

REFERENCE
FOR USE IN LIBRARY ONLY

C. C. I. W.
LIBRARY

ACRES CONSULTING SERVICES LIMITED
Niagara Falls, Ontario

March 1974

CANADA CENTRE FOR INLAND WATERS
Burlington, Ontario

Examination of Methods
of Treating Contaminated
Bottom Sediments

EXAMINATION OF METHODS OF TREATING
CONTAMINATED BOTTOM SEDIMENTS

This report has been prepared under contract to the
Canada Centre for Inland Waters, Burlington, Ontario, Canada, by
Acres Consulting Services Limited of Niagara Falls, Ontario.

The views expressed are those of the Consultant, and do
not necessarily reflect those of the Canada Centre for Inland Waters.

This report is provided on a confidential and restricted
basis to both Canadian and United States members of the joint,
international, Working Group on Dredging and Disposal and Dumping
of Materials in the Great Lakes.

It is requested that any use of this report, or the material
contained herein, receive proper reference and acknowledgement of
source.

Agencies interested in follow-up related to the experimental
aspects of this report are invited to contact the Canada Centre for
Inland Waters, for further discussions. At the time of acceptance
of this report (March 1974) the extent of implementation (if any) is
not known.

P.G.Sly
Lakes Research Division
C.C.I.W.
March 12, 1974




TABLE OF CONTENTS

	<u>Page</u>
1 - DESCRIPTION OF WORK	1
2 - BACKGROUND AND APPROACH	2
3 - RATING AND SELECTION OF BASIC TREATMENT PROCESSES	4
3.1 - Summary	4
3.2 - Criteria and Rating System	6
3.3 - Weighting of Criteria	10
3.4 - Processes Considered	11
3.5 - Selection of Processes for Further Evaluation	14
3.5.1 - Extreme Conditions	15
3.5.2 - Other Conditions	17
3.5.3 - Other Treatment Processes	18
3.6 - Selection of Test Procedures	19
4 - RECOMMENDED TEST PROGRAMS	22
4.1 - Summary	22
4.1.1 - Laboratory Test Program	22
4.1.2 - Combined Laboratory and Field Program	23
4.2 - Program of Chemical Testing in Laboratory	23
4.2.1 - Turnover	23
4.2.2 - In Situ Chemical Stabilization	26
4.3 - Aquarium Design and Biological Test Procedures	28
4.4 - Decision on Continuing with a Test Procedure	29
4.5 - Procedure for Selecting Field Program	30
5 - ESTIMATED COST OF LABORATORY TEST PROGRAM	33

TABLES

FIGURES

APPENDIX I - LIST OF REFERENCES

APPENDIX II - TERMS OF REFERENCE

APPENDIX III - SEDIMENT SAMPLING AND ANALYSIS

APPENDIX IV - COMBINED LABORATORY AND FIELD TEST PROGRAM

1 - DESCRIPTION OF WORK

This study examines and rates alternative methods of treating contaminated bottom sediments, and recommends a program of work to evaluate selected processes with high potential.

The full terms of reference defining the scope of the study are given in Appendix II.

2 - BACKGROUND AND APPROACH

The potential for treatment of contaminated bottom sediments by dredging and removal was examined in a previous study (Acres 1972)¹. This study indicated that the environmental impact of dredging operations to improve navigation can be reduced, and that there is a possibility of using planned dredging for the specific purpose of improving the environment (S. Bjork 1972)². The cost involved in removal of contaminated sediments and their deposition in a manner that would not cause subsequent pollution is, however, high. So would be the cost of permanently covering the contaminated sediment with a stable layer of imported material. As an alternative to the above, the study recommended further investigation into the treatment of contaminated sediment in situ.

In the present study, which emphasized in situ methods of treatment, it is recognized that contaminated sediments can cause or accentuate many different environmental problems (Ku & Foess 1973)³, therefore, particular attention is placed on basic methods that are broadly applicable to a variety of conditions. The complexity of treatment of a wide range of contaminants and their separate and synergistic relationships to natural water chemistry, however, will require additional consideration to be given to individual cases.

The report is divided into two parts. In the first, basic treatment processes are rated and a selection made of those processes that merit further evaluation. In the second, a laboratory test and field program is recommended for the technical evaluation of these selected processes.

The principal recommendations made in the report are:

- (a) Where contaminated sediments are underlain by clean sedimentary deposits, contamination of the water body can be retarded by progressive turnover by dredging so that the contaminated material is covered by the clean sedimentary deposit.
- (b) This method of treatment is applicable in a variety of situations. Laboratory tests should be made in aquaria to determine its chemical and biological potential, and the results correlated, if possible, with field tests. If the method proves effective pilot tests could be used for process development.
- (c) Treatment of heavy metal-contaminated sediments by chemical stabilization could prove to be both economical and effective in reducing contamination of the surrounding water body.
- (d) Chemical stabilization by anion exchange of hydrogen sulphide adsorbed to an anion exchange support could reduce soluble release of many heavy metal ions. The process of hydrogen sulphide adsorption should be developed by laboratory tests, and the treated materials tested in aquaria to determine their effectiveness.

If the method proves effective, and correlates with field test data, pilot tests would be in order.

- (e) Progress of research and development on other methods of treatment, such as agglomeration and on-barge oxidation techniques, should be kept under observation for use in special conditions.

3 - RATING AND SELECTION OF BASIC TREATMENT PROCESSES

3.1 - Summary

The procedure used to select basic treatment processes with potential that could merit further evaluation is based on:

- (a) Adoption of six nearly independent considerations as criteria to be used in judging the merits of basic treatment processes.
- (b) The weighting of these criteria to reflect the relative importance of each criterion.
- (c) Assigning to each process a separate rating (0 - 4) pertaining to each of the criteria. Zero being the most favorable rating.

As not all criteria merit equal weight in the selection process, each is given a weight reflecting its relative importance. The six criteria and the weights assigned to them are given below:

<u>Criteria</u>	<u>Weight</u>
Short-term releases to water column	0.1
Long-term releases to water column	0.5
Effect on Benthic Development	0.5
Flexibility of Operation	0.2
Required Technical Development	0.5
Cost	1.0

Four basic processes are considered:

- Agglomeration
- Turnover
- Chemical Stabilization in situ
- Dredging, Processing and Replacing

A comparison is made for two very dissimilar conditions that are known to occur in the Great Lakes.

- (a) A silt-sand material in oxygenated water with release of heavy metals to the food chain.
- (b) A thick industrial harbor deposit with high concentrations of hydrocarbons and industrial wastes of recent origin.

Comparative ratings, given in Tables 1 and 2, indicate that for the above conditions consideration should be given to further evaluation of in situ chemical stabilization of sediments contaminated by heavy metals, and to perfecting methods of overturning heavily contaminated harbor deposits so that they can be effectively sealed, using the original uncontaminated material directly below them.

The weights given to the various criteria favor processes feasible with present technology and capable of direct implementation. The weighting system selected, however, must not be allowed to stop development of other processes such as agglomeration or sophisticated dredging techniques, that have more specialized applications.

3.2 - Criteria and Rating System

As outlined in the preceding summary, six considerations were selected as criteria to be examined in choosing basic treatment processes.

The following paragraphs give the basis upon which the six criteria were selected, and considerations that were taken into account in establishing a rating under each criterion.

(a) Short-Term Release
to Water Column

In most cases, if the sediment is disturbed or mixed with the overlying water, some of the contaminant can be released from the surface of the sediment particles or the interstitial water. In rating treatment processes, each process is considered from the point of view of the mixing likely to take place before final stabilization. In establishing a process rating for this criterion, account must also be given to the role of the redox potential in minimizing the release of soluble phosphorus during the mixing period.

