Proposal to General Motors Corporation

General Motors Technical Center, Warren, MI &
General Motors Central Foundry, Massena, NY

ENVIRONMENTAL CONTROL OF PCB DECHLORINATION IN ST. LAWRENCE RIVER SEDIMENTS

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Estimated start date: As early this fall as possible

Duration: 3 years

OVERVIEW OF PROJECT

Recent work has indicated that PCBs can be reductively dechlorinated by a biological process in at least some anaerobic environments. This process can both eliminate the most toxic PCB congeners and make PCBs more disposed to aerobic degradation. The environmental factors that control dechlorination are, however, poorly understood. We propose to analyze the environmental controls on PCB dechlorination in contaminated sediments in the St. Lawrence River below the outfall of the General Motors Central Foundry plant in Massena, N.Y. This work will have two phases. In the first we will correlate the extent of PCB dechlorination to likely environmental and biological factors that may control dechlorination. The factors to be considered include sediment texture, aeration status, nutrient level, microbial population, and the dechlorinating ability of the extant population. In the second phase we will use sediment cores containing either "fresh" or "old" PCBs to measure the rates of dechlorination under both controlled laboratory conditions and *in situ*. These experiments will indicate the role of O_2 supply and other environmental parameters on dechlorination patterns in nature. By combining these results with the results of the first phase, we should have the data necessary to model the course of PCB dechlorination in sediments and thus to make realistic predictions on the fate of PCBs in the St. Lawrence River sediments.

INTRODUCTION & BACKGROUND

The fate of PCBs in aquatic sediments is an important environmental concern. Sediments are a major environmental sink for PCBs, and it was thought that PCBs in sediments were undegradable and constituted a possible source of PCBs for the human food chain (Brown et al., 1987). However, there is recent evidence that PCBs are dechlorinated in anaerobic Hudson River sediments (Brown et al., 1984, 1987a,b). This process occurs primarily by removal of meta and para chlorines, converting the PCBs into less toxic (McKinney and Singh, 1981; Safe et al., 1982) and more aerobically degradable congeners (Brown et al., 1984).

Other aquatic sediments show evidence of PCB dechlorination as well. Congener analysis of PCBs from Silver Lake, MA (Brown et al., 1984, 1987a,b) and Waukegan Harbor, IL (Stalling, 1982) suggests that dechlorination has occurred in these sites. Our interpretation of the existing PCB data on the sediments just below the General Motors Central Foundry outfall in Massena, NY is that PCB dechlorination has also occurred at this site. The sediments contain congeners that are not found in Aroclor 1248, as indicated by the apparent occurrence of Aroclor 1232 (Report to GM by RMT inc., project 269, 1986). These lesser-chlorinated congeners presumably resulted from the dechlorination of Aroclor 1248, as neither GM nor Reynolds Aluminum, immediately upstream of the GM foundry, reported using Aroclor 1232.

Current work in our laboratory shows that PCBs can be dechlorinated anaerobically by a biologically mediated process (Quensen et al., 1988; manuscript attached). Briefly, in lab experiments, we found extensive dechlorination using a "transfer technique"; organisms eluted from a PCB contaminated Hudson River sediment were added to "clean" sediments spiked with

Aroclor 1242. Approximately 75% of meta + para chlorines were removed within 8 weeks when the PCB concentration was 700 μg PCB/g sediment, although negligible dechlorination occurred at a PCB concentration of 14 μg/g. At 140 μg/g the dechlorination was intermediate. Dechlorination did not occur in autoclaved control samples, indicating that the process is biological. Biological PCB dechlorination can therefore occur rapidly under the right conditions.

