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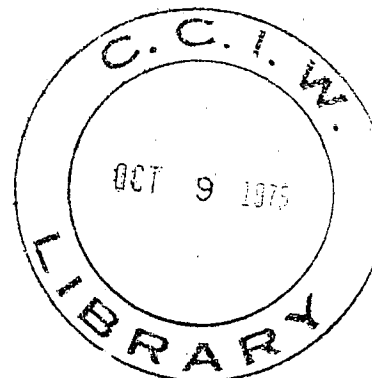


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DREDGING STUDIES: ELUTRIATION EXPERIMENTS
AND THE AVAILABILITY OF
Fe, Mn, P, Zn AND DISSOLVED ORGANIC CARBON
FROM DREDGED SPOILS
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DREDGING STUDIES: ELUTRIATION EXPERIMENTS
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V. CHEAM and P. G. SLY

Canada Centre for Inland Waters
Process Research Division
Burlington, Ontario

August 1975

ABSTRACT

It has been demonstrated that disposal of dredged sediments by dumping in open lake waters (oxic, pH 7-8) results in the release of Mn, P, Zn, dissolved organic carbon, and possibly Fe. The larger the body of receiving water, the greater the amount of release and the smaller the resulting concentration. Even though the highest percentage release does not appear to exceed 1% of total sediment load for the above elements, the net amount released can be large (especially where sediments are highly "polluted"). Nutrient releases may significantly affect local trophic states, especially where conditions are already critical (particularly where receiving waters are already stratified and exhibit D.O. stress or depletion).

It would seem that the rate of dilution is of major importance when considering the disposal of dredged materials in Great Lakes' waters.

INTRODUCTION

In both Canada and the United States, dredging and the disposal of dredged materials are subject to regulation. Recent studies (IWG final report)* have suggested, however, that it is not possible to detail a single set of criteria which may be satisfactorily applied to all cases of dredging activities. To assist in the provision of more effective guidelines for the issue of permits, the U.S. Environmental Protection Agency (E. P. A.) and the U.S. Corps of Engineers (U. S. C. E.) have suggested that, in addition to the use of bulk sediment composition (E. P. A.), further assessment be based upon the use of the standard elutriate test (U. S. C. E. and E. P. A.).

In a case examination of a theoretical dredging project, Cheam et al.¹ have shown that a further improvement of the methods is desirable (At the time of completing the final revisions to this text, it is understood that revisions to the standard elutriate test will soon be brought into effect).

The objectives of the studies reported here are:

- 1) To analyze selected sediment samples and elutriates for Cd, Fe, Hg, Mn, P, Pb, Zn, and organic matter, using the methodology proposed by E. P. A. and U. S. C. E. (above);

* International Working Group (IWG) on the abatement and control of pollution from dredging activities. Final report in preparation. Submitted in compliance with Annex 6 of the Great Lakes Water Quality Agreement (June 1975 Draft).

- 2) To compare the resultant concentration values with those established by E. P. A. and U. S. C. E. (as criteria/guidelines);
- 3) To assess the implications of using such criteria based upon a series of simulatory test cases and to discuss the validity of such an approach.

In attempting to meet these objectives, the report first describes, briefly, the experiments and methods; following this, the results and discussions centre around the release behaviour of P, heavy metals, and organic carbon, complexing capacity and stability; further comments with respect to DO, Eh, pH and temperature are also drawn together (based largely on data from the Chemex report^{5b}). Conclusions and comments provide an assessment of our present level of understanding and give some guidance as to the need for future research.

EXPERIMENTAL

Small Scale Elutriation Experiments

The procedures outlined by Keely and Engler^{2a} were closely followed and some suggestions by Lee and Pumb^{2b} on varying the ratio and time of mixing were also incorporated. The experimental definitions are given in Table 1, where mixing, settling,

and centrifugation time are given for each sediment-water mixture. The % water used for a particular mixture is defined as: $(100 \text{ volume water added}) / (\text{Volume water added} + \text{volume wet sediment})$. For convenient reference, the standard elutriate is designated by X_4 , where 4 refers to four volumes of disposal site water mixed with one volume of wet sediment (Table 1).