A rating of zero (0), under this criterion, would entail no disturbance of the surface layer, two (2), the removal of the surface layer by controlled dredging, and, four (4), complete mechanical mixing to stimulate rapid decomposition of the contaminant.

(b) Long-Term Release
to Water Column

The release of contaminants from treated bottom sediments will be modified by the chemical and physical changes that occurred during the treatment process.

Generally, long-term releases in undisturbed sediments are controlled by the diffusion rate in the interstitial water (Stumm & Chen)⁴. Also, as the sediment consolidates, further releases can occur by displacement of the interstitial water. Wave and ship action in shallow water can result in the periodic mixing of sediments with resultant contaminant release.

The role of micro-organisms as agents of methylation is an extremely important one. Through their activities, heavy metals such as mercury are released from the sediments in a form which is utilizable by other organisms. In addition, higher organisms can cause vertical transfer of contaminants by physical movements. For example, tubificid undulations, diffusion through rooted plants and the feeding activities of forage fish.

In rating a treatment process the following factors are taken into consideration:

- (i) Change in chemical stability and concentration of contaminants in the surface layer.
- (ii) Change in stability against physical disturbance.
- (iii) Consolidation of sediment after initial settlement.

A rating of four (4) would entail no change in the rate of long-term release, and zero (0), complete removal or permanent stabilization of the contaminant; intermediate numbers being used to index rates of release between these two limits.

(c) Effect on Benthic Fauna

Treatment of the contaminated sediment can result in modification to the benthic fauna, and may be undertaken for this purpose⁵. For instance, treatment that caused bias toward pollutant tolerant species, such as tubificids or some chironomids, would be judged undesirable because it restricts the full development of benthic fauna.

Treatment that encouraged an increase in the number of species, including those less tolerant to low oxygen condition, would be rated beneficial to the benthic fauna.

The rating of zero (0), under this criterion, indicates a wide diversity of species, and four (4) indicates conditions that would not support any form of benthic fauna.

(d) Flexibility to Operate under a Range of Environmental Conditions

The methods examined in this report for treating contaminated bottom sediments pertain to open water conditions.

Additional site factors that could influence the choice of method, or restrict its use to specific conditions only, are:

- (i) Depth of water
- (ii) Exposure to waves and currents
- (iii) Obstruction to navigation
- (iv) Proximity of structures
- (v) Mechanical strength of the sediment

The method of treatment selected for further investigations should be applicable to a variety of site conditions.

A rating of zero (0) under this criterion implies that the same equipment, with minor modifications could be applied in all situations. Four (4) implies that a number of separate types of equipment are required to utilize the method under a variety of conditions found in Canadian lakes and slow flowing rivers.

(e) Required Technical Development

There are obvious merits in any approach that uses only existing equipment. The development, manufacture and use of new equipment entails costs and uncertainties in design, training and contractual procedures. Treatment processes that in part employ standard components are to be preferred over those that require special equipment that is normally not in continued demand.

In rating processes under this criterion, zero (0) implies no equipment development, and four (4), the complete design and development of new equipment.

(f) Cost

Experience has shown that the range of cost of treatment varies widely. Oxygenation of a thin layer of contaminated sediments in a small bay or lake can be effected for a cost of about \$10,000 per square kilometre. Over \$1,000,000 per square kilometre has been spent on inplant treatment of a heavily contaminated sediment. Some typical costs for unit operations relating to dredging and inplant operation have already been published (Acres 1972)¹.

In rating the cost criterion of treatment, zero (0) implies negligible direct costs, reliance being placed on the natural process of oxygenation once the source of pollution is stopped. Ratings one (1) to four (4), for the four treatment processes considered, being in the order of their incremental cost. The cost of treatment for any given rating will naturally depend on the degree of contamination, the composition and depth of the deposit.

3.3 - Weighting of Criteria

The criteria selected for rating basic treatment processes were chosen as being independent of each other so that a choice could be made, either on the basis of one criterion or a combination of several. In most instances the equal weight would not be given to individual ratings under each of the six criteria.

For example, in most cases the major disbenefit to any method of treatment is its cost. The major potential benefits of treatment of contaminated sediments relate to reducing the long-term contamination of the water body and improving the diversity of bottom fauna (benthic development). In this study, therefore, cost has been given the weight of 1.0, and each of the above two major benefits a weight of 0.5. Reduction of the short-term release of contaminants to the water body has been given the lesser weight of 0.1.

The need for further technical development can have a major impact on scheduling and the reliability of cost estimates. Rating under this criterion was also given a weight of 0.5. Flexibility of operation, being of lesser importance, was for this study rated at 0.2.

All the above weightings are subjective only, but are deemed to be representative of weights that would be allocated in many situations when an immediate solution is desirable.

3.4 - Processes Considered

Four processes were selected for consideration as being suited to Canadian conditions, and not yet developed through use in other countries. The processes are described in the following paragraphs.

(a) Agglomeration

In this process fine contaminated sediments or loose floc are treated to form larger particles or pellets that are essentially inert. As presently envisaged, the contaminated material would be carefully dredged, and treated by one of the following methods:

- (i) Appropriate addition would be mixed with the material to form, on settling, insoluble solid particles of appropriate size.
- (ii) The sediments would be pelletized into larger particles which could later be stabilized by a surface coating of inert material.

In either case, the agglomerate would be returned to the lake or river bed and spread in an even layer.

(b) Turnover

In this process contaminated material is buried under clean sediments brought up from below. The approach is to trench, partially backfill with contaminated sediments, and cover again with clean material. Equipment is available to perform these operations (Acres - Faldi)⁷, but its rate of performance is limited. The development of a continuous process along the lines shown in Figure 3 to increase the efficiency and economy of turnover, would be warranted if the initial investigation indicated that the process is effective.

The method is most clearly applicable where there is a readily dredged clean substratum, under a contaminated layer, and the contaminated sediments are dense and not in the form of a loose floc.

(c) Chemical Stabilization
In Situ

Chemical or biochemical treatment of the contaminated sediments can be done in situ by:

- (i) Spreading or mixing an additive with the contaminated material. An example would be the use of a treated anion exchange support to adsorb metal ions.
- (ii) Oxygenation of the lower layer of water to raise its redox potential. This could result in absorption of organic materials, and a reduction in the solubility of phosphorous compounds.
- (iii) Biological seeding: when the water chemistry is favorable, micro-organisms can be introduced to promote the breakdown of certain contaminants.

(d) Dredging, Processing
and Replacing

This process is similar to the agglomeration insofar as the contaminated material is dredged, treated and returned to the lake or river bottom. Processing is done, however, through a treatment plant to remove the contaminant. The contaminant could be removed by rapid oxidation or solvent extraction. An appropriate treatment would have to be designed for each type of problem sediment. The capital cost of a treatment plant with the required flexibility and throughput would be considerable (Everett 1973)⁸.

The following processes were specifically excluded from consideration in this study for the reasons outlined below:

- (i) Dredging and removal of sediments - this had been considered previously (Acres 1972)¹ and a controlled field test completed (S. Bjork 1972)².
- (ii) Covering the sediment with imported clean material - experiments have been made in Sweden (Acres 1972)¹, and work is continuing on a larger scale in Germany under the direction of Professor Ohle⁶.
- (iii) Sealing the sediment surface - this method could be expected to have a long-term adverse effect on benthic growth.
- (iv) Reducing the impact of contaminants - this would normally be a preliminary to any consideration of sediment treatment, or removal of contaminants by plant harvesting. The latter approach has been field tested and equipment developed (S Bjork)².