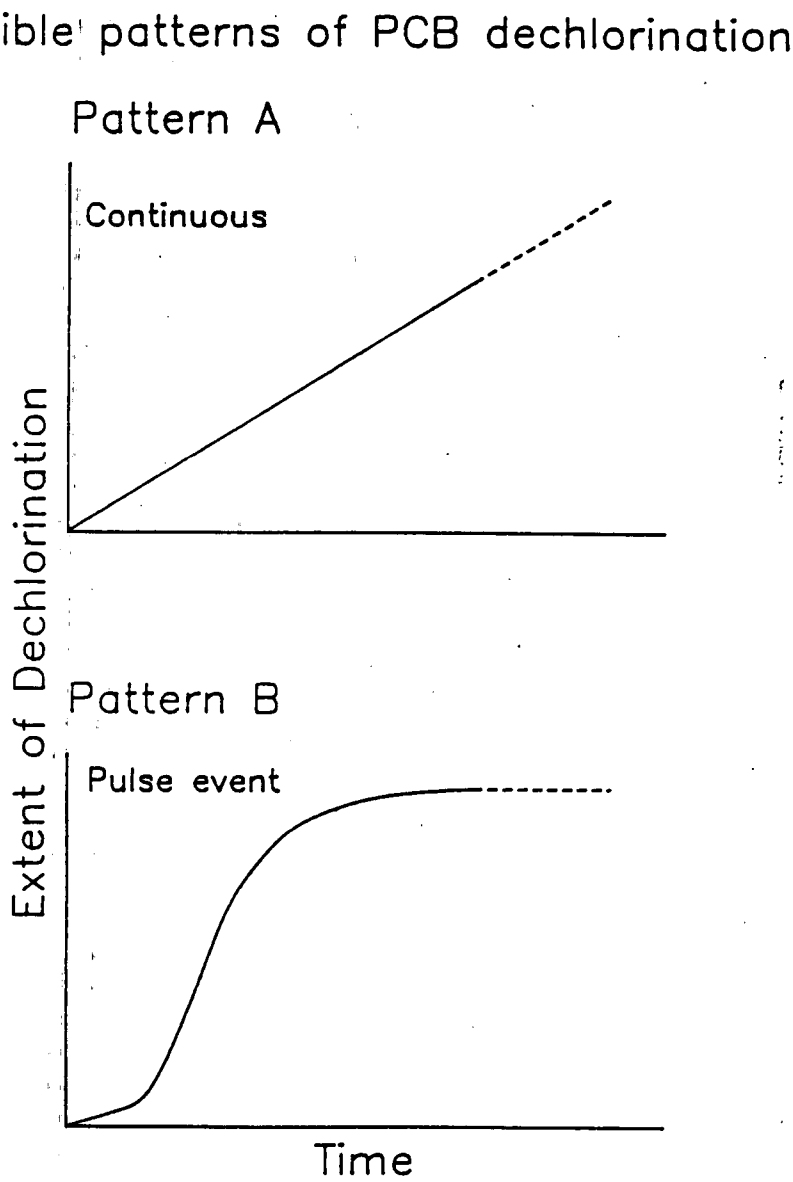
While the occurrence of biological PCB dechlorination in anaerobic sediments has thus been verified, the kinetics of the process remain a major question. In the approximately 15 years since PCB input into the Hudson ceased, the extent of dechlorination is no greater than we observed in the lab in four months. There are two possible explanations for this apparent discrepancy between lab and field data:

A. PCB dechlorination could be a slow continual process with the rate determined by environmental factors.

B. Dechlorination could have occurred in a rapid pulse, perhaps shortly after PCBs were deposited and an active dechlorinating population established, but slowed or ceased thereafter.

The two patterns are diagrammed in Figure 1. Which is correct is unclear, and it is possible that different patterns apply in different circumstances. Furthermore if the second pattern predominates, it may be possible to restart the pulse event. Determining the kinetics of dechlorination *in situ* is therefore important to understanding the long-term behavior of PCBs in nature and to predicting the best course for dealing with contaminated sediments. Addressing the above issues is the next important step in research on PCBs in contaminated sediments.