To generalize, an elutriate is here defined as the filtrate (through 0.45 μ membrane filter) of the liquid part of a certain sediment-water mixture, which has been prepared according to predetermined specifications as defined in Table 1. The elutriates X_N , prepared from N volumes of disposal site water and one volume of wet sediment, are characterized by 30 minutes mixing time, one hour settling time, and one hour centrifugation time. X_N also represents a certain parameter -- say phosphorus concentration -- in the elutriate X_N . Within this generalization, X_∞ is used to refer to the disposal site lake water whereas X_0 may be used to represent pore water. (Note: Ideally, X_∞ should represent distilled water, whereas X_∞' the disposal site lake water; in the same fashion, X_0 should represent dry sediment, whereas X_0' pore water. This way, X_∞ (smallest concentration) and X_0 (greatest concentration) would, as they should, overlap X_∞' and X_0' in plots of concentration vs. % water. Then X_N would ideally refer to an elutriate prepared from distilled water and X_N' to that prepared from disposal site

lake water. As in this report lakewater is almost exclusively used, the "prime" should appear on most elutriates, but for convenience sake, is omitted throughout).

The characteristics of other elutriates -- V_N , Y_N , Z_N , X_N , CS_N -- are also given in Table 1. (In all cases, sediment samples are representative of proposed dredging sites.)

An unfiltered sample is defined as the supernatant obtained immediately before the filtration step. The volume of water used in each test was usually less than 10 litres.

Large Scale Elutriation - Lake Column Simulators

Description: The simulator consists of a group of eight vertical cylindrical open-topped tanks (columns), a working platform structure with access ladder and work tables, refrigeration for cooling the lower section of each tank, overhead fluorescent lighting (2 per tank), sediment transfer pump and loop piping, and 1000-lb. hoist on a monorail servicing four columns. The detailed specifications are listed in Techwest Operation Manual (Techwest Enterprises Ltd., Vancouver, Canada: Operation Manual for Lake Column Simulator). For each column, the main features of interest are: diameter = 1 meter; height 4.5 meters; volume 3.5 m^3 ; sampling ports at 10 mm intervals. Temperature can be controlled to $\pm 1^\circ\text{C}$ by the cooling jacket enveloping the bottom 2 metres of

each column, thus permitting the development of thermal stratification within each simulation column.

Experiment:

The elutriation experiments were designed to simulate the response of disposal site water columns which received disposal of dredged sediments by surface dumping. To simulate dumping, we used plastic buckets holding 10 Kg of wet sediment. In total, 40 Kg of wet sediment were added to a stratified column; 100 Kg to a mixed column; and 180 Kg to an initially mixed but subsequently stratified column. Characteristics of these elutriates, which are designated by CS_N , are also given in Table 1. It should be noted however that here there was no vigorous mixing as in the small scale experiments but instead, a more gentle agitation induced by air bubbling.

The sediment samples used in simulators were taken from Kettle Creek at Port Stanley, Lake Erie (see also Chemex report^{5b}). Mixing of the simulated column water was effected by bubbling air about 1/3 meter below the thermocline at a rate fast enough to produce visible movement at the water surface. E_h , DO, pH and temperature were measured using a Hydrolab Surveyor, Model 6D; the sonde (model 700), containing the probes was slowly immersed to the desired depth and probe stabilization at test depths required 2-5 minutes. After use, the sonde was stored in a bucket of clean

water, preferably distilled water. Water samples were taken just before, one hour after, and 10 days after sediment dumping and were analyzed at C.C.I.W. together with those elutriates described above.

Most chemical analyses were provided by Water Quality Branch, C.C.I.W., using the methods described by Traversy³. Complexing capacity was measured using anodic stripping voltammetry⁴. XAD-2 (neutral macroreticular resin beads) columns were kindly provided by M.E. Fox, C.C.I.W.

RESULTS AND DISCUSSIONS

In case elutriation tests involving Hamilton Harbour sediment and Lake Ontario water¹, it was observed that for total P, $X_4 > 1.5 X_{\infty}$. Following these, additional and similar experiments were performed with the hope of further appreciating the release mechanism of phosphorus as well as other constituents from the sediment. The results of these tests are shown in Tables 2-6 (small scale experiments) and Table 7 (Lake Column simulators).