3.5 - Selection of Processes for Further Evaluation

Processes with potential warranting further evaluation were chosen for rating under each of the criteria outlined in Section 3.2. Evaluation was made for extreme conditions that occur in the Great Lakes and other conditions that are common in small lakes and reservoirs and also in some major rivers. Continued review is suggested of all treatment processes with potential, as their use could be appropriate in special conditions.

3.5.1 - Extreme Conditions

Ratings and overall comparisons were made for two extreme conditions that are known to occur in the Great Lakes:

- A - A contaminated silt-sand material in oxygenated water with release of heavy metals to the food chain.
- B - A thick (> 1 metre) industrial harbor deposit with high concentrations of hydrocarbons and other industrial wastes (> 10 per cent organics, > 10 per cent metals), all of recent origin.

Results of the two comparisons are given in Tables 1 and 2. Four processes outlined in Section 3.4 were rated, and the rating under each criterion was weighted as outlined in Section 3.2 to give a composite overall rating. The individual and composite ratings were used as follows for comparison of processes, and evaluation of their potential for treatment of specific conditions.

Condition A

Heavy Metal Contamination
of Upper Layer in Well-
Consolidated Silty Sand

The overall rating on Table 1 shows that for Condition A, in situ treatment is considered most likely to be successful and economically feasible. A second alternative would be turnover, which could be more suitable in locations where the sediment was not likely to be disturbed by currents or wave action.

Other reasons for this choice are:

- (i) In situ chemical stabilization and turnover provide potentially the lowest cost alternatives.
- (ii) Both will restrict long-term contaminant releases to acceptable values.
- (iii) Chemical stabilization will minimize short-term releases of contaminants, but could have deleterious effects on benthic development.
- (iv) Turnover, while causing more immediate release of contaminants to the water body would allow acceptable benthic development on clean sediments.
- (v) The technical development required to validate either process is within practical limits.
- (vi) The overall cost of in situ chemical stabilization is estimated to be less than that of turnover.

Condition B

Thick Contaminated Deposit in
Harbor with High Concentration of
Hydrocarbon and other Industrial Wastes

The overall rating on Table 2 indicates that for the deep deposit of mixed industrial waste, Condition B, turnover is most likely to be successful

and economically feasible. Very considerable technical development is required if any other process is considered. Success of the method, however, depends on the availability of suitable uncontaminated sediment under or adjacent to the contaminated deposit. Should there be no such material available, nor a suitable disposal site for the contaminated material, consideration would have to be given to dredging and on-site treatment, probably using two or more unit processes. Agglomeration or in situ chemical stabilization would not likely be successful for a heterogeneous mixture of contaminants.

It is, therefore, recommended that a laboratory and field test program be developed to further examine the feasibility, and determine design parameters for treatment by:

- (a) Turnover for heterogeneous deposits.
- (b) Chemical stabilization for heavy metal-contaminated deposits.

3.5.2 - Other Conditions

Less extreme conditions of sediment contamination that should also be considered are:

- (a) Deposits with organic contaminants only.
- (b) Hydrocarbon-saturated sediments.

For the first of these, oxygenation is the treatment most commonly employed. Normally, the whole water body is aerated⁹, but, where this could encourage algae blooms, or other undesirable conditions, aeration can be focused on the hypolimnion (Bjork 1972)².

The second, hydrocarbon-saturated sediments, represents a more stable condition (U.S. Corps of Engineers)¹⁰, but not necessarily a more desirable one. Oil-saturated deposits support little colonization by any organisms¹¹. However, it has been reported that tubificids can survive in oil-contaminated sediments, and strains of bacteria have been found to partially degrade crude oil-contaminated deposits¹².

As dredged oil-contaminated materials cannot generally be used as fill material, treatment of such deposits, if required, might warrant in-plant treatment either by solvent extraction or oxidation at elevated temperatures. This could be done at the dredging site, but would require extensive equipment development.

It is therefore recommended that, outside of the laboratory test program, the behaviour of the reservoirs treated by oxygenation should be kept under constant review. Other studies currently in progress on the underwater degradation of hydrocarbons^{11,12} should be kept under observation.

3.5.3 - Other Treatment Processes

Although further laboratory and field tests have not been suggested for treatment of contaminated sediments

by agglomeration, or processing on a barge by rapid oxidation or solvent extraction, their use in special conditions must not be ignored.

Development work now under way¹³ on solidification of phosphate-contaminated sludge from municipal sewage treatment indicates the possibility of economical agglomeration if the carbonaceous content does not exceed 12 per cent. In such cases the larger particles formed through the agglomeration process could provide a more acceptable substrate for aquatic fauna than prior to treatment.

Rapid oxidation of hydrocarbons and other organic contaminants by incineration is becoming more feasible. Increased development of the fluidized bed¹⁴ as a combustion system gives stability to the incineration process, and allows it to operate more economically.

Also, as mentioned in Section 3.4(b), much development work remains to be done on dredging equipment to make it more suitable for handling of contaminated materials.

3.6 - Selection of Test Procedures

As the processes recommended for further studies have not been extensively used, small-scale testing is required to determine their feasibility. Approximate design parameters are also required prior to initiating large-scale field studies.

Questions that can be answered in part by small-scale tests are:

- (a) The release of material to the water column following treatment.
- (b) The resistance of the sediments to disturbance by currents or wave-induced shear.
- (c) Suitability of the treated sediments as a habitat for various selected invertebrate species.

Several approaches are possible: in situ testing; bench testing and various combinations of the two. An example of in situ testing has been described by Hallberg¹⁵. This method involved regular diving for samples. The major advantage of this approach is that samples of undisturbed material can be taken.

A more common first approach is to bench test, using aquaria containing reconstituted samples of the sediment for the determination of sediment water reaction. This method is suggested for the initial studies that are proposed for examination of the two selected processes. Also, if required, in the laboratory separate tests on the physical stability of the treated surface can be run in a small flume that simulates hydrodynamic shear on the bed, but this is not recommended in the initial test program.

The use of aquaria is advantageous in that it facilitates sampling and gives the operator maximum control over the experimental environment. It has weaknesses, however, in that it is possible to only partially simulate the natural system and, therefore, extrapolation from the aquarium to the lake is potentially misleading.

In aquaria the effect of treatment on biota can be examined by determinations of survival and proliferation of selected species. The same organisms could be used to determine a potential path of contaminant release by measurement of its concentration within the species' bodies.

In addition to periodic measurements in aquaria pertaining directly to the process under examination, data would be obtained to characterize the sediment type. Particular parameters that could affect the treatability of sediments are:

- (i) Minerology
- (ii) Particle size distribution
- (iii) Ion exchange capacity
- (iv) Water content
- (v) Organic content
- (vi) Elemental analysis

It is also possible to combine a series of laboratory tests with field measurements, thereby increasing the reliability of the information obtained.

4 - RECOMMENDED TEST PROGRAMS

4.1 - Summary

The objective of the test programs is to determine the feasibility of in situ treatment of contaminated sediments to reduce the adverse environmental impact. The described programs include purely laboratory testing as well as a combination of laboratory and field experiments.

Two methods of treatment are examined, namely:

- (a) Turnover of heterogeneous deposits.
- (b) Chemical stabilization of heavy metal contaminants.

4.1.1 - Laboratory Test Program

A flow diagram for the proposed laboratory test program is given in Figure 1.

Phase I, which examines treatment by turnover, includes tests for contaminant release, physical stability and support of benthic fauna. Using a single sample, the Phase I test program could be completed in 10 weeks.

Phase II, which examines chemical stabilization, requires a larger test period, as the metal contaminant is traced through the biochemical process.

