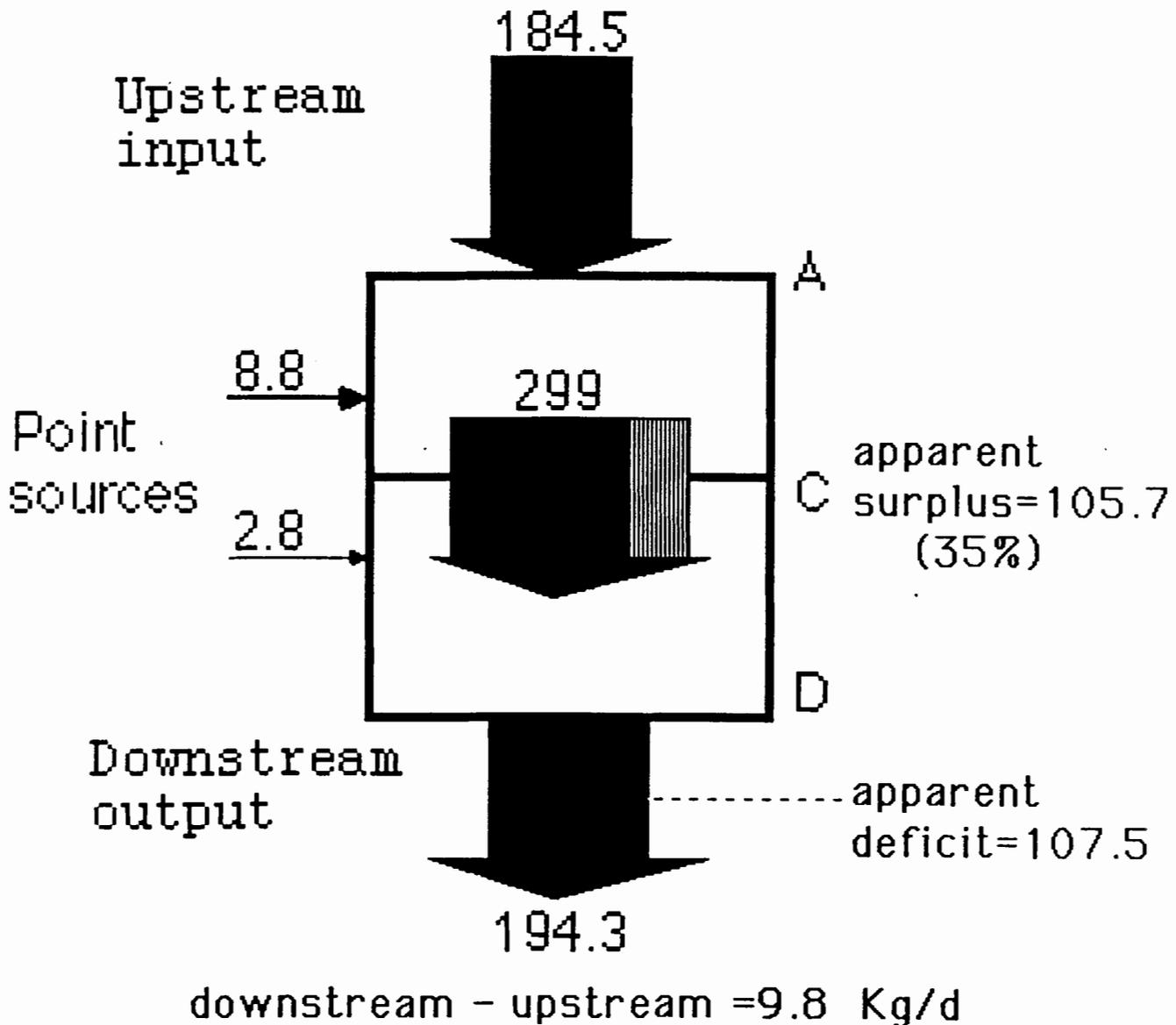


downstream - upstream = 14 MT/d

Entire area is not a statistically significant source of chloride although the C-A area is a significant source.

TRENTON CHANNEL SURVEY II

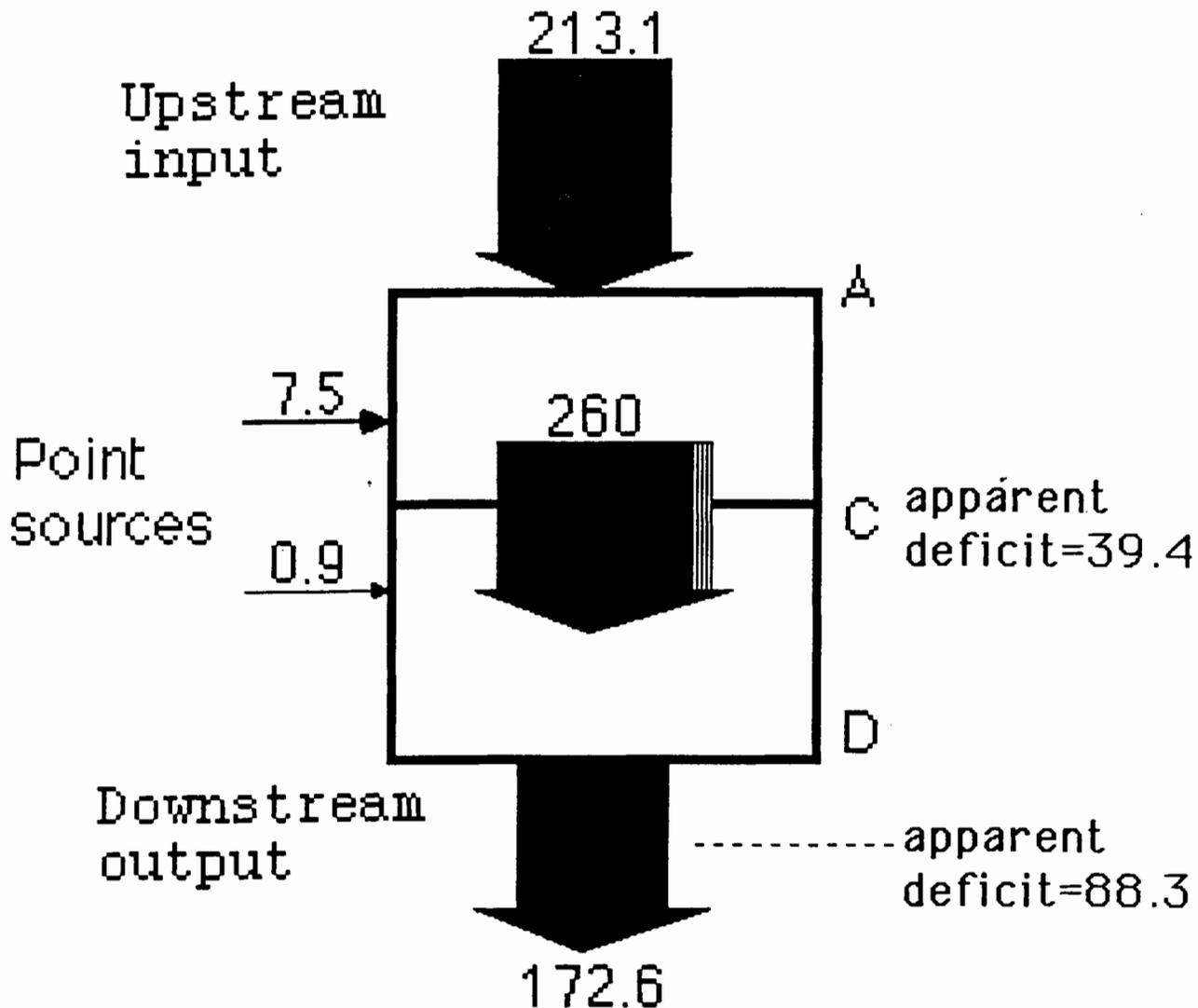
Copper, Total (Kg/d)



Entire area is not a statistically significant source of copper. Significant accumulation occurred in the D-C area.

TRENTON CHANNEL SURVEY III

Copper, Total (Kg/d)