The concentrations of all chemical constituents in unfiltered solutions are often higher than the corresponding filtered solutions. However, these unfiltered samples were not regularly obtained as part of the experiment and their results

are not treated in detail in the following discussions.

The Release Behaviour of Phosphorus

The concentration of total P in X and CS elutriates is plotted vs. % water used in Fig. 1, where the points representing a particular test and sediment sample are differentiated from others by use of symbols. In this figure, one can see that the P concentrations in the original waters range from 10 to 100 ppb (most are between 10-30 ppb), whereas those in the elutriates range from 20 to 300 ppb. In this data there is a definite indication that increasing concentrations of P are related to decreasing % water used. Except for the magnitude, the general release pattern is the same for all sediment samples used.

With the exception of the Lake St. Clair case, which will be discussed later, one sees that $X_4 > 1.5 X_{\infty}$ (apparently unacceptable cases according to ocean dumping criteria) yet most values of X_4 probably do not exceed the maximum permissible limit for drinking water or aquatic life as defined by existing requirements. If the bulk composition criteria (E. P. A.) shown in Table 8 are applied to these sample data, it may be seen that in each sample case some constituent concentrations exceed the criteria while others do not. In a real situation, should one consider the issuance of a dredging permit or not, based on this

type of evidence, evidently the situation is not clear.

It should be noticed, also, that in the V and Y tests the concentration of 1:4 elutriate is greater than 1.5 times the original concentration (Tables 2-5). In fact, all the 1:8 tests show the same inequality, including the Z₈ test which used a 50-50 mixture of waters from dredging and disposal site (Table 5). In Fig. 1 we have also plotted the results from the V tests. Although these indicate P release, they do so in a somewhat more irregular fashion as compared to the X tests. We have decided, therefore, to discuss further points, mainly in references to X tests (unless otherwise specified). Results from lake column simulators, CS, are also plotted in this figure and they fit well with the other Port Stanley-Kettle Creek points in spite of the fact that there was little vigorous mixing in these experiments. It should be noted, however, that in ten days, P values decreased significantly in all three CS elutriates.

While absolute values are immediately useful, knowledge of the concentration ratios is also often informative. Thus we have plotted the ratio $\frac{(\text{ppm})_x}{(\text{ppm})_{\text{sed}}}$ vs. % water used, where $(\text{ppm})_x$ is the concentration of P in ppm in the elutriates X and $(\text{ppm})_{\text{sed}}$ is that in corresponding sediments (Fig. 2). Again, even though the points are scattered, a definite trend is evident. One can imagine a curve starting at point (100%, 2.5) and rising steadily to (80%, 8-10). Lacking data at % water added lower than 80%, we

can only speculate what might be in this range. But we have plotted, on the same figure, the data of interstitial waters (IW)⁶ and corresponding sediments^{7a} at 0% water added. It may be seen that the ratio of 80% water used is practically the same as that at 0% water used (IW), which suggests that the concentration of P in interstitial water may be the saturation value with respect to P in sediment. If this is so, then one may tentatively express it in the following equation:

$$P_{sed} \rightleftharpoons P_{IW} \dots\dots\dots (1)$$

A series of elutriation tests on the whole range of % water added and at similar conditions to those of IW would be highly desirable. It may be possible, then, to discern whether the ratio continues to rise after 80% water. If it does not rise, equation (1) is probably valid, and this may be a useful technique to derive concentrations in pore waters.

We tried to analyze these data in terms of a linear least square fitting of the form:

$$\begin{aligned} \text{(concentration ratio)} \cdot 100,000 = & a + b (\% \text{ water}) \\ & + c (\% \text{ water})^2 \\ & + d (\% \text{ water})^3 \dots\dots\dots (2) \end{aligned}$$

Although both the second and third order equations give better fit than the first order, they do give a < 0 which is irrelevant to actual

cases. The first order equation gives an intercept of 35 ± 4 , corresponding to a hypothetical ratio of 35×10^{-5} for $(\text{ppm})_{IW}/(\text{ppm})_{sed}$. We have used this number to calculate the variation of $(\text{ppm})_{IW}$ with $(\text{ppm})_{sed}$, which is shown in the following table:

$(\text{ppm})_{sed}$	250	500	1000	1500	2000
$(\text{ppm})_{IW}(\text{calctd})$.088	.175	.35	.53	.70

Compared to interstitial water values of Nriagu and Dell⁶, these calculated $(\text{ppm})_{IW}$ are high and do not appear to be representative P values for Lake Erie pore waters.