The time required to complete both phases is 30 weeks. The aquaria that would be used for the test program is

shown diagrammatically in Figure 2. The estimated cost of the proposed test program is \$34,500.

4.1.2 - Combined Laboratory and Field Program

The alternative approach, that of combining the results obtained from complementary laboratory and field studies, is likely to yield the greatest amount of information, and be the most reliable, but involves a considerable expenditure of time and effort to set up and maintain. Such an approach is generally described in Appendix IV.

4.2 - Program of Chemical Testing in Laboratory

The following program of sampling, simulation and chemical tests is proposed.

4.2.1 - Turnover

- (a) Sampling - Sufficient undisturbed cover will be taken from the site to charge the aquaria (0.6 metres square). The cores will extend to at least 0.2 metres beyond the zone of contamination. The sample will be sealed and refrigerated to prevent deterioration. Sufficient water will be taken from the lake to charge the experimental system.
- (b) Simulation of Turnover - The upper 0.15 metres of the contaminated core will be removed, homogenized

and screened to remove the invertebrate fauna. The contaminated sediment will be placed to a thickness of 0.05 metres on the bottom of the experimental vessels in the aquaria (Figure 2), and the vessels filled with lake water.

The lower 0.15 metres of uncontaminated core will then be removed and reworked to break down any structure. The reworked material will be ejected into the water at low velocity and allowed to settle on separate sets of samples of the contaminated sediment to a depth of 0, 0.05 and 0.15 metres respectively.

(c) Analysis

- (i) Before treatment--consolidation, compaction and other physical tests will be done on sediment samples.

Samples from the top 10 millimetres, 10 - 30 millimetres and 30 - 100 millimetres will be taken, homogenized and analyzed for C.O.D., benzene extractables, PO_4 , N, carbon, sulphur, pH, Eh, heavy metals, water content and any other contaminants considered likely in the particular location. Samples of interstitial water will be extracted at depths at 5, 10, 20 and 65 millimetres, and analyzed for the same parameters plus B.O.D. Additional control samples will be obtained for biological testing.

- (ii) During the treatment a sample of the material to be used for covering the sediments will be taken and subjected to the same analyses as the underlying sediments.
- (iii) Seven days after turnover the physical parameters will be examined, and sediment and interstitial water samples will be taken from the top and bottom of the cover layer and the top 10 millimetres of the original layer. These will be subjected to the same analyses as the original samples. The tests will be repeated after a further period of 28 days..
- (iv) In addition to the above tests the overlying water will be sampled before turnover, immediately after the top layer has settled, and at 7 days and 35 days after turnover. Analysis will be for B.O.D., PO_4 , N and heavy metals. During the period of testing, the pH, D.O. and temperature of the overlying water will be maintained constant at the values found in the water column at the sampling area. Additional water used above the sediment samples will be obtained at the time of sampling from the sampling site at a height of 1 metre above the bed.

During the experimental incubation period the aquaria will be aerated, and the water within them circulated to prevent stagnation and to maintain water quality.

If available, the CCIW lake column simulators would be used in lieu of the aquaria. These would optimize experimental control and sampling, as well as increasing the scale of the study.

General methods used in sampling, and chemical and physical analysis are given in Appendix III.

4.2.2 - In Situ Chemical Stabilization

- (a) Sampling - Initially, grab samples will be taken of the contaminated layer for analysis and the design of the treatment process. Later, sufficient undisturbed cores will be taken to charge the aquaria.
- (b) Development of Suggested Treatment Process - It is known that strongly basic anion exchange resins such as Amberlite 1R - 4B, when placed in contact with hydrogen sulphide (H_2S), form stable products containing up to 12 per cent H_2S ¹⁶. These hydrogen sulphide saturated materials are employed to separate selectively the ions of mercury, antimony, cadmium, copper, lead, arsenic and bismuth. These are retained on the surface of the exchange material as metallic sulphides. Early studies of the adsorption of anions¹⁷ by soil clays indicate a relationship between the $SiO_2:R_2O_3$ ratio and the degree of adsorption. As the ratio decreased, the adsorption of anions increased. Possibly, the adsorption power is associated with the presence of

Fe and Al compounds, the adsorption by clay minerals being through the replacement of OH from the clay mineral surfaces¹⁷. Detailed information on the selectivity of these types of clays, and on the intensity of H₂S adsorption, is not presently available, but could be determined by laboratory tests.

It is suggested that clays capable of adsorbing H₂S be used as carriers in the treatment of metal-contaminated sediments. After treatment to adsorb H₂S, they would be mixed with an appropriate ratio of sand to make them most effective in scavenging soluble metals from the overlying water through precipitation as metallic sulphides.

Merits of this approach are:

- (i) Maintenance of free or ionized H₂S in the body of water to acceptable levels.
- (ii) High settling rates due to formation of sulphide layers around clay particle nuclei.
- (iii) Practically inert solid product with no significant change of pH in the sediment.
- (iv) The ratio of sand to clay and adsorbed H₂S can be adjusted for maximum efficiency.

Initial development tests would determine, by measurement of soluble and total sulphide in the surrounding water, the optimal mixture of sand, clay and adsorbed H₂S.

- (c) Simulation and Testing - On development of an optimal mixture of sand, clay and adsorbed H_2S , the aquaria will be charged with reconstituted samples of the top 0.05 metres of metal-contaminated sediment. The contaminated sediments will be covered with 0, 0.05 and 0.10 metres of the optimal mixture, kept under 0.10 metres of water with slow mixing. Dissolved oxygen will be controlled at normal in situ values, and analysis at one-day intervals of sulphide ion maintained. Analysis of water for heavy metals will be made for 1, 2, 7 and 35 days after treatment for comparison with concurrent biological tests.

4.3 - Aquarium Design and Biological Test Procedures

For both the in situ chemical stabilization procedure and the turnover method, the biological analysis procedure to determine the effectiveness of the treatment and the suitability of the resulting substrate as a faunal habitat, will depend in part upon the existing contamination. With sediments treated for toxic components or extensive organic enrichment, survival would be the most significant criterion of suitability for benthic fauna.

Bottom-dwelling invertebrates such as tubificids, amphipods, isopods, chironomid larvae, ephemeropteran larvae, sphaeriids or nematodes could be used, the specific organisms being chosen according to their availability and ease of culture. Generally, three different organisms would be used for each sediment type and treatment tested, and the biological tests

would all have a minimum of three replications. The survival procedure would have a duration of 35 days, with subsampling being done at 2, 7, 14 and 35 days after the initiation of the experiment. The apparatus would be as shown in Figure 2, with each subsampling unit containing five to ten animals (depending upon availability).

At the four prescribed subsampling times, one unit is removed from each block. This yields three replicate subsamples for each organism. The number of living and dead organisms is recorded following screening to remove them from the sediment material. Added information can be gained by blotting and weighing the live animals from each unit (collectively) so that an indication of weight gains can be made. This sampling is continued to the completion of the incubation period.

Should all of the experimental animals be found dead after the first subsampling period, additional live ones could be introduced at 2-day intervals to determine at what point the treated sediments stabilize sufficiently to support fauna. This would largely depend on the sediment and water interface conditions.

4.4 - Decision on Continuing with a Test Procedure

As each specific approach is pursued, two indicators can be used to determine whether the effort should be continued.

These are:

- (a) The release of contaminants to the overlying water body should be reduced by a factor of at least two.
- (b) The treated substrate should support at least as wide a variety of animal species as the controls. Where the controls support no animal life, the test material should support at least one of the test species.