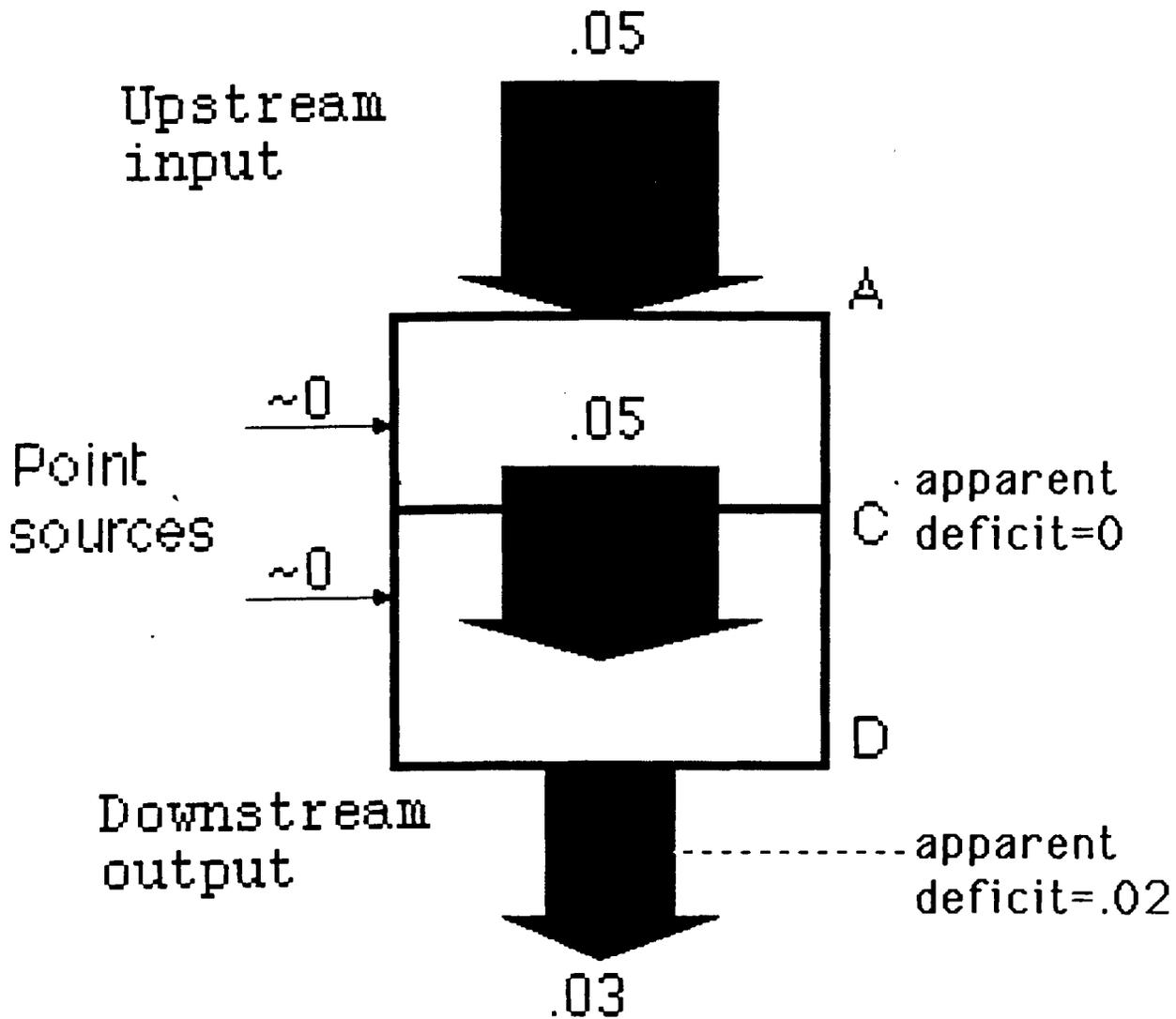


downstream - upstream = 40.5 Kg/d

Entire area is not a statistically significant source of copper. Significant accumulation occurred in the D-C area.

TRENTON CHANNEL SURVEY II

HCB (Kg/d)

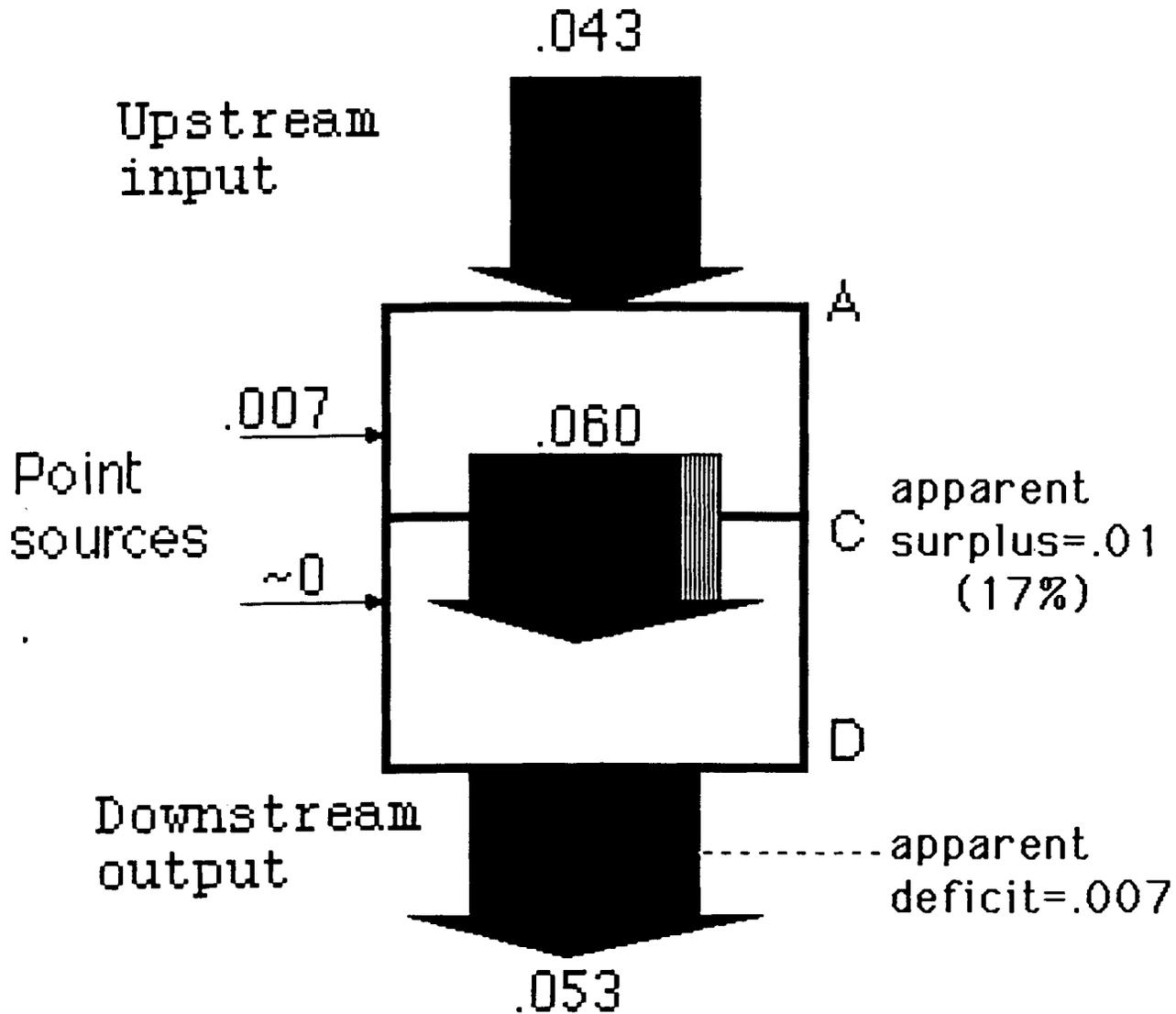


$$\text{downstream} - \text{upstream} = .02 \text{ Kg/d}$$

Entire area is not a statistically significant source of HCB.

TRENTON CHANNEL SURVEY III

HCB (Kg/d)

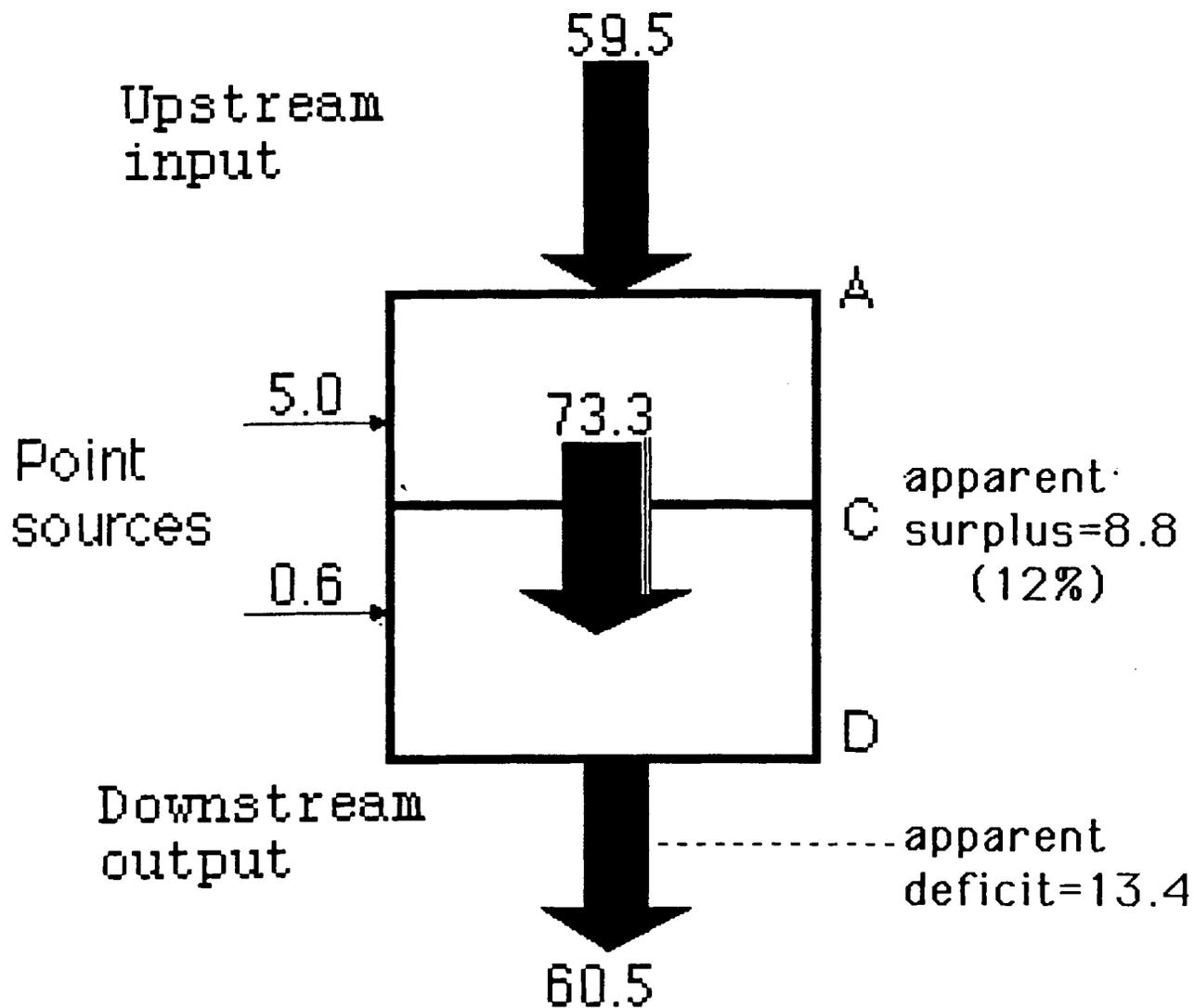


$$\text{downstream} - \text{upstream} = .01 \text{ Kg/d}$$

Entire area is not a statistically significant source of HCB although the C-A area is a significant source.