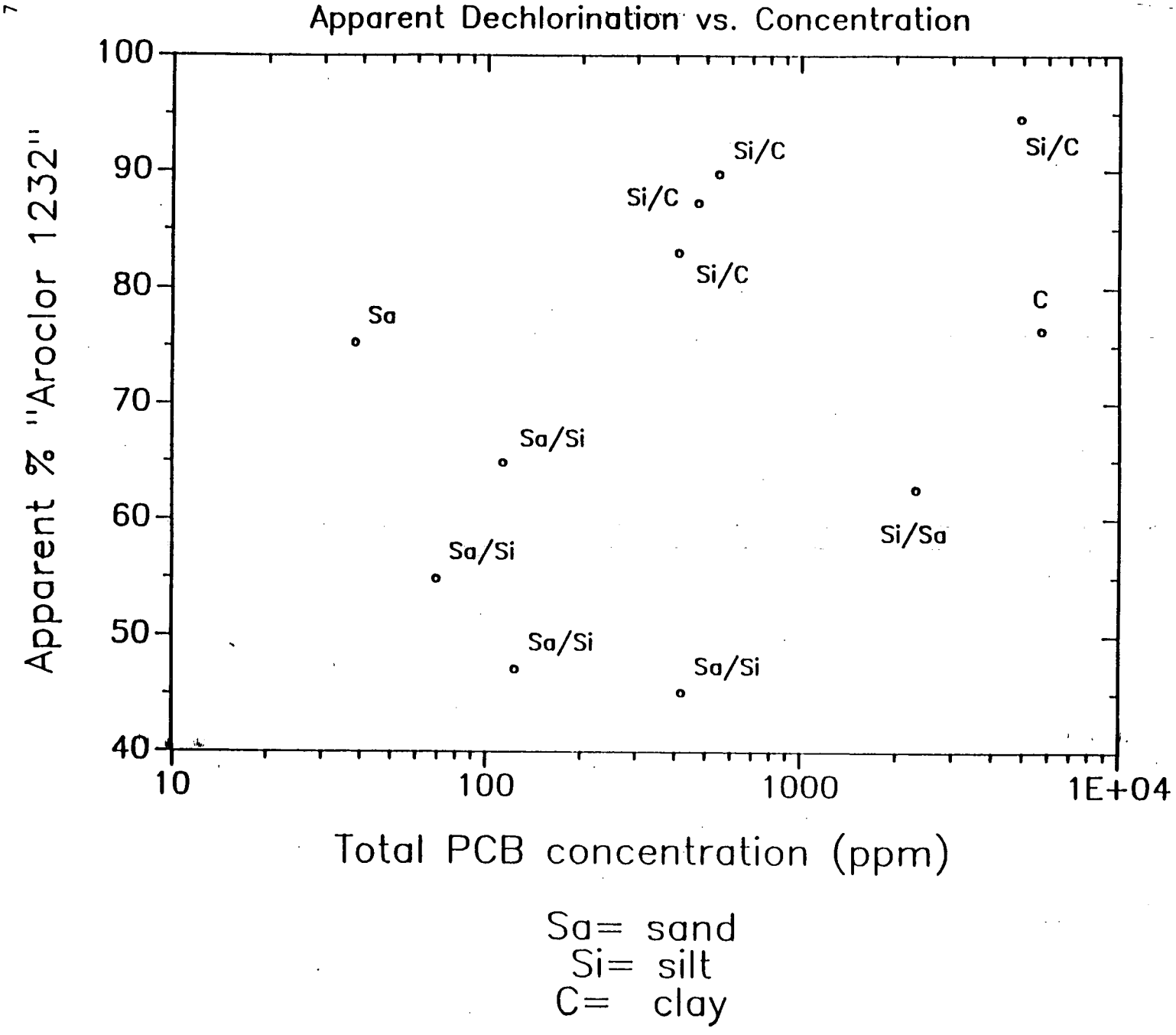
Figure 1.