Where a treatment process fails either of these criteria as determined after one month, it can be assumed to have failed and be abandoned. If the tests carried out 7 days after treatment fail the criteria, then the analysis should continue to the end of the month, but work should immediately commence on a modified procedure likely to improve the situation.

4.5 - Procedure for Selecting Field Program

The outcome of the preliminary test program will be recommendations for a full-scale field program to determine the feasibility and results to be expected in a prototype operation. In addition to questions of feasibility, the selection should be based on testing the appropriate approach in an area that is clearly a problem. One potential site for testing the concept of turnover, for example, might be found in Hamilton Harbour. Sites for testing metal release might be found in the basin of the Wabigoon River system.

From the previous tests a decision should be made on whether to proceed with in situ chemical stabilization or turnover. In the event that the site selection is open and both methods turn out to be successful, it is suggested that in situ

stabilization be selected for initial testing, since it is likely to involve the least initial capital expenditure.

The test data should be interpreted, and for in situ stabilization the flow rates, location of chemical addition and accuracies required will be specified. For turnover the minimum vertical control, extent of clearance between removed layer and contaminant, and minimum depth of cover should be specified.

Based on the above parameters, an appropriate apparatus should be selected to treat an area at a rate of 500 square metres per 8-hour day, in depths up to at least 13 metres or the maximum depth at the test site. The field equipment, to be feasible for general application, must satisfy the following requirements in addition to the treatment parameters:

- (a) The width of the treated swath must be at least five times the maximum error in horizontal position.
- (b) Horizontal velocity control must be accurate within the errors permitted in the rate of application of material.
- (c) Overlapping swaths must not place contaminated material back on the surface.
- (d) Variations in underwater topography should be accurately followed.
- (e) The depth of treatment and, in the case of turnover, the depth to cut of clean material, and the depth of the cover layer should be readily controlled from the surface.

- (f) The apparatus should be reliable and capable of operation under adverse conditions, i.e., submerged timber, rocks and rough weather may stop operation temporarily, but should not seriously damage the equipment.
- (g) To the maximum extent possible, equipment previously used in the marine environment should be used.

The dimensions of the field program should be sufficient to allow long-term monitoring of the effectiveness of the treatment. For this purpose the treated lake or bay should be well defined, with a minimum transfer of sediments in and out. In addition, it should either directly support itself or be in close proximity to an area supporting a wide diversity of benthic fauna.

5 - ESTIMATED COST OF
LABORATORY TEST PROGRAM

<u>Classification</u>	<u>Man-Days</u>	<u>Per Diem Rate</u> \$	<u>Cost</u> \$
Executives	15	250	4,000
Project Engineer	20	225	4,500
Chemist/Engineer	30	150	4,500
Biologist	25	150	3,750
Drafting	10	120	1,200
Laboratory Technician	50	120	6,000
Secretarial	10	100	<u>1,000</u>
			<u>24,950</u>

Experimental

Processing of Water and Sediment	6,000
Samples for Biological, Physical and Chemical Parameters, Aquaria and Miscellaneous Supplies for Experimental Work	<u>1,000</u>
	<u>7,000</u>

Estimated Disbursements

Travelling Expenses	800
Communication	550
Report Production	<u>1,200</u>
	<u>2,550</u>

We estimate the total cost for these laboratory studies will be \$34,500. Only one type of sediment would be treated in each phase.

TABLES

TABLE 1

Rating of Basic Treatment Processes -
Condition A - Heavy Metal Contamination
of Upper Layer in Well-
Consolidated Silty Sand

Criteria	Short-Term Release to Wtr Column	Long-Term Release to Wtr Column	Effect on Benthic Develop't	Flexibility of Operation	Required Technical Develop't	Cost	Overall Rating (Weighted Average)
Weight	0.1	0.5	0.5	0.2	0.5	1.0	-
<u>Processes</u>							
Agglomeration	2(0.2)	1(0.5)	2(1.0)	3(0.6)	4(2.0)	3(3.0)	3(1.22)
Turnover	2(0.2)	2(1.0)	2(1.0)	3(0.6)	2(1.0)	2(2.0)	2(0.96)
Chemical Stabilization in situ	0(0.0)	2(1.0)	3(1.5)	3(0.6)	2(1.0)	1(1.0)	1(0.85)
Dredging, Processing & Replacing	2(0.2)	1(0.5)	2(1.0)	3(0.6)	4(2.0)	4(4.0)	4(1.38)

Notes: 1 - Process rating given in full type.
 Weighted rating given in brackets;
 e.g., 4(0.8)

2 - Most favored process has lowest
 weighted average.

TABLE 2

Rating of Basic Treatment Processes -
Condition B - Thick Contaminated (>1.0m)
 Deposit in Harbor with High
 Concentration of Hydrocarbons
 and Industrial Wastes

Criteria	Short-Term Release to Wtr Column	Long-Term Release to Wtr Column	Effect on Benthic Develop't	Flexibility of Operation	Required Technical Develop't	Cost	Overall Rating (Weighted Average)
Weight	0.1	0.5	0.5	0.2	0.5	1.0	-
<u>Processes</u>							
Agglomeration	2(0.2)	2(1.0)	2(1.0)	3(0.6)	4(2.0)	4(4.0)	4(1.42)
Turnover	2(0.2)	2(1.0)	2(1.0)	3(0.6)	3(1.5)	1(1.0)	1(0.88)
Chemical Stabilization in situ	0(0.0)	3(1.5)	3(1.5)	4(0.8)	4(2.0)	2(2.0)	3(1.30)
Dredging, Processing & Replacing	2(0.2)	1(0.5)	2(1.0)	3(0.6)	4(2.0)	3(3.0)	2(1.22)

Notes: 1 - Process rating given in full type.
 Weighted rating given in brackets;
 e.g., 4(0.8)

2 - Most favored process has lowest
 weighted average.