TRENTON CHANNEL SURVEY II

Lead, Total (Kg/d)

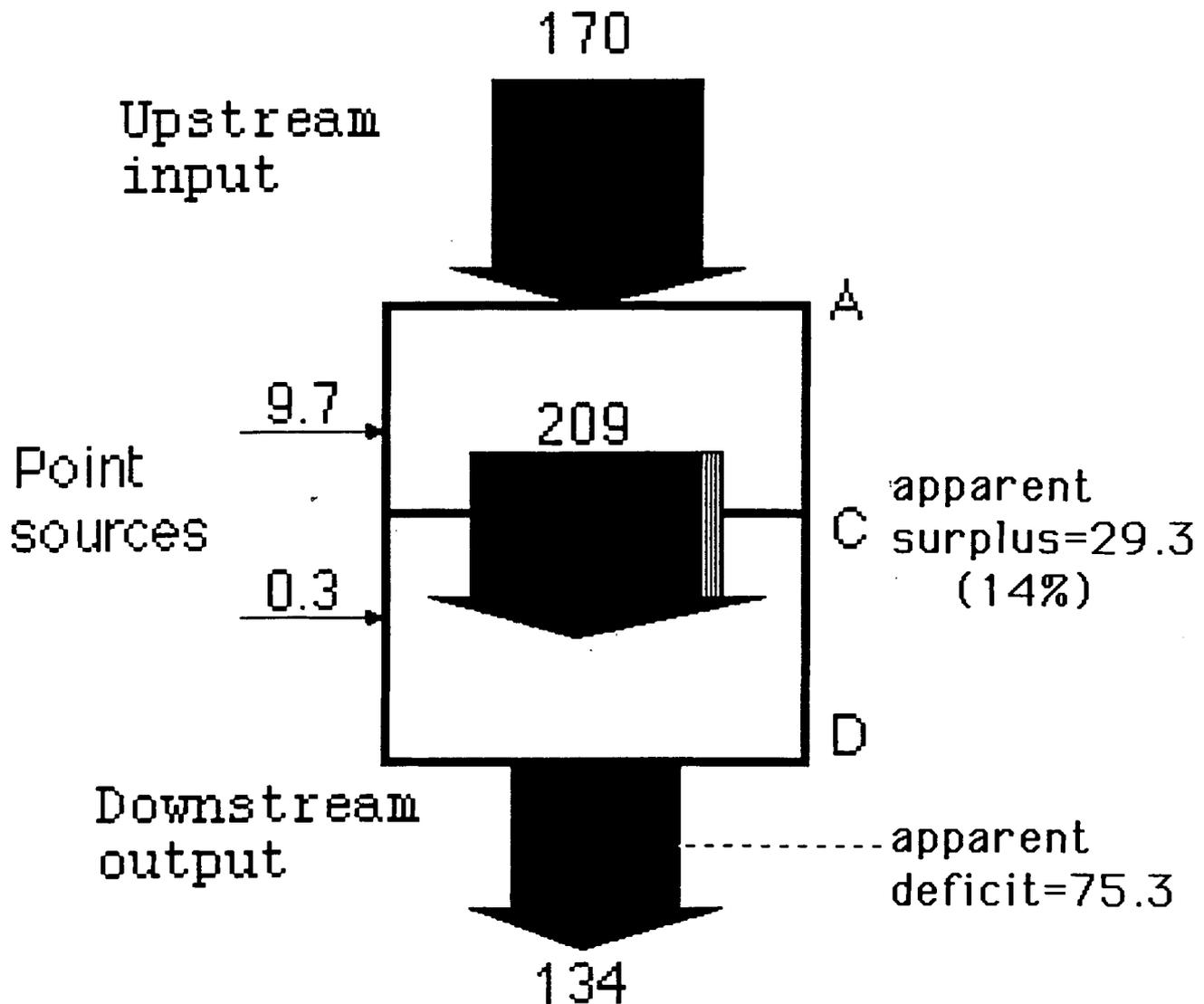


$$\text{downstream} - \text{upstream} = 1.0 \text{ Kg/d}$$

Entire area is not a statistically significant source of lead although the C-A area is a significant source.

TRENTON CHANNEL SURVEY III

Lead, Total (Kg/d)

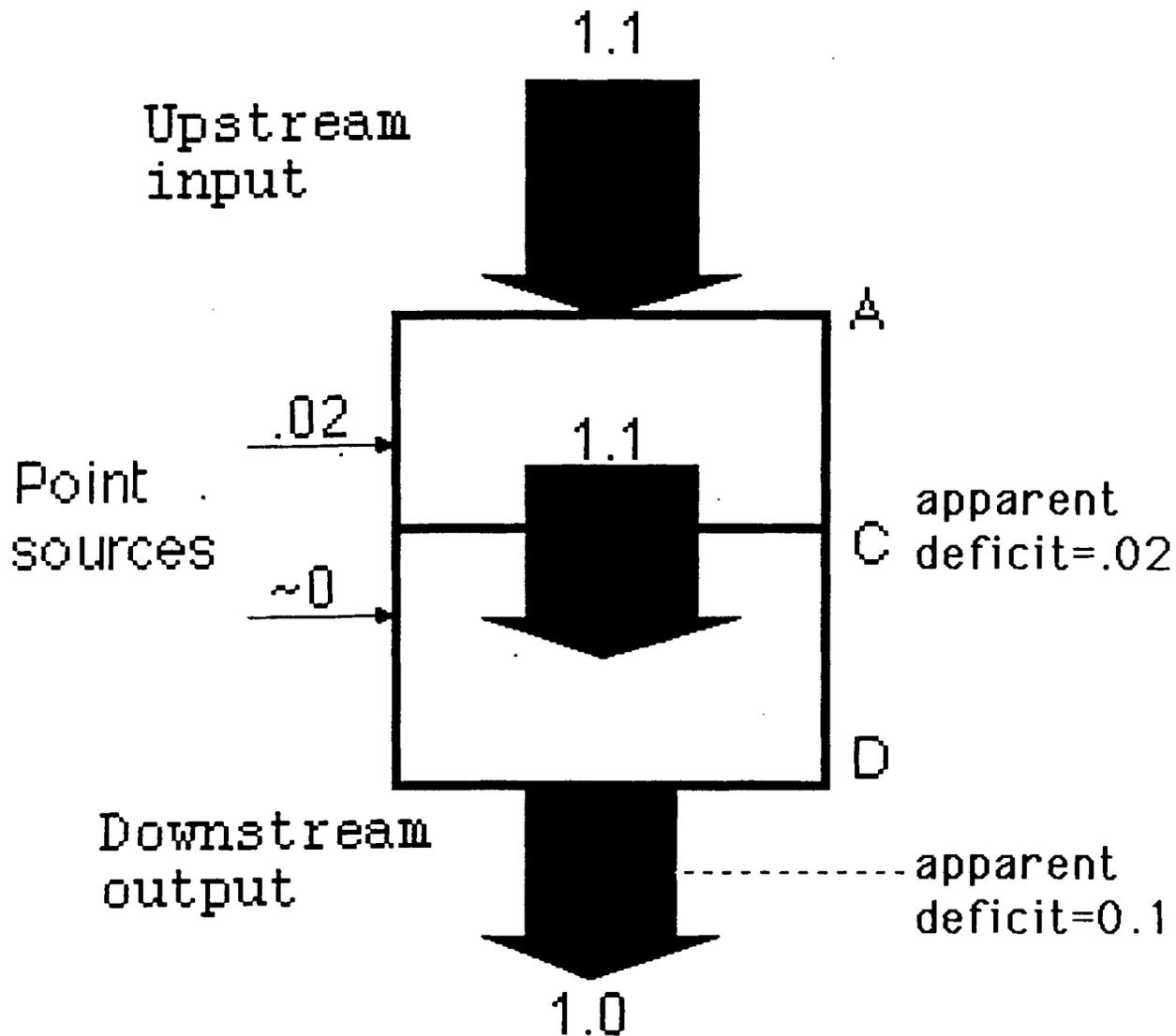


$$\text{downstream} - \text{upstream} = 36 \text{ Kg/d}$$

Entire area is not a statistically significant source of lead although the C-A area is a significant source.

TRENTON CHANNEL SURVEY II

Mercury, Total (Kg/d)