SPECIFIC RATIONALE

As previously mentioned, dechlorination appears to have occurred in the St. Lawrence sediments. Since the "Aroclor 1232" identified by RMT inc. probably represents dechlorination products of Aroclor 1248, the apparent proportion of "Aroclor 1232" in the total PCB mix can be used as an index of dechlorination. Figure 2 shows a plot of apparent percent of "Aroclor 1232" in surface sediments vs. total PCB concentrations in those sediments, with the texture of the sediment indicated as well. There are correlations between the concentration of PCB, the extent of dechlorination and the texture of the sediment; fine textured sediments have generally higher concentrations of PCBs and show more apparent dechlorination than do coarse sediments. The association between texture and dechlorination may therefore result from either a concentration-activity relationship, a texture-activity relationship, or both. If it is a texture relationship, it probably results from more strongly anaerobic conditions in the fine textured sediments. The clayey texture reduces O_2 diffusion rates and should also enhance organic matter (carbon substrate) concentrations in the sediments. Thus, in the fine sediments, greater numbers of anaerobic dechlorinators are likely, and O_2 is less likely to limit their activity as well. These relations need more intense analysis to determine the strength and the actual cause of the observed relationships.

Figure 2.


Apparent Dechlorination vs. Concentration
Apparent % "Aroclor 1232"
100
90
80
70
60
50
40
10
100
1000
1E+04
Total PCB concentration (ppm)
Si/C
Si/C
Si/C
Si/C
Sa
C
Sa/Si
Si/Sa
Sa/Si
Sa/Si
Sa/Si
Sa= sand
Si= silt
C= clay

OBJECTIVES

The overall goal of this study is to improve our understanding of the controls and rates of PCB dechlorination in nature. This will greatly improve our ability to wisely plan remedial action for PCB contaminated sediments. There are three major objectives:

1. Verify that PCB dechlorination has occurred in the St. Lawrence River sediments by analysis of PCB congener profiles.
2. Evaluate relationships between the sediment characteristics, the extent of dechlorination of existing PCBs, and the dechlorinating ability of the existing microbial population.
3. Measure dechlorination rates *in situ* and relate these to known controlling factors and rates measured in the laboratory.

In the proposed work, we will carry out studies on sediments from the St. Lawrence River near the outfall of the GM Massena plant. This work will have two phases. The first phase will address objectives 1 & 2. This will provide us with the information and sediments necessary for the *in situ* experiments proposed under objective 3, which will constitute phase 2. Together, these will provide the first experimental study analyzing the actual dynamics of PCB dechlorination in aquatic sediments.

By measuring the rate of dechlorination and determining the major environmental controls we should have the essential information for reasonable predictions on the eventual fate of PCBs in the St. Lawrence River. It is particularly important to determine the fate of the most specifically toxic congeners: 34-34, 2345-4, 234-34, and 2345-34 chlorobiphenyl. The knowledge gained from this work will assist in determining what, if any, remediation measures are necessary for the St. Lawrence sediments.

APPROACH & METHODS

First Phase- Characterize sediments

The purpose of the first phase is to relate the extent to which dechlorination has occurred to the physical and biological characteristics of the St. Lawrence sediments near the Massena plant. Cores will be taken from sites which have previously shown high concentrations of PCBs (determined from Map sheet 5-3, project no 269.07- Sediment distribution, pipeline locations and sampling stations).

Thirty pairs of cores (30 cm deep) will be taken from sediments outside the plant outfall. These will be collected in a grid covering the area just below the GM plant outfall, and covering a variety of sediment textures and PCB concentrations. Within each pair, the cores will be taken as close together as practicable. One core from each pair will be sectioned into several depth increments and the following analyses performed on each section:

Sulfide concentration
Sediment texture (particle size analysis)
Organic carbon
Nutrients- NO_3^-, SO_4^{2-}
Bacterial numbers
Microbial activity
PCB concentration
PCB congener distribution