FIGURES

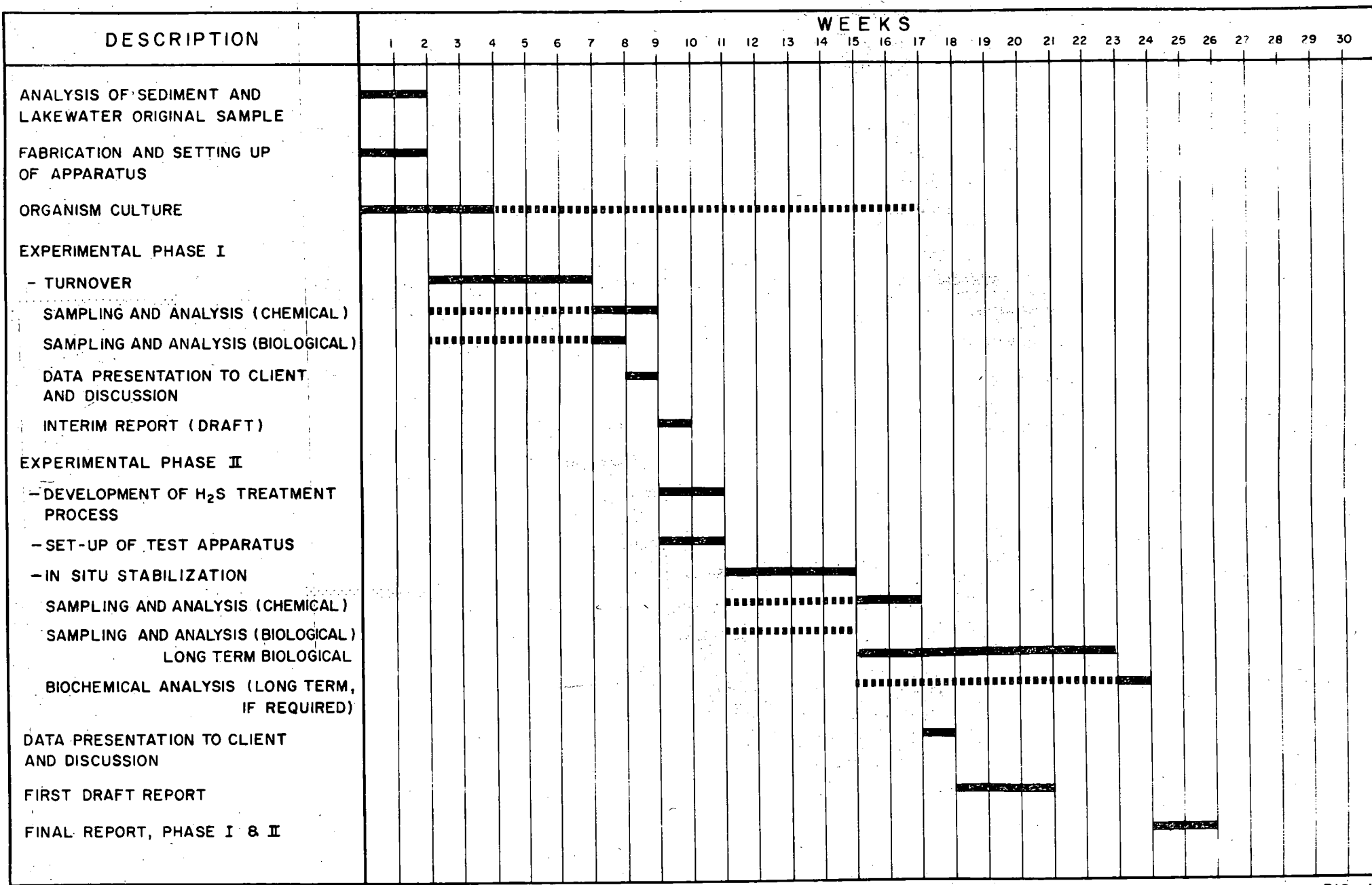
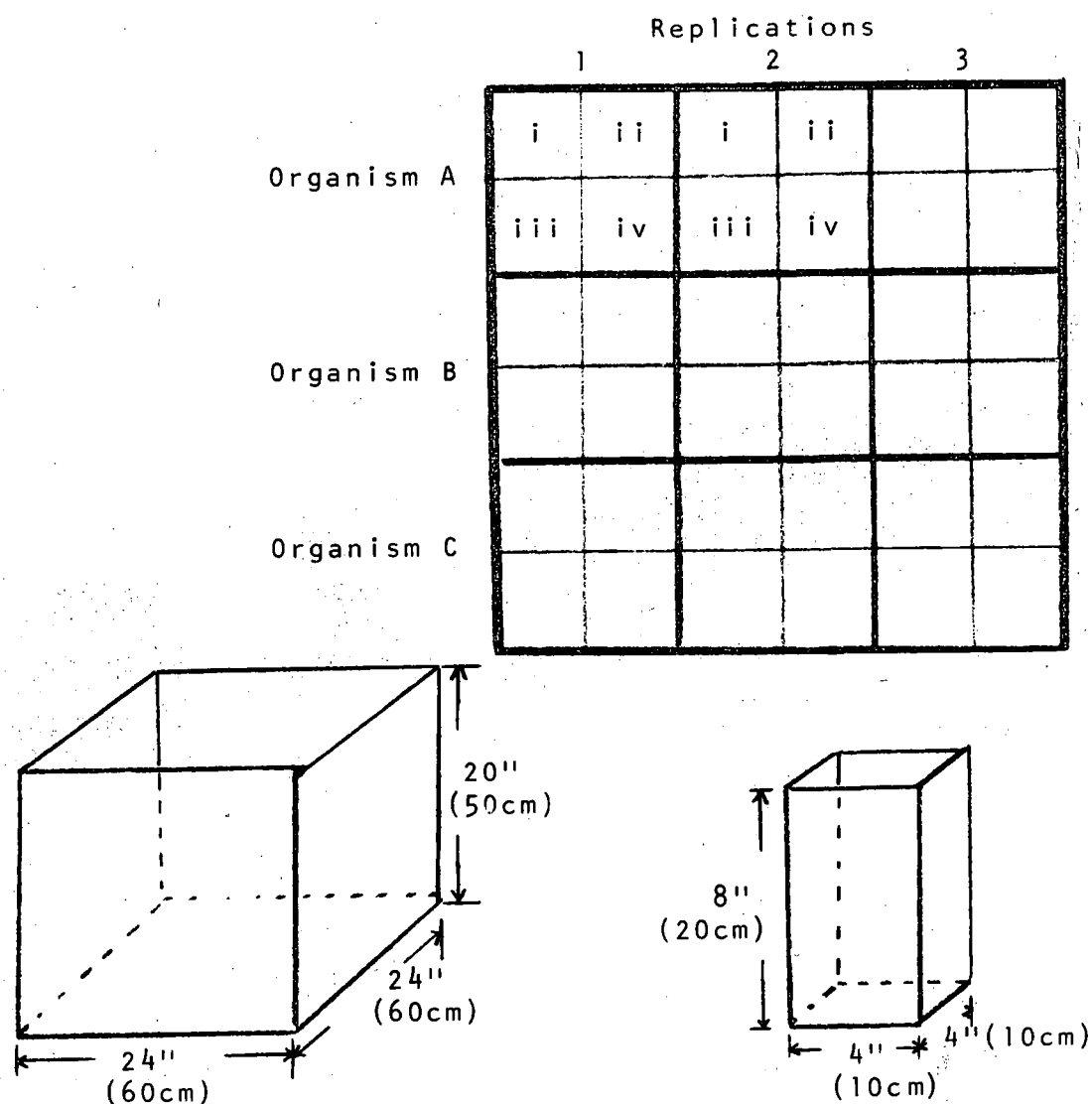


FIGURE 2 - EXPERIMENTAL APPARATUS



The Complete Vessel

A Single Subsampling Unit

For the turnover technique, this apparatus is repeated for each of the three treatments and each subsample (i - iv) consists of a separate 4" x 4" x 8" container. These are all placed within the main experimental vessel; the vessel is filled with approximately 10" (25cm) water and the sediment material is added. Five to ten animals (depending upon availability) are added to each subsampling unit, and the incubation period commenced.