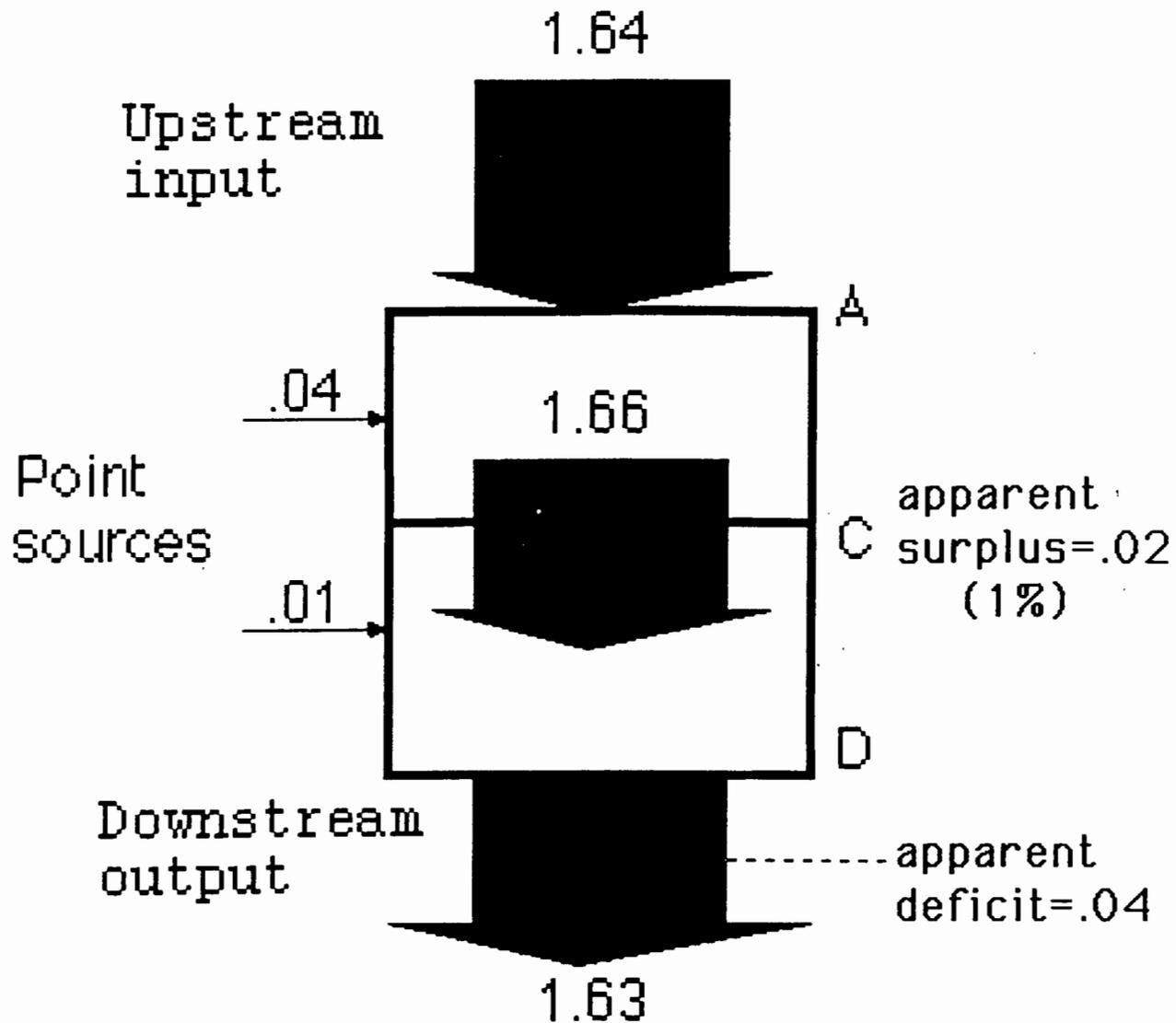


$$\text{downstream} - \text{upstream} = 0.1 \text{ Kg/d}$$

Entire area is not a statistically significant source of mercury.

TRENTON CHANNEL SURVEY III

Mercury, Total (Kg/d)

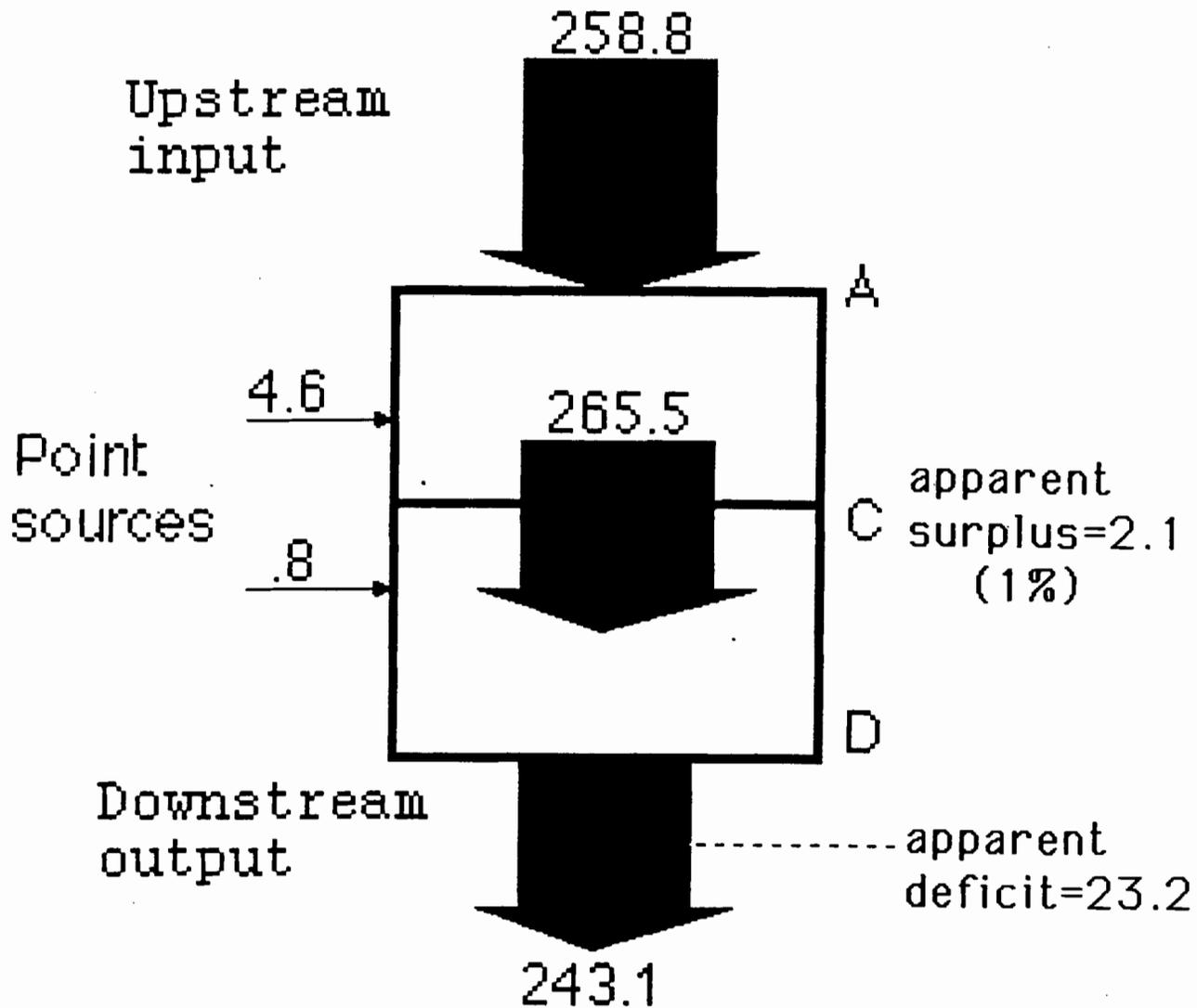


$$\text{downstream} - \text{upstream} = .01 \text{ Kg/d}$$

Entire area is not a statistically significant source of mercury.

TRENTON CHANNEL SURVEY II

Nickel, Total (Kg/d)

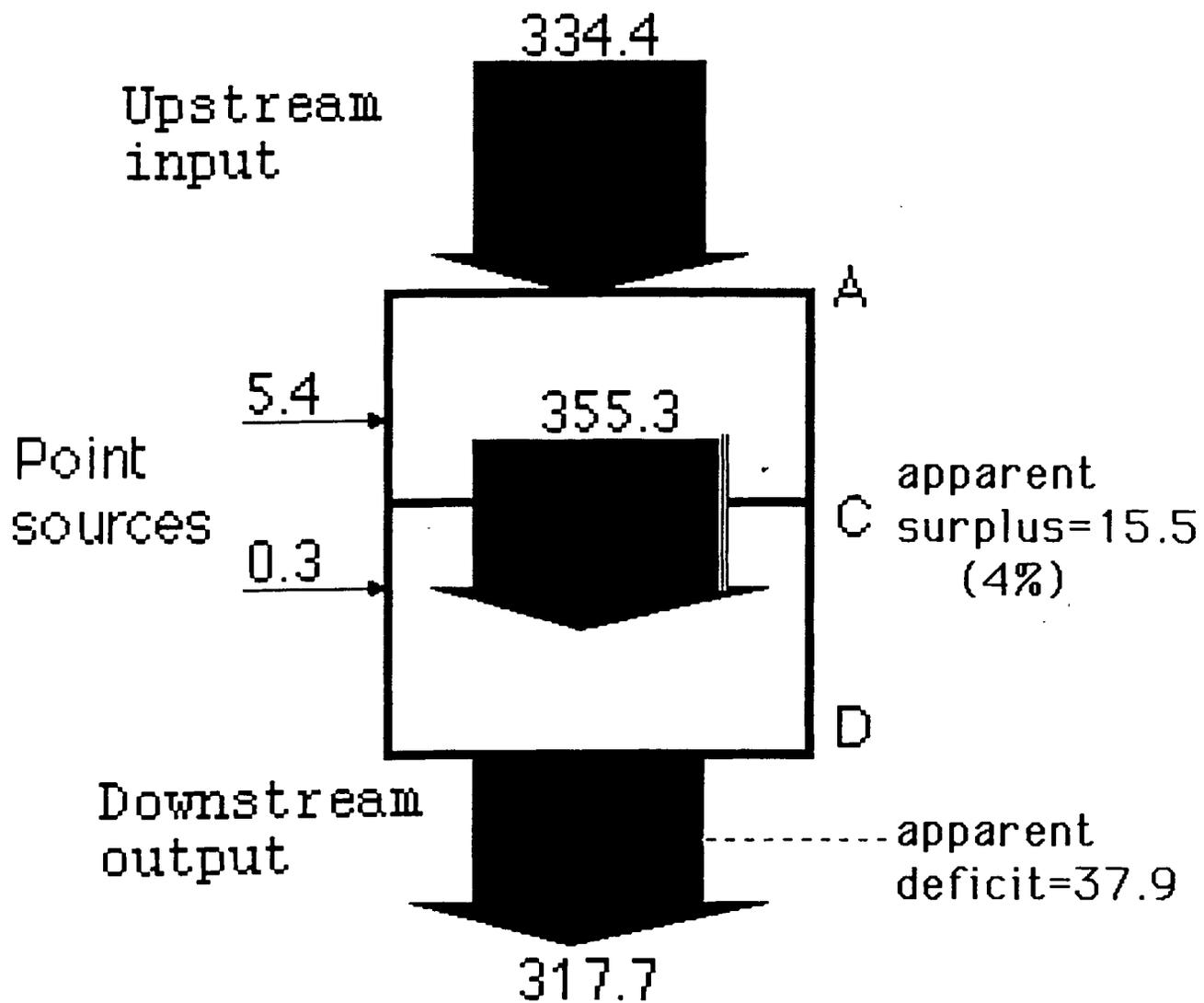


downstream - upstream = 15.7 Kg/d

Entire area is not a statistically significant source of nickel.