These analyses will enable us to examine in more detail the relationship between sediment texture and dechlorination (Fig. 2), and to determine the underlying mechanism of this relationship. PCBs will be extracted from the sediment by refluxing with hexane-acetone and congener specific analysis will be performed using capillary gas chromatography with an electron capture detector (Quensen et al., 1988). These analyses will

indicate whether, and to what extent, dechlorination has occurred in the sediments; they will also indicate the concentration and fate of the specifically toxic congeners. Sulfide concentrations will be measured as an index of redox potential (aeration status; Alexander, 1977). We will not measure redox potential directly as sulfide poisons the platinum electrode used in redox measurements. Organic carbon will be measured by combustion (Nelson and Sommers, 1982). Organic carbon is important both as a substrate for microbial growth and as the major factor controlling PCB adsorption in sediments. Microbial activity will be measured by incubating samples and measuring CO_2 and CH_4 production. Sulfate has been found to inhibit dechlorination by the bacterium DCB-1 which dechlorinates chlorobenzoic acid derivatives (Linkfield, 1985); soluble SO_4^{2-} concentration is therefore useful information in this analysis. Sulfate will be extracted from the sediments and analyzed by ion chromatography (Dionex Corporation, 1984). Nitrate will be extracted with KCl and analyzed colorimetrically (Keeney and Nelson, 1982). Bacterial numbers will be counted by direct microscopy using the fluorescent stain acridine orange (Ramsay and Bawden, 1983).

The second core from each pair will be maintained under anaerobic conditions. This core will be divided into the same sections as the first core. Each section will be mixed and a portion will be used to prepare an inoculum of eluted bacteria, which will then be tested for the ability to dechlorinate PCBs by using the "transfer" technique as described earlier (Quensen et al., 1988). The remainder of the core will be maintained under anaerobic conditions and used for the *in situ* experiments described below.

The "transfer" approach should provide an index of dechlorinator population size. Fresh PCBs (500 $\mu g/g$), inoculum, and uncontaminated

sediments are slurried in reduced anaerobic mineral medium. These tubes are incubated anaerobically at 25° C to measure the rate of dechlorination (Quensen et al., 1988).

This technique will be refined by using a PCB test mixture that has been depleted of low boiling, low chlorine content congeners. Since these substances are typical dechlorination products, their removal will increase assay sensitivity by providing a "clean slate" for the measurement of dechlorination products. We will try to further simplify and standardize the dechlorination bioassay by developing a more general solid support than the uncontaminated sediments used previously in the "transfer" technique. Possibilities are various mixtures of sand, vermiculite, ceramic chips, peat, and wood chips.

Data from these cores will be analyzed using multiple regression to determine correlations between factors important in controlling the extent of dechlorination in the sediments. This will help in identifying important controls on dechlorination, which will be valuable in modeling PCB behavior in river sediments.

In Situ Studies

Fine textured sediments that show reasonably high PCB concentrations and dechlorination ability will be composited and used for further studies. The core experiments will be done with fine-textured sediments for two reasons: they have generally higher concentrations of PCBs and dechlorination has apparently proceeded further than in the sandy sediments (Fig. 2). These experiments will address two basic questions relating to dechlorination kinetics in nature:

1) How rapidly can dechlorination occur in natural sediments with fresh deposits of PCBs?

2) Is dechlorination still occurring in those St. Lawrence sediments with active populations of dechlorinators?

By examining dechlorination of both "fresh" and "old" PCBs we will separate the possibilities that dechlorination is a slow, ongoing process rather than a pulse phenomenon that only occurs when both fresh PCBs (unadsorbed by organic matter and hence more degradable; Unterman et al., 1988) and an active population are present together.

The first question will be addressed by a technique similar to the transfer experiments. An inoculum will be prepared by eluting organisms from the composited sediments. This inoculum will be added along with fresh PCBs (at the same concentration as in the composited contaminated sediments) to uncontaminated sediments collected from the St. Lawrence. These will be packed into plastic columns (10 cm of sediment x 5 cm diam.) and covered with water as described below. Three sets of cores will be prepared. One set of will be incubated anaerobically in the lab, one will be incubated exposed to the atmosphere (open top), and the last set will be replaced in the field. The field cores will be placed in the sediments in the fall of 1988. Cores will be harvested each spring and fall for up to three years to ensure that even if dechlorination is slow, we will be able to detect it, and the long incubations will provide a more complete view of dechlorination kinetics over time. At the time cores are harvested, we will measure sulfide concentrations, bacterial numbers, PCB congener concentrations, and PCB dechlorination potential.