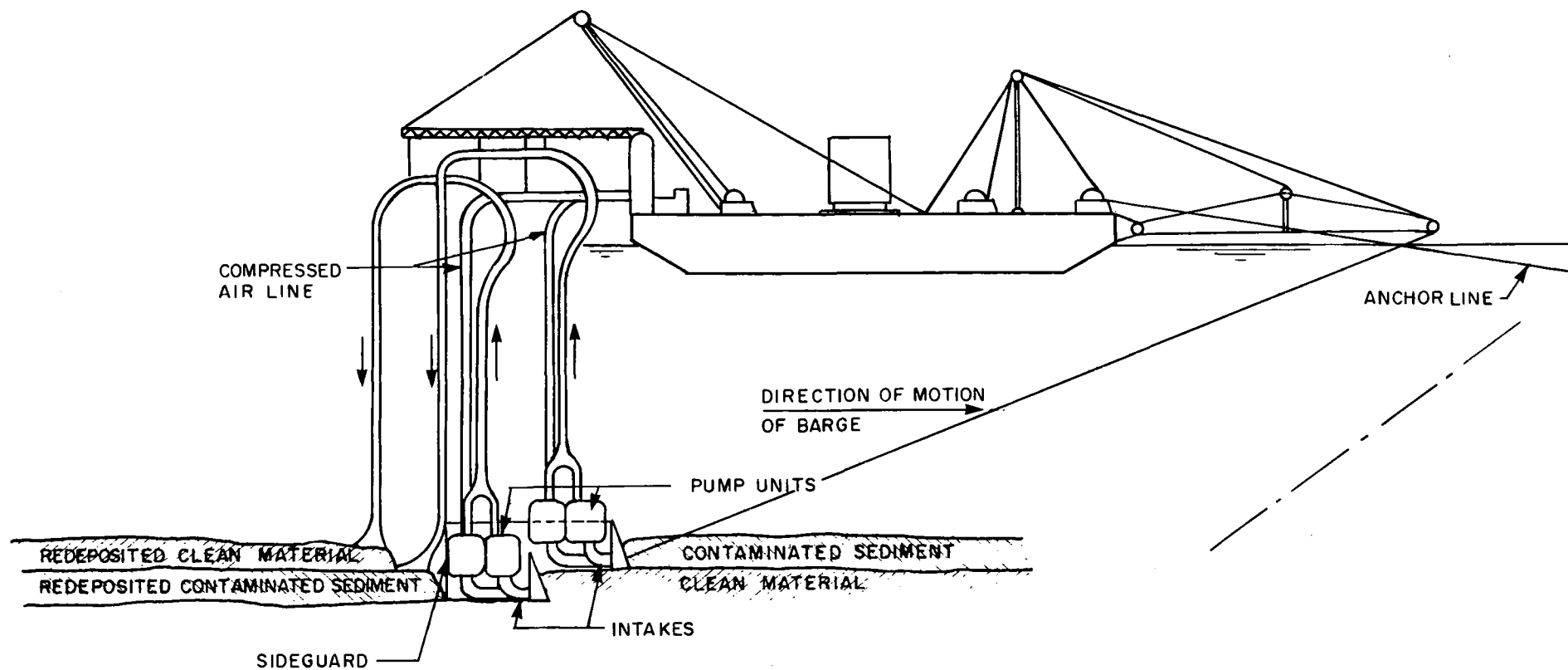


FIGURE 3 - CONTINUOUS PROCESS OF TURNOVER USING TWO AIR PUMP (PNEUMA) UNITS

APPENDIXES

APPENDIX I

LIST OF REFERENCES

- ¹Acres Consulting Services Limited, Niagara Falls. Evaluation Procedures for Removing and Decontaminating Bottom Sediments in the Lower Great Lakes. Report prepared for the Canada Centre for Inland Waters, Dept. of the Environment, Canada, 1972.
- ²S. Bjork. Swedish Lake Restoration Program Gets Results. Ambio, Vol. 1(5), 1972.
- ³W. C. Ku and G. W. Foess, Literature Review on Aquatic Sediments, Journal of Water Pollution Control Federation, Vol. 45(6), p. 1301.
- ⁴W. Stumm and Y. S. Chen, Unpublished data from Harvard University.
- ⁵G. Andersson, G. Cronbert and C. Gelin. Planktonic Changes Following the Restoration of Lake Trummen, Sweden. Ambio Vol. 2, No. 1-2, 1973.
- ⁶W. Ohle. Private Communication, Max-Planck Institut fur Limnologic, Plon, Holstein, Germany.
- ⁷Faldi. Private Communication, SIRSI, Firenze, Italy
- ⁸J. G. Everett. Recent Developments in Heat Treatment. J. Water Pollution Federation, Vol. 72(4), 1973
- ⁹D. Beal and A. Clark. An Evaluation of the Effects of the Scotch Block Reservoir on the Water Quality of Middle Oakville Creek, Water Quality Branch of the Ministry of the Environment, 1973.
- ¹⁰U.S. Corps of Engineers. Dredging and Water Quality Problems in the Great Lakes, Vol. 1-12, 1969/70.
- ¹¹L. Bengtsson and H. Berggren. The Bottom Fauna in an Oil Contaminated Lake. Ambio, Vol. 1(5), 1972.
- ¹²H. Kater et al. Microbial Degradation of a Louisiana Crude Oil in Flaska and under Simulated Field Conditions. Proc. API/EPA/USCG Joint Conference on Prevention and Control of Oil Spills, Amer. Petroleum Inst. 1971

- ¹³ Acres Consulting Services, Niagara Falls, Ontario. Solidification of Phosphate Sludges Using Industrial Sulphate Waste & Fly Ash. Prepared for the Canada Centre for Inland Waters, Department of Environment, Canada. 1972.
- ¹⁴ Copeland Process Limited. Modern Fluid Bed Combustion Techniques Applied to the Destruction of Industrial and Municipal Wastes.
- ¹⁵ R. O. Hallbert, L. E. Bagander, A. G. Engrall and F. A. Schippel. Method for Studying Geochemistry of Sediment - Water Interface, Ambio, Vol. 1(2), 1972.
- ¹⁶ Gaddis, S. J. Chem. Ed., 13, p.327-328. 1942.
- ¹⁷ F. E. Bear. Chemistry of Soil, 2nd Ed. Reinhold Pub. 1964, Chpt. 4 - Cation and Anion Exchange Phenomena.
- ¹⁸ Standard Methods, APHA, Ed. 13, 1971, p. 495.
- ¹⁹ Standard Methods, APHA, Ed. 13, 1971, p. 254.
- ²⁰ Standard Methods, APHA, Ed. 13, 1971, p. 257.
- ²¹ J. A. Maxwell. Rock and Mineral Analysis, John Wiley & Sons, N. Y. pp. 430 - 433, 1968.
- ²² Standard Methods, APHA, Ed. 13, 1971, p. 453.
- ²³ Standard Methods, APHA, Ed. 12, 1965, p. 531.
- ²⁴ Standard Methods for the Examination of Water and Waste Water. 13th Edition, 1971, p. 555.
- ²⁵ T. O. Meiggs. A Revised Method for the Determination of Total Sulphide in Water and Bottom Sediments. Lake Michigan Basin Office, Chicago, Illinois, 1966.
- ²⁶ Y. K. Chau and H. Saitoh. Determination of Submicrogram Quantities of Mercury in Lake Waters. Environmental Science and Technology, Vol. 4, No. 10, 1970, p. 839.

- ²⁷ W. R. Hatch and W. L. Ott. Determination of Submicrogram Quantities of Mercury by Atomic Absorption Spectrophotometry. Analytical Chemistry. Vol. 40, No. 12, 1968, p. 2085.
- ²⁸ W. T. Oliver and H. S. Funnell. The Quantitative Determination of Mercury in Animal Tissues. Journal American Veterinary Research, Oct. 1958, p. 185.
- ²⁹ Standard Methods, APHA, Ed. 13, 1971, p. 64.

APPENDIX II

TERMS OF REFERENCE

Requirements

Examination of methods of treating contaminated bottom sediments, and preparation of a program of work designed to identify and develop processes with high potential.

Scope of Work

Potential methods of treating contaminated bottom sediments that release undesirable material to the water column, or exert a high oxygen demand, will be briefly examined. This examination will include full consideration of methods of mechanical inversion of the bottom layers to effect burial of contaminated material, and treatment such as pelletizing and chemical stabilization to reduce the rate of contaminant release. Reference will be made to previous studies on methods of dredging and disposal, and only cursory consideration will be given to methods of bottom sealing that could have a long-term adverse effect on the biota.

Following the examination of potential methods of treatment, a program will be developed to evaluate selected process with respect to:

- Requirements and availability of mechanical equipment to handle bottom sediments in conformity with process needs.
- Physical stability of treated sediments under the action of winds and currents.
- Rate of chemical release from treated sediments.
- Suitability of treated sediments as substrata for various forms of aquatic fauna.