TRENTON CHANNEL SURVEY III

Nickel, Total (Kg/d)

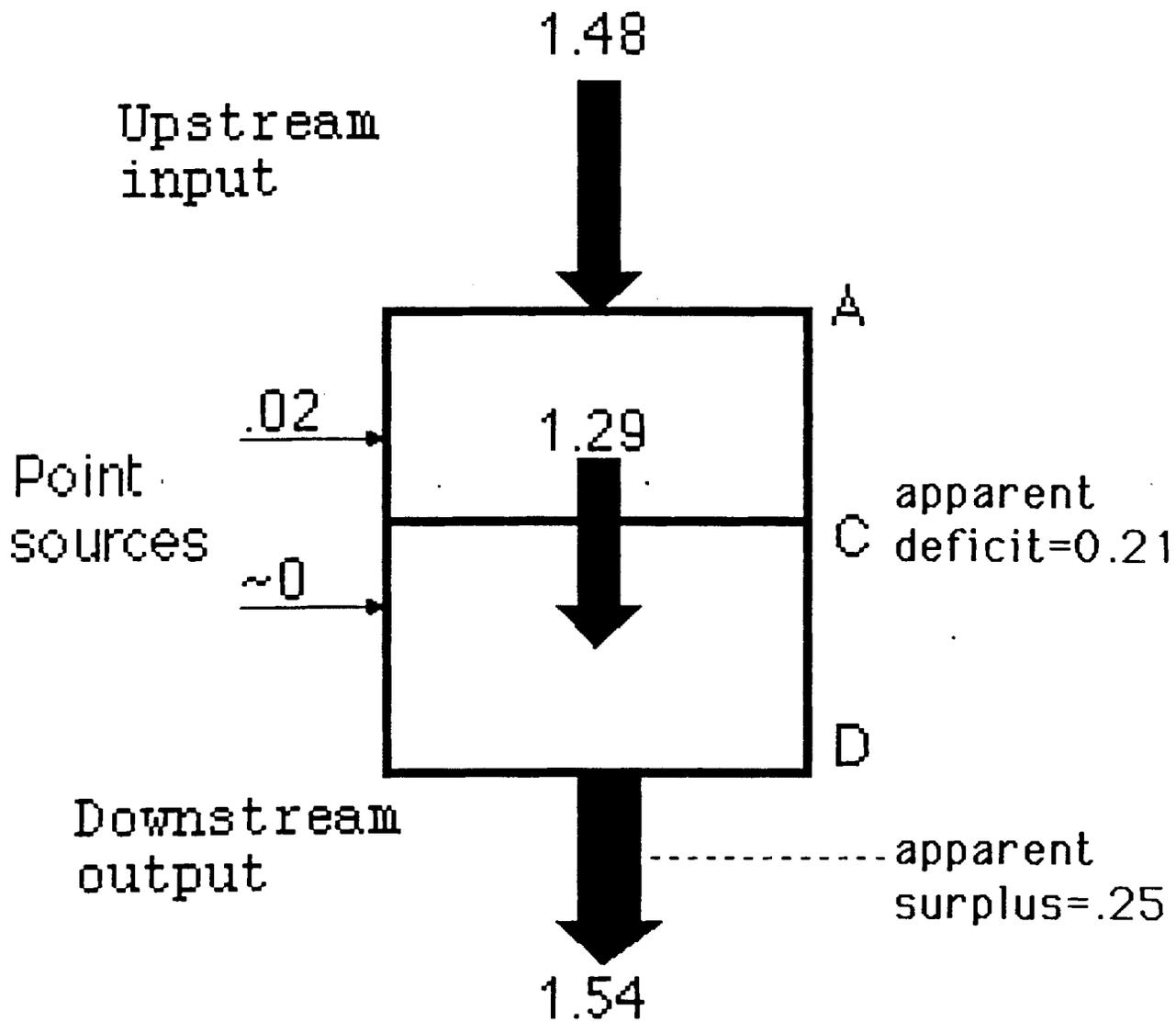


$$\text{downstream} - \text{upstream} = 16.7 \text{ Kg/d}$$

Entire area is not a statistically significant source of nickel.

TRENTON CHANNEL SURVEY II

Total PCB's (Kg/d)

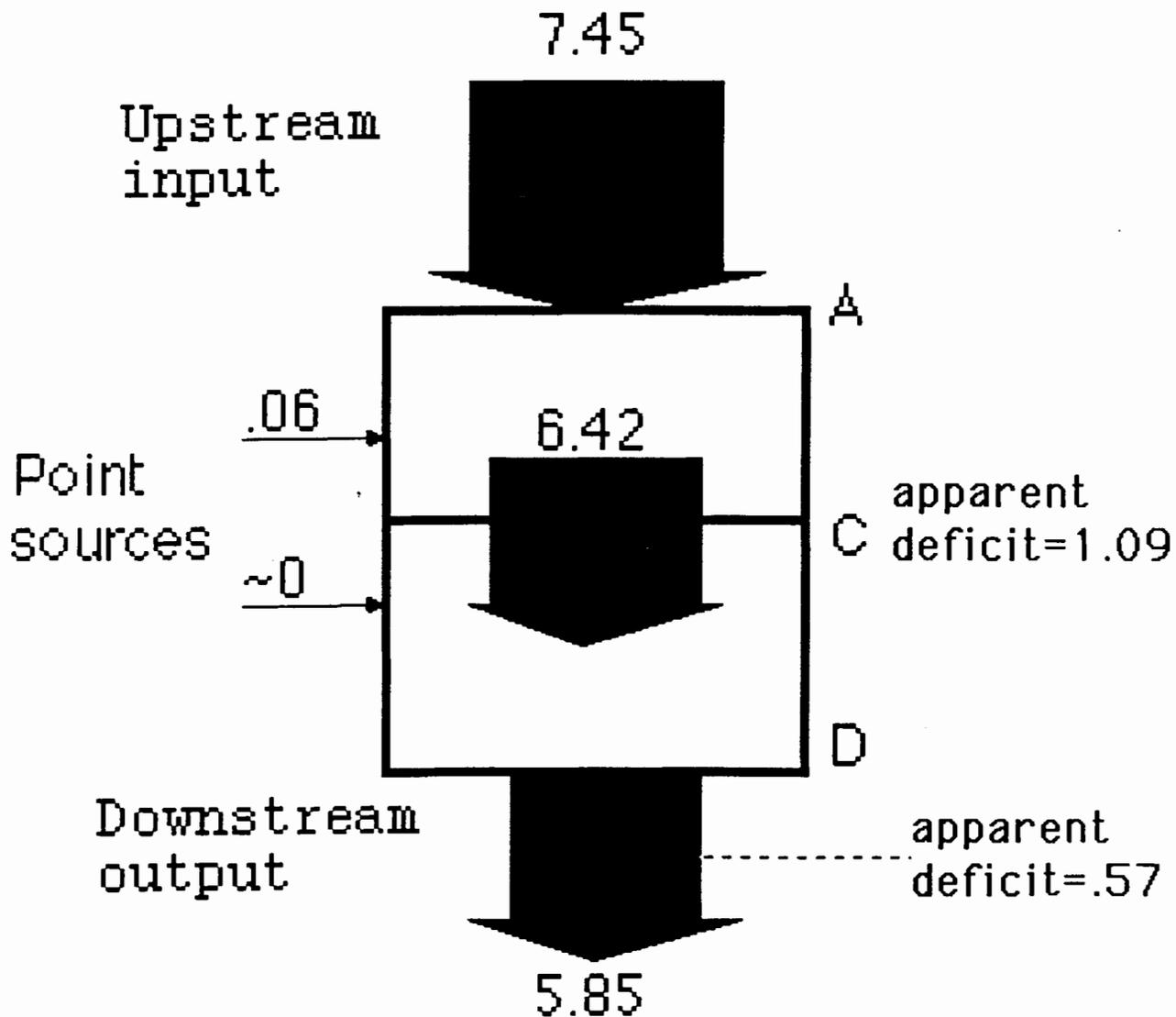


$$\text{downstream} - \text{upstream} = .06 \text{ Kg/d}$$

Entire area is not a statistically significant source of PCB.

TRENTON CHANNEL SURVEY III

Total PCB's (Kg/d)