The three core treatments will allow us to determine the various factors controlling dechlorination (Fig. 3). The anaerobic assay measures the maximum potential rate of dechlorination while the field treatment measures the actual rate of dechlorination. The exposed treatment is intermediate, to bridge the gap and help determine controlling factors:

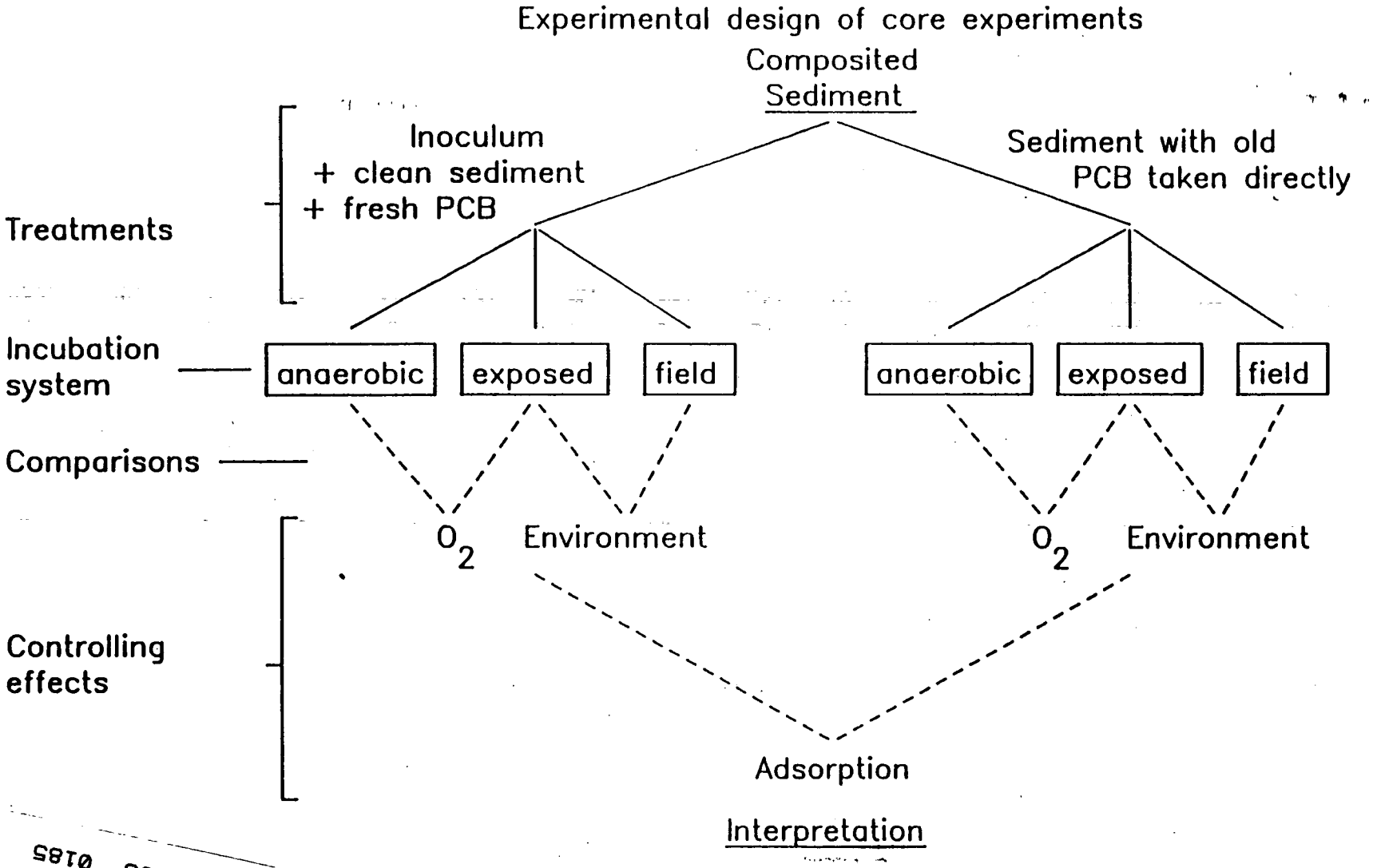
anaerobic vs. exposed cores: effects of sediment structure on limiting O_2 diffusion.

exposed vs. field cores: effects of other environmental factors- temperature, nutrient supply from the river, etc.