The program to be developed will include bench testing of promising processes, laboratory investigations on the rate of chemical release from treated sediments and response of biota to the resultant product. The program will also include examination of the engineering feasibility of selected processes and cost studies of process development and operation.

APPENDIX III

SEDIMENT SAMPLING AND ANALYSIS

A brief description of the chemical analysis procedures recommended for determining particle size, ion exchange capacity and other parameters are given in the following paragraphs.

(a) - Sample Preservation and Preparation

Sediment cores require special handling to ensure minimal chemical changes. Cores, including the turbid surface layer, should be sealed and frozen as quickly as possible after collection.

Some chemical changes would occur on the outer surface of the samples, as indicated by an oxidized layer of iron. This outer surface would be removed before the sample is mixed or homogenized.

The pore water from the sediments should be removed for analysis by applying a vacuum to a known quantity of sediments, taking care to minimize any disturbance of the sediments.

(b) - Oxidation-Reduction Potential (Eh)

Eh should be measured by inserting the standard platinum electrode just under the surface of the undisturbed sediments (about one-half inch).

(c) - Chemical Oxygen Demand

This is measured using a standard potassium dichromate oxidation method as described in Standard Methods. (18)

(d) - Oxygen Levels

Dissolved oxygen can be measured using an oxygen-sensitive electrode and meter.

(e) - Oil and Grease

Oil and grease, as separated by benzene extraction following acidification, would be ascertained by standard procedure as described in Standard Methods (19).

(f) - Carbon

Gravimetric measurement of the carbon dioxide formed from the ignition of carbon-containing materials is used to evaluate the total carbon (20).

(g) - Inorganic Carbon

Inorganic carbon is determined using the common gravimetric method described by Maxwell (21).

(h) - Organic Carbon

Organic carbon is calculated by taking the difference between the percentage of total carbon and that of organic carbon.

(i) - Nitrogen

Free ammonia nitrogen is determined by a standard titrametric technique (22) and organic nitrogen is determined using a standard Kjeldahl technique.

(j) - Phosphorus in Sediments

Total soluble phosphate is determined using a standard ammonium molybdate colourimetric procedure (23), while total phosphate is also colourimetrically ascertained following work-up.

(k) - Total Sulphide

After preparation according to Standard Methods (24, 25), total sulphide is measured colourimetrically.

(l) - Trace Metals

Trace metals, excluding mercury, cadmium, lead mercury, arsenic, zinc and total mercury, are measured using an atomic absorption spectrophotometer (26, 27, 28).

(m) - Arsenic

Inorganic arsenic is reduced to arsine and measured using a colourimetric technique (29).

(n) - Cadmium, Lead, and Zinc

Cadmium, lead and zinc will be determined by atomic absorption spectrophotometry.

WATER SAMPLE

The water samples for various chemical parameters are analyzed in accordance with the recommended procedures by the Water Quality Division, Department of Fisheries and Forestry, Ottawa, American Public Health Association and the Environmental Protection Agency.

CATION EXCHANGE CAPACITY (CEC)

The metal ions are leached from a known amount of sediments with NH_4OAc . The leachate obtained is used for the determination of exchangeable metal ion on an atomic absorption spectrophotometer. The sediments are then washed with ethanol and leached with sodium chloride solution. This final leachate is analyzed for NH_4 .

PARTICLE-SIZE ANALYSIS OF BOTTOM SEDIMENTS

The distribution of particle sizes larger than 75 microns (retained on a No. 200 sieve) can be determined by sieving, and particles between 75 and 5 microns in size should be determined by sedimentation, using an hydrometer to secure the necessary data. The clay fraction of less than 5 microns is determined by a conventional pipette method or by microscopic technique.

APPENDIX IV

COMBINED LABORATORY AND FIELD TEST PROGRAM

The laboratory aspect of this program would be essentially the same as described in Section 4 of this report. The scope of the bench study could be somewhat reduced however, in view of the additional information to be gained from the field experimentation.

1 - Field Tests

The initial site selection for the small scale field testing would be governed by the procedure to be tested. For example, the turnover process would be tested in an area with a layer of well-consolidated industrial deposits (along the south shore of Hamilton Harbour for example), and in waters approximately 10 metres deep.

The in situ stabilization process would be tested in an area preferably of silty-sand, which contains high concentrations of heavy metals. The Western Niagara Basin of Lake Ontario offers likely locations.*

Such factors as thermal stratification, oxygen tension, bottom topography, subsurface currents and circulation, will have an influence on where and when the field programs are executed. The final site selections for either process would be made following an examination of the chemistry, biota and physical characteristics of the sediments and overlying water.

(a) - Turnover

During the initial site selection, the sediments would be tested for consolidation, texture, chemistry, and biotic components, the overlying water would be chemically examined and the submerged currents and general contour of the site would be examined. These would be used to ascertain the suitability of the site and to optimize the size of the treatment area with respect to the current velocities at the sediments/water interface.

*The Distribution of Mercury in the Sediments of Lake Ontario, R.L. Thomas, Canadian Journal of Earth Sciences, q, 636 (1972).

The next phase would involve the development of a suitable device and manual method of turnover which creates only minor disturbance and which results in the smoothest possible surface upon completion. The exact field site would then be designated and marked both at the bottom as well as at the water surface.

The turnover technique would involve:

- Hand turnover (by a diver) of a submerged circular plot approximately 10-foot (2.5 m) radius.
- The exact dimensions to be large enough to allow boundary layer stability to be attained across the treatment zone.
- A partial limno-corral, or no enclosure at all, would be employed so that natural exchanges across the sediment/water interface could occur. The system would be left open to allow recolonization of the treatment zone by benthic fauna from outside.
- The "control" would be a similar-sized plot in the same general area as the treatment plot, but which had not been turned over.
- Both the control and the treatment plot would be sampled prior to testing to make a detailed evaluation of the sediment chemistry and physical composition, the chemical character of the overlying water, as well as an examination of the biotic complement of each. They should be similar initially.
- Sampling would be carried out prior to turnover, during the turnover process, one hour after its completion, five hours, two days, one week, two weeks, five weeks, generally in keeping with the laboratory sampling schedule. Sampling over a longer term would be decided after the first five weeks.
- Sampling would either be carried out by a diver or by remote devices such as corers, Ekman dredges or Kemmerer water bottles. The former would be required for the "during process" samples, as well as for micro-sampling of interstitial water and samples from the sediment/water interface.

(b) - In Situ Stabilization

Following the initial site selection, similar tests on the water quality, sediments, and biota would be carried out as described for the turnover process. The methodology would be basically the same with a partial limno-corral likely employed to contain the treatment area. The treatment, once decided upon using the aquarium set-up would be manually applied to a circular plot, similar to that described for the turnover process. The sampling regime would continue for several months, with samples being taken before treatment, during treatment, six hours, one day, two days, one week, five weeks, ten weeks after treatment. At the end of this time, incubation could be maintained if warranted by the information gained. With the stabilization process the maintenance of normal circulation within the test plot is especially important due to the highly important role played by living organisms in the uptake and release of heavy metals.

2 - Combining Results

The aquarium testing program would have its greatest reliability for short-term investigation, since maintenance of water quality within the test vessels will be difficult. For this reason there would be greater weight placed upon the long term (greater than one week) data obtained from the field study.

There is an advantage in utilizing both a field and a laboratory program in that it allows the experimenter to check the reliability of his lab set-up against the "real" situation as well as pointing out specific areas where lack of control in the field situation could be potentially misleading, e.g. stratification, or unusual bottom topography.