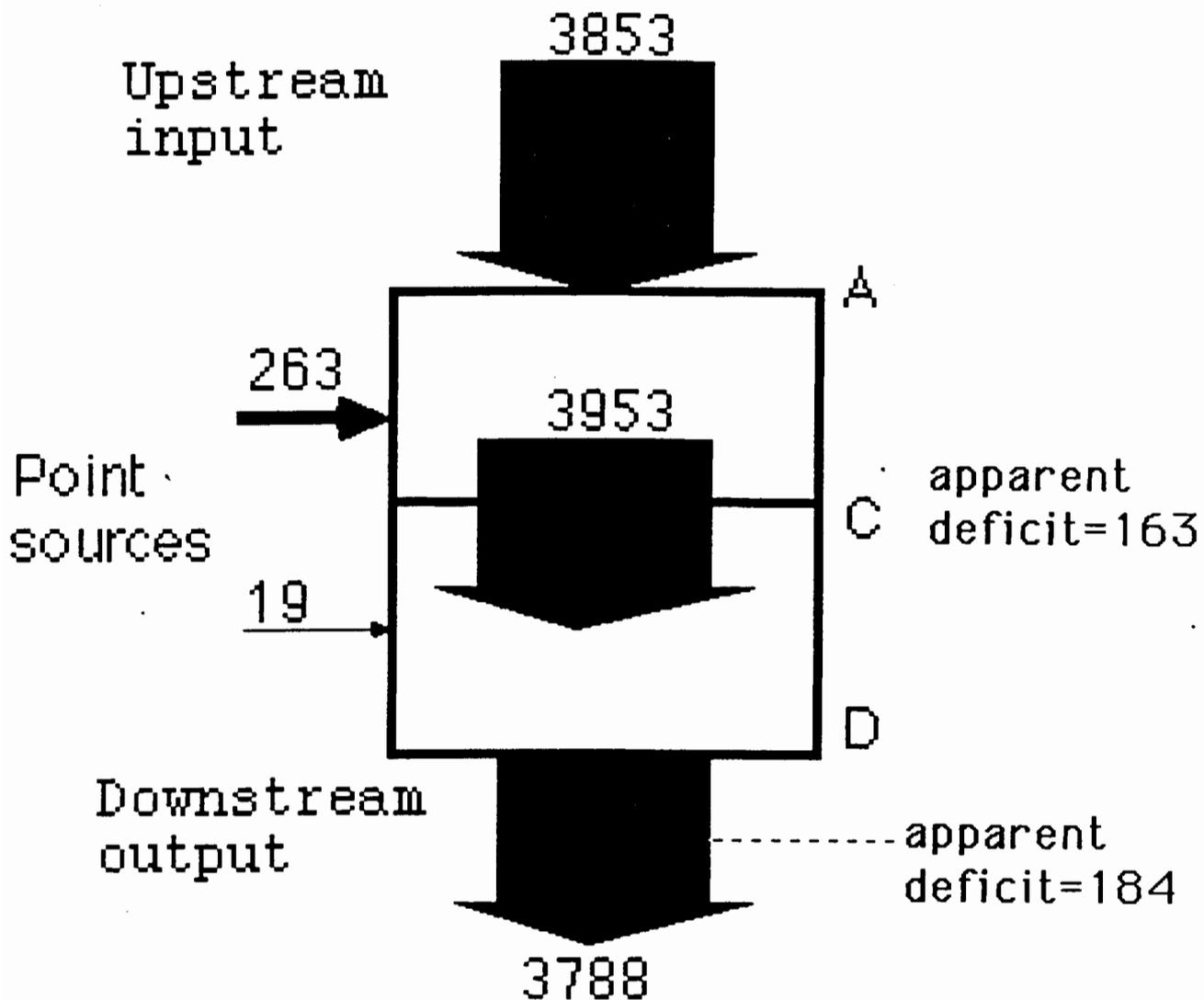


$$\text{downstream} - \text{upstream} = 1.6 \text{ Kg/d}$$

Entire area is not a statistically significant source of PCB.

TRENTON CHANNEL SURVEY II

Phosphorus, Total (Kg/d)

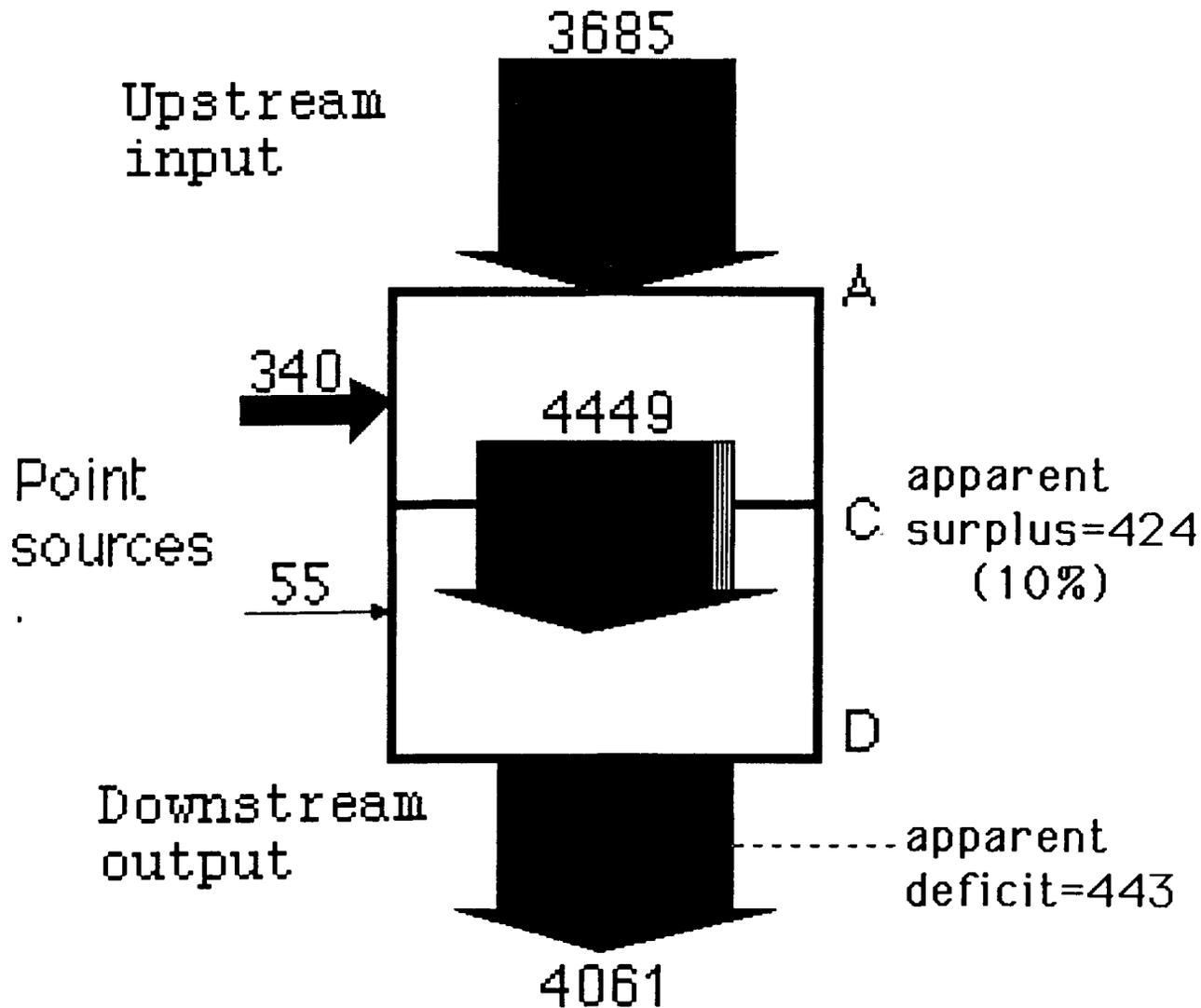


downstream - upstream = 65 Kg/d

Entire area is not a statistically significant source of phosphorus.

TRENTON CHANNEL SURVEY III

Phosphorus, Total (Kg/d)

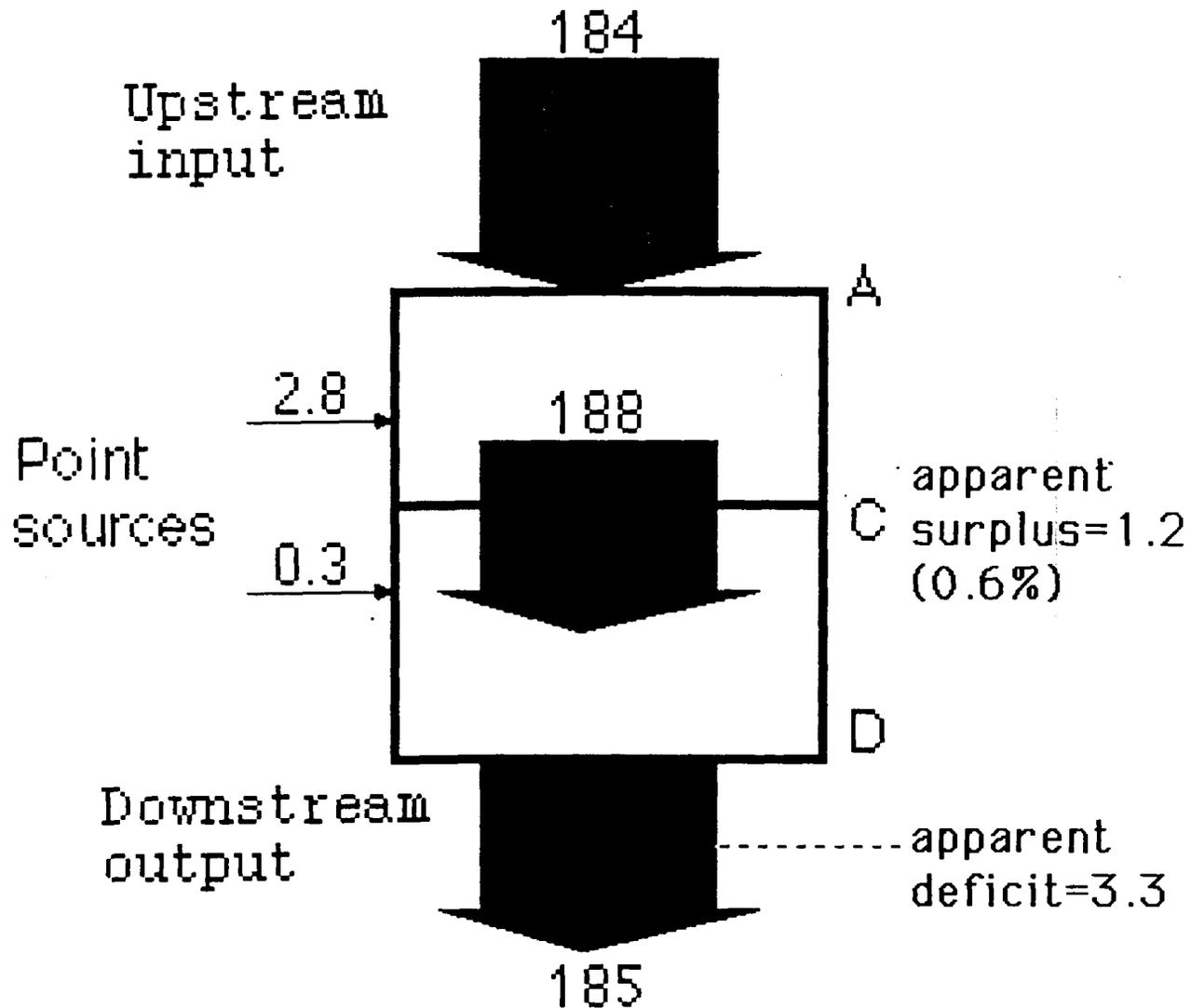


$$\text{downstream} - \text{upstream} = 376 \text{ Kg/d}$$

Entire area is not a statistically significant source of phosphorus although the C-A area is a significant source.