Dechlorination won't occur under aerobic conditions, so if dechlorination rates in exposed cores are rapid, then it suggests that O_2 supply is not fast enough to limit dechlorination. The "native" PCBs then either dechlorinated rapidly after development of an active population, or some environmental factor limited the rate, most likely PCB adsorption into mineral/organic complexes before the population developed. If dechlorination in the exposed core is significantly slower than in the anaerobic core, then it suggests that the rate of O_2 supply limits the rate of dechlorination, in which case dechlorination would likely be slow but ongoing.

The current dechlorination rate of "native" PCBs in in contaminated sediments will be addressed by core experiments using the composited PCB-contaminated sediments. Three core treatments will be established as in the "fresh" PCB experiments. The same assays will be performed as were described for the fresh PCB cores, allowing examination of the control of ongoing PCB dechlorination. Again, the comparisons of anaerobic, exposed, and field cores will allow determination of the relative roles of O_2 and other factors on dechlorination of "old" PCBs.

Figure 3.



By using cores with known PCB concentrations and congener mixes we will be able to determine both rates of dechlorination and loss of the PCBs in the cores. If there is significant loss of PCBs by degradation or dissolution over the period of the incubations, it should therefore be measurable.

All cores will be made out of polycarbonate cylinders 5 cm diameter by 12 or 20 cm long. These will be sealed on the bottom to prevent material from falling out. They will also be fitted with caps so that the cores can be maintained anaerobically for transport; the caps will be fitted with septa so that the headspace can be purged with N_2. The sediment (for both experiments) will be packed 10 cm deep into the cores and will be covered by a screen mesh to hold the sediments in while allowing free diffusion between water and sediment.

Lab cores will be 20 cm long to allow standing water over the sediment. Anaerobic cores will be filled with water, sealed, purged with N_2 and incubated in the lab. Exposed cores will be filled with water, covered with foil, and incubated in the lab. Field cores will be 12 cm long. The packed sediment cores will be topped off with water, capped, and purged with N_2. They will then be transported to Massena, uncapped, and replaced in the field. The cores will be placed into a stainless steel box, segmented into individual compartments for each core. Sediment will be packed into the spaces around each core. One box will be used for the "old" and one box for the "fresh" PCB experiments. The boxes will be buried in the sediments and anchored in place. The location will be marked by a post driven solidly into the sediment. At harvest times, individual cores will be removed from the boxes without removing the box (to avoid disturbing other cores).

Sets of triplicate cores will be removed periodically, capped, purged with N_2, and returned to East Lansing. Cores will be harvested spring and fall for up to three years. This will allow determination of the the annual rate of dechlorination, as well as the seasonal dynamics of the dechlorinating population and its overwinter survival.

Data Interpretation and Modelling.

The data from the survey, the *in situ*, and other experiments currently going on in our laboratory will be used to construct a simple model of dechlorination kinetics in river sediments. The model will probably use the multiple regression output from the survey experiments to adjust the measured field rates for various environmental conditions. A more sophisticated model of PCB dechlorination kinetics would require more information than we can collect in this project. Nevertheless, a simple model would allow workers to perform several assays on a contaminated site and then estimate the likely course of PCB dechlorination, providing the first realistic predictions of the fate of PCBs in these environments. The proposed model would thus be an invaluable aid in making decisions on the management of PCB contaminated sediments, such as those in the St. Lawrence River near Massena.

Reporting

We will provide General Motors a brief written report every six months, an oral report each year, and a final written report. We will also provide phone updates or key summary data whenever it is available and of interest to GM.