Sutherland et al.⁸ observed that, for water extracted from four bottom sediment samples, phosphorus concentrations represent water exactly in equilibrium with respect to hydroxyapatite. This implies that equation (1) is valid only if hydroxyapatite is present in sediments as the dominant phosphate mineral. This is probably not the case since, according to Nriagu and Dell⁶, the stable phosphate minerals in the Great Lakes sediments are vivianite, reddingite and anapite. It is questionable, therefore, if equation (1) may be appropriate under these circumstances.

The fact that we have a definite slope in the portion 100% - 80% in Fig. 2 should tell us that, although $P_{sed} \gg P_{IW}$, only a small portion of P_{sed} is released following each test. The next question is then what the releasable fraction is.

Fig. 3 could shed some light on this question. Here we plot the percentage of P released, defined as $100 P_{\text{released}}/P_{\text{sed}}$ against % water added, where P_{released} is the amount of total P released after each elutriation process and is assumed to be:

$$P_{\text{released}} = V (C_f - C_i) \dots\dots\dots (3)$$

in which

V = volume of lake water used in each test,
expressed in liters -- relative to one
litre of wet sediment;

C_f = concentration of P in elutriate, ppm;

C_i = concentration of P in original water, ppm;

P_{released} = weight in mg of total P released (contribution from interstitial water, dissolution or desorption; under our experiment conditions, the contribution order is probably: desorption > IW > dissolution);

P_{sed} = weight in mg of total P in one litre of wet sediment calculated from: concentration in ppm, % water content, and particle density which is assumed to be 2.6 g/cm^3 (Mudroch's thesis)⁹.

In Fig. 3, the stars represent the PS2 elutriate data points where a smooth representative curve could be drawn as shown. The intercept of 100% water added could be ~9, whereas that of 0% water should

be zero according to equation (3). The solid triangles of PSI points (samples from Port Stanley-Turning Circle) which again might be represented by a smooth curve somewhat similar to the star symbols. Another similar curve could be drawn for the solid squares (Wheatley Harbor sediments, PPI). If we draw another similar line passing through the coordinates (80%, 4), one sees that most points fall within that strip of area limited by the curves passing by coordinates (80%, 1.5) and (80%, 4).

As the lines should originate at (0%, 0) point, the range of intercepts of % P_{released} - axis could be large. In our Fig. 3, the range may be 5-15, suggesting that the P_{released} could be 0.15% of total P in sediment at infinite dilution, where the effective concentration approaches the predisposal value (Fig. 1). This means that the dumping of dredged materials containing high concentration of P into these waters would result in large amount of P released, even though the post-disposal concentration is low. In short, the higher the degree of dilution, the greater the % release and the smaller the effective concentration.

Referring now to the two circle points that are outside the aforementioned area, the solid circle represents this work, whereas the other is taken from the Chemex report^{5a}; the sediments are from Lake St. Clair in both cases. One feature characteristic of Lake St. Clair sediment is that there is a large variation in particle mean

size and in total P as compared to sediments from Port Stanley and Bronte Harbor^{5a}. Without suggesting that this is the only cause or saying that the two points are wrong, we feel that more refined experimentation would bring the points closer to the stated area.

Heavy metals: Fe, Mn, Zn, Hg, Cd, and Pb

Williams^{7a} has postulated that there is a relationship between orthophosphate, iron and manganese in sediments of Lake Erie and of some other locations in the Great Lakes. This correlation is such that there are many more Fe atoms than P and Mn. In interstitial waters⁶, a similar relationship was observed; in μ mole/l, the overall ratio is Fe:Mn:P = 25:15:1. But our observations indicate that some P and Mn concentrations may be higher than that of Fe (Figs. 4, 1). Furthermore, although the star symbols indicate release of these elements, the squares (Wheatly Harbor sediment) indicate removal of Fe (with release of P and Mn). These observations may be explained by oxidation and subsequent precipitation of iron hydroxide since the medium is oxic and the mixing-shaking steps can only speed up an already fast oxidation reaction.

On the other hand, if the dissolved oxygen level is low, one might expect to see release of Fe from sediment back into the water body. The following observation, though not yet conclusive, appears to be indicative of this trend. In Fig. 6, the dissolved oxygen level has decreased appreciably in the stratified column

(in particular, the hypolimnion) ten days after the dump of sediment, and indeed, the release of Fe was observed then (Figs. 1 and 3), whereas in the mixed columns, limited decrease or no change of Fe levels was observed. However, according to Burns (N.M. Burns, personal communication), DO has to be reduced to about 0.5 ppm before large regeneration may occur.

The recent Chemex report (Chemex report, Table 8 - stratified column)^{5b} indicates that at day 21, when DO is relatively low, the concentrations are such that $Fe > Mn > orthoPO_4$, a trend toward the ratios in sediments^{7b} (where $Fe > Mn \approx PO_4$) and in interstitial waters. And it is also reported^{5b}, that in the mixed column at day 21, the similar behaviour as above was observed at a relatively high DO level. However, in our experiments we observed that by day 14 there was an increase in organic carbon (O.C.) in all three columns (Figs. 1 and 3). It looks as if OC also plays a role in the release of Fe back into the water body; after all, it is well known that Fe-fulvic acid complex is a very strong one. This seems to call for more extensive studies under anoxic conditions also, which should also be aimed at understanding the relation between DO, Fe, Mn, P, and DC in sediments, interstitial waters and elutriates.

Also, it is interesting to note that 10 days after the sediment dumps, the simulator column results indicate decrease in P and increase in Mn in both stratified and mixed columns. The plots of % release (Fig. 3) clearly show that Fe is present in the elutriates

(in particular, those of PS2 sediment) to a much lesser extent than P, and certainly Mn, which indicates release of at least 0.15% at infinite dilution. The X and V tests for PS2 samples indicate % Mn release much higher than 0.15% -- at least 0.5% at $X_{N \rightarrow \infty}$. Although the CS and X tests for Mn do not produce results which form a smooth curve as in the case of phosphorus, they do individually indicate that the highest % release is realized in the most dilute solution -- much the same way in which % P release behaves.

Regarding Zn release, three out of five cases show release such that $X_4 > 1.5 X_{\infty}$ whereas the other two indicate removal (Fig. 1). However, in one of the two latter cases, the X_{∞} value (solid triangle) appears to be unusually high and it could well be 4.2 rather than 42. If that were the case, X_4 is again $> 1.5 X_{\infty}$. Furthermore, the PS2 sample shows a release of 0.16% in X_{16} elutriate (Fig. 3). Thus Zn could be another constituent of concern in open water disposal.

For Hg, Cd and Pb, the elutriate concentration is in general low and often below the detection limit.

Organic carbon, complexing capacity, and stability

We have plotted the dissolved organic carbon (DOC) concentrations in elutriates against the corresponding values of complexing capacity in Fig. 5. As can be seen, there appears to be little meaningful correlation between the two parameters.

However, an important observation was recorded --- that the XAD-2 columns apparently remove many of the complexing sites as previously suspected¹ (thus producing low complexing capacity values) even though two of the XAD-2 points indicate presence of high content of organic carbon. According to Fox (M.E. Fox, personal communication), this is probably due to the fact that these two columns were not properly washed with distilled water before use, thereby leaving behind some of the organic solvent used in preparing the columns. Utilizing techniques based upon these errors, it may, therefore, be feasible to prepare the "zero" complexing capacity solution which, in turn, should permit accurate measurements of conditional stability constant.

Again, as can be seen in Fig. 1, $X_4 > 1.5 X_{\infty}$ in most cases. Although the percentage release behaviour is not quite as obvious as that of P, the general trend is apparent in particular with the points of solid triangles. The column simulators appear to produce points within reasonable expectation and it seems, therefore, that further study of changes in organic carbon, complexing capacity and stability with time