TRENTON CHANNEL SURVEY II

Silica, Filtered (MT/d)

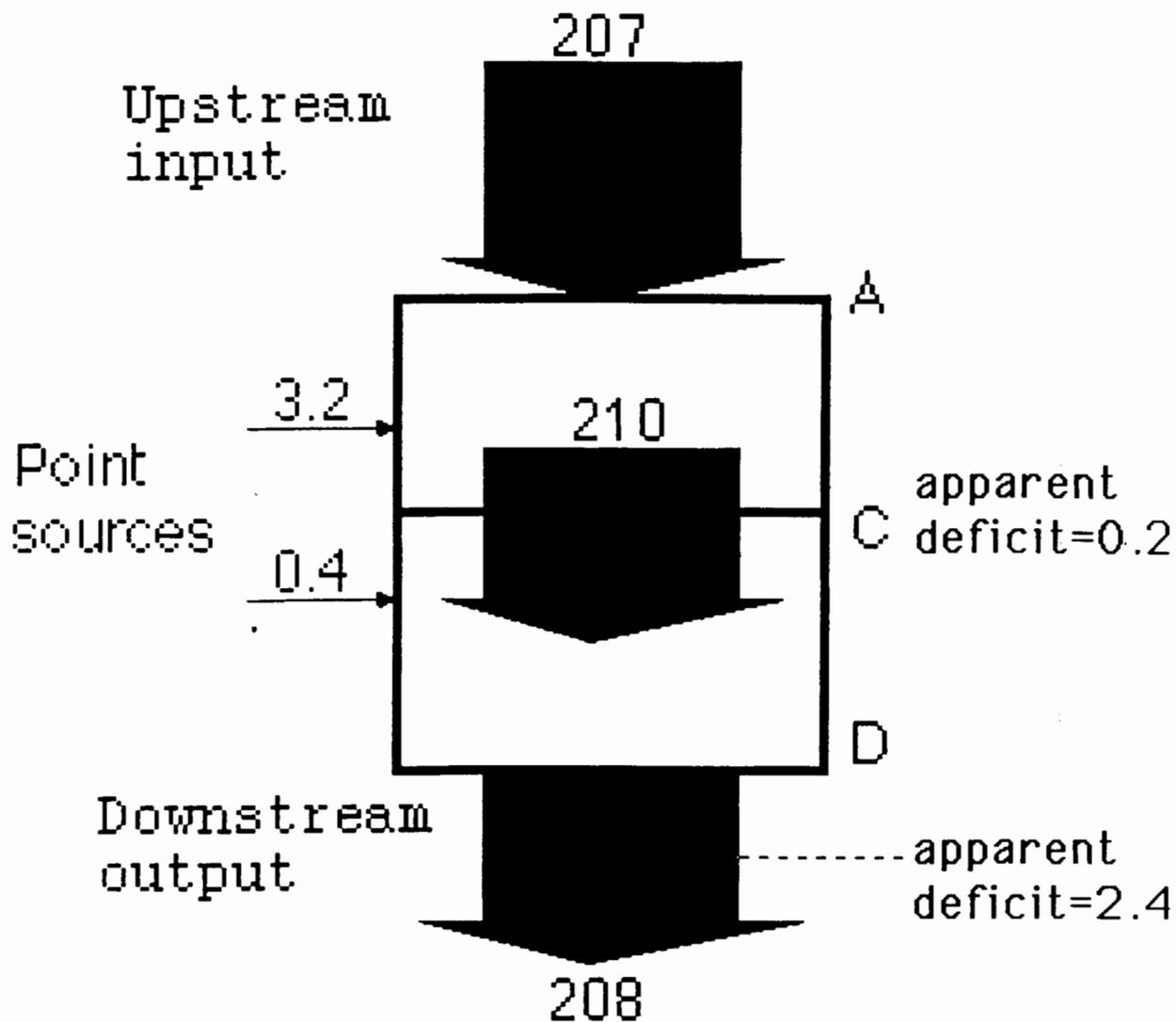


downstream - upstream = 1.0 MT/d

Entire area is not a statistically significant source of silica.

TRENTON CHANNEL SURVEY III

Silica, Filtered (MT/d)

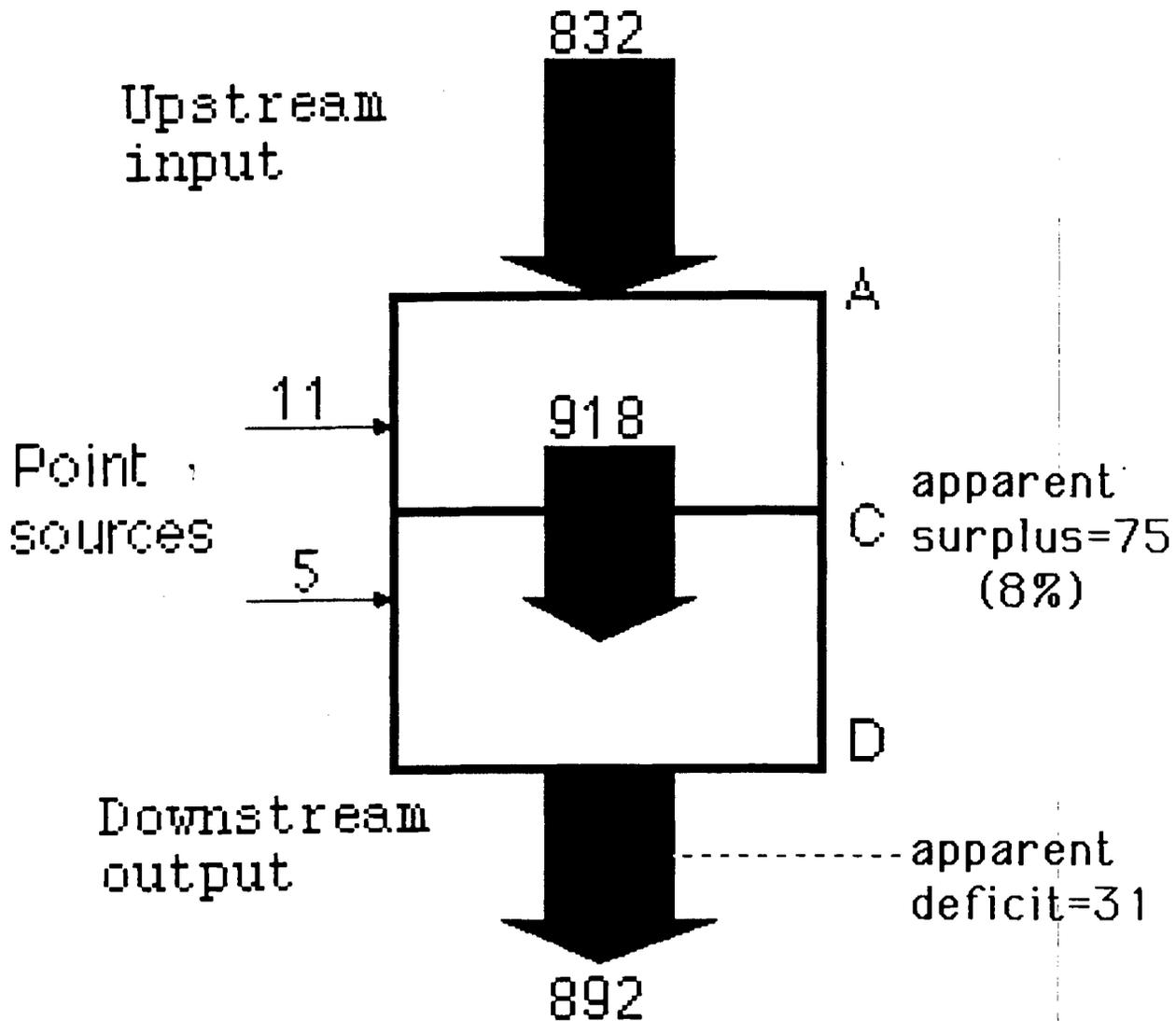


downstream - upstream = 1.0 MT/d

Entire area is not a statistically significant source of silica.

TRENTON CHANNEL SURVEY II

Suspended Solids (MT/d)

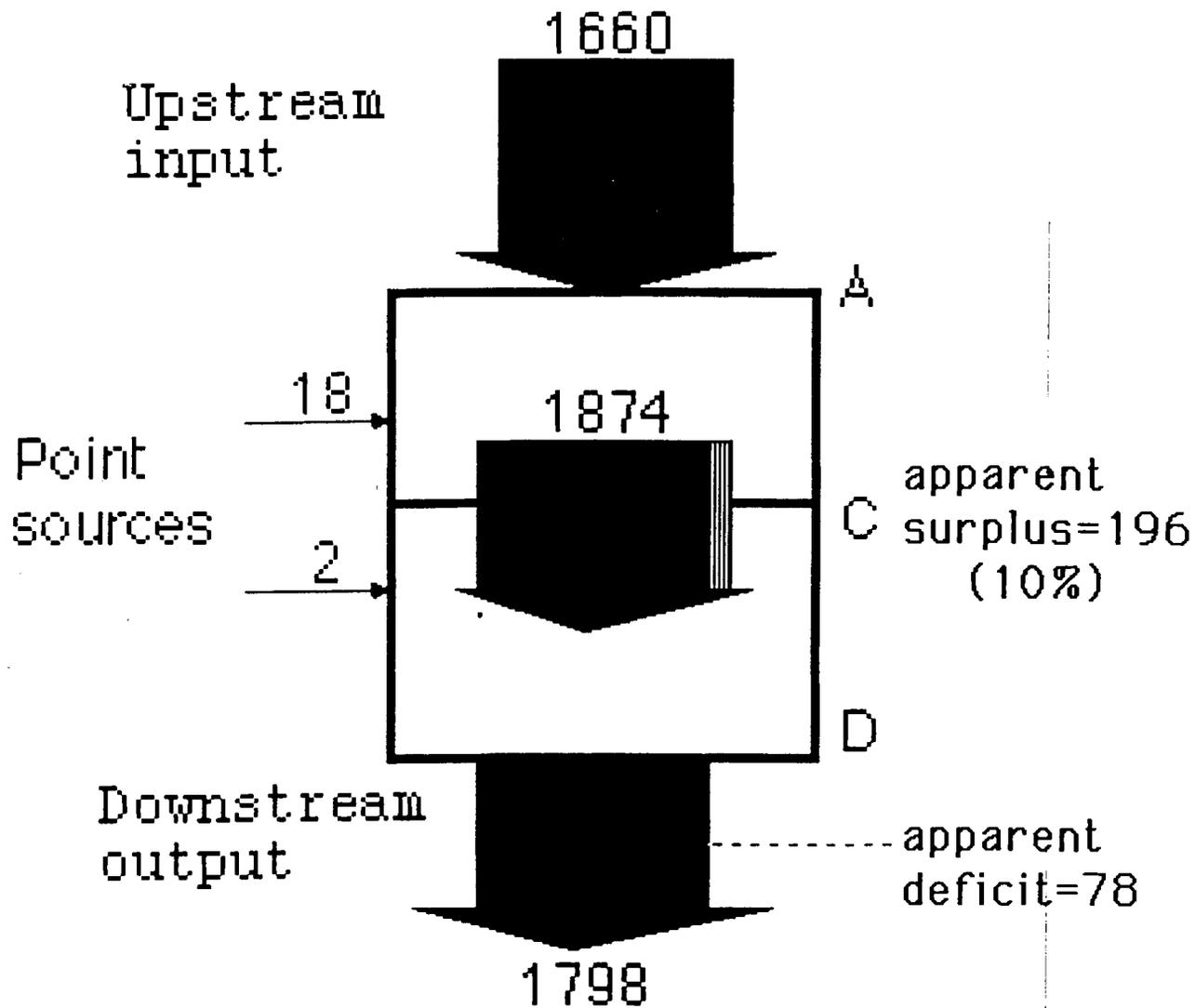


$$\text{downstream} - \text{upstream} = 60 \text{ MT/d}$$

Entire area is not a statistically significant source of TSS.

TRENTON CHANNEL SURVEY III

Suspended Solids (MT/d)

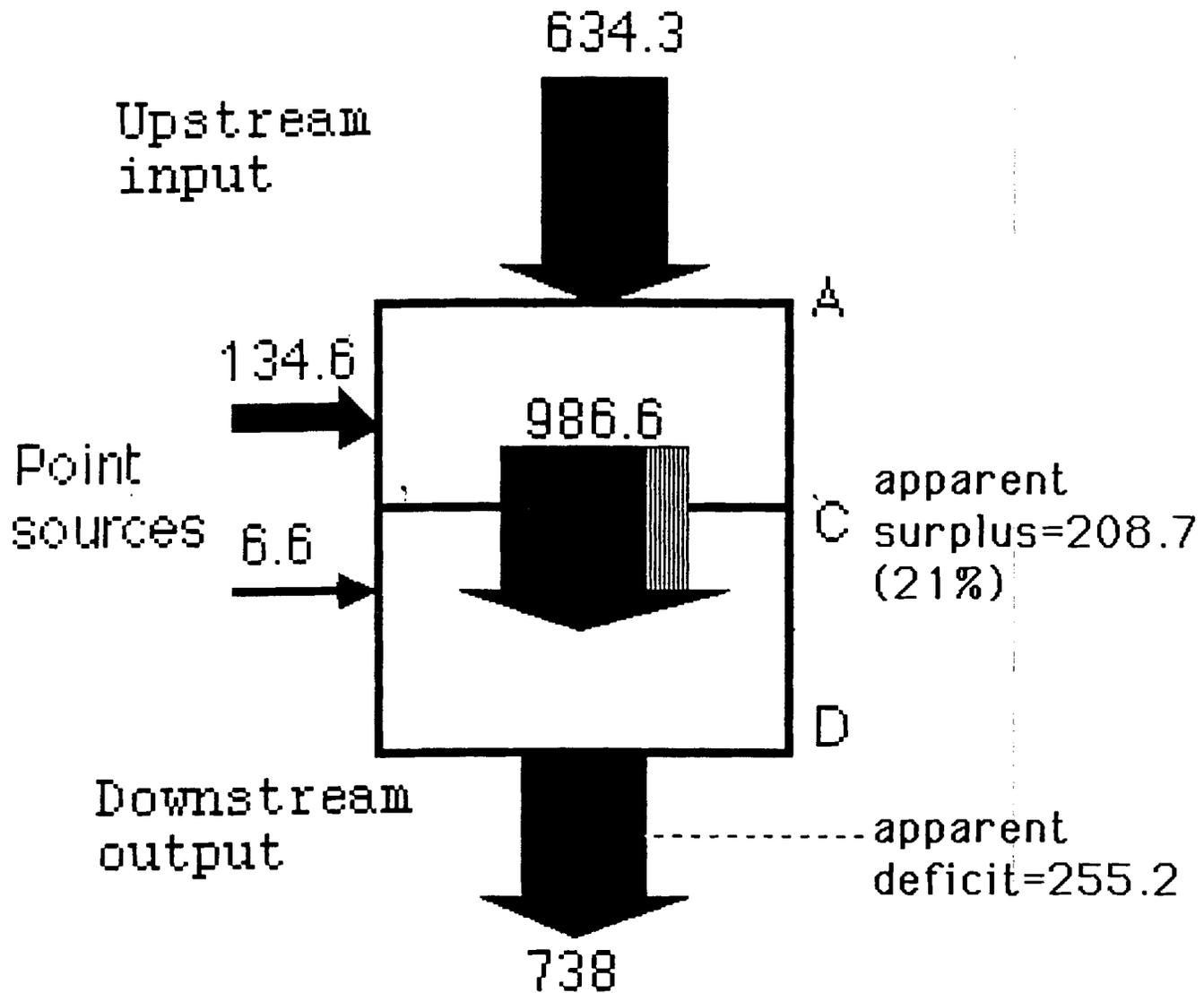


downstream - upstream = 138 MT/d

Entire area is not a statistically significant source of TSS.

TRENTON CHANNEL SURVEY II

Zinc, Total (Kg/d)

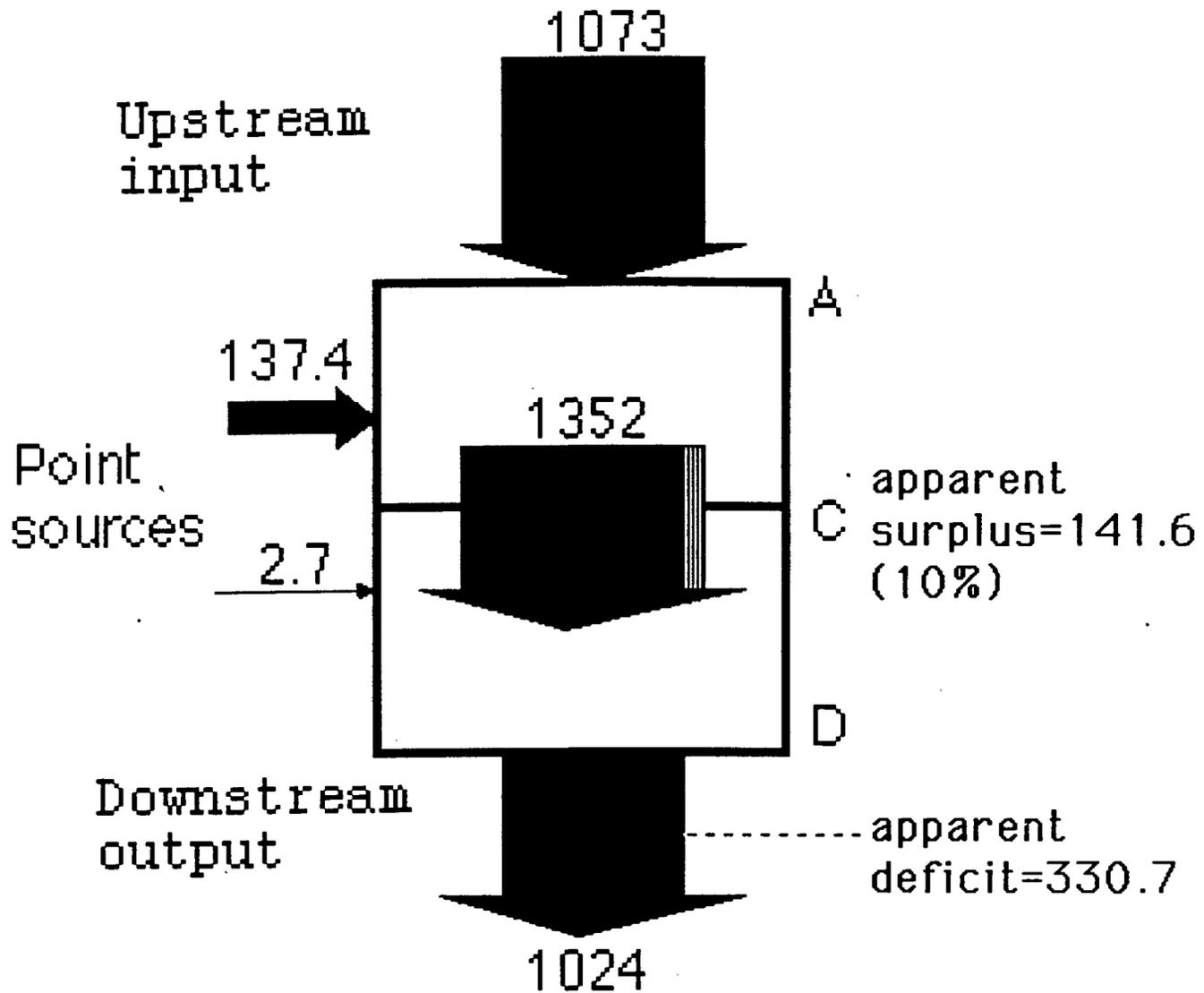


downstream - upstream = 94.7 Kg/d

Entire area is not a statistically significant source of zinc although the C-A area is a significant source and the D-C area is a significant sink.

TRENTON CHANNEL SURVEY III

Zinc, Total (Kg/d)



$$\text{downstream} - \text{upstream} = 49 \text{ Kg/d}$$

Entire area is not a statistically significant source of zinc although the C-A area is a significant source.