As for any State University there can not be restrictions on publicatior of any new and significant scientific knowledge. General Motors will,

however, have the right to review, provide suggestions, and negotiate on the content of any manuscripts on this research.

The contract is for the scientific investigation of PCB dechlorination in the St. Lawrence River, and any of our time associated with this research effort is provided as part of the contract. However, should there be the desire by GM for personal effort beyond the contract, eg. in testimony or for advice on specific applications, this would be contracted on a consulting basis.

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Equipment-

The capillary gas chromatograph we presently use for PCB analysis is nearing its capacity to process samples. Other chromatographs are available, but without the necessary data handling capacity for the complex PCB spectra. An integrator interfaced to an IBM compatible microcomputer is an inexpensive way to ensure that we have the sample processing capability required for this project. The computer will also be used for data analysis and for the statistics and modelling component of the project.

A soxlet extraction block is necessary for extracting PCBs from sediment.

Initial Sample Collection-

This is to be contracted by GM as we do not have the resources to collect samples in water as deep as it is over the main contaminated zone of the St. Lawrence River sediments (see specifications on last page).

CORE DRILLING-

To be contracted separately by GM.

Specifications-

Thirty pairs of cores will be taken from the area marked in Fig. 4. Twenty pairs should be taken from the central sampling zone and ten from the outer sampling zone. The members of each pair will be taken as close together as practicable. Each core should be 30 cm (12") deep by 7.5-10 cm (3-4") diameter. After collection, the cores must be closed with air impermeable caps (eg. butyl rubber stoppers) which fit tightly over the cores. These should then be sealed with duct tape to prevent them from becoming aerated. The cores should be labeled with the location from where they were collected and pairs should be indicated. The cores should be shipped to Michigan State as soon as possible after collection.

Further samples of fine textured sediment (clay to silt) should be collected from nearby but uncontaminated sediments. These may be collected from several hundred meters downstream just off the small inlet by control station "OSI-2". These sediments may be collected by shovel or dredge from the surface 30 cm (12") of the sediments. These sediments should immediately be loaded into containers and sealed (paint cans work well for this) and shipped to MSU. Ten gallons of sediment should be collected.

POSSIBLE ENVIRONMENTAL HAZARDS

Input of material into the St. Lawrence River-

In the field experiments, we will be replacing PCBs contaminated sediment into the St. Lawrence River. Forty cores will be placed in the river, half containing "old" and half containing "fresh" PCBs. Each core will contain approximately 200 g of dry sediment with ≈500 μg-PCB/g sediment. Thus the total amount of PCB to be replaced into the river is at most 4 g, of which half is PCBs that were removed from the sediments during sampling. The amount to be placed in the river is absolutely insignificant with respect to what is already in the sediments, will be less than that removed during initial sampling, and all the cores will be removed over the course of the project. There is therefore no environmental hazard from the proposed experiments.

SHEET TITLE: SEDIMENT DISTRIBUTION, PIPELINE LOCATION AND SAMPLING STATIONS		
DRAWN BY: CLG	SCALE: 1" = 100'	PROJ. NO. 269.07
CHECKED BY:		DRWG. NO.
APPROVED BY:	DATE PRINTED: 1/3/86	SHEET OF
DATE:		

RMT INC

Suite 124
1106 East Washington Ave
Madison, WI 53703
Phone: 608-255-2134

SCALE: 1" = 100'
0 100 200 300 FEET

PARALLEL GRAVEL/COBBLE RIDGES WITH GRAVEL/COARSE SAND

COARSE SAND/GRAVEL

N 1818186.5
E 396497.3

COARSE SAND WITH MINOR GRAVEL

SL-25
SL-24
SL-23
SL-14
SL-26
SL-2
SL-20
SL-27
SL-11
SL-12
SL-19
SL-18
SL-17
RL-3

Inner sampling zone

Outer sampling zone

INTAKE PIPELINE

"OSI-1"
N 1,817,970.355
E 396,214.324

PLANT OUTFALL
N1817978
E 396650

Figure 4. Map of Sampling zones.

24

0194 S00 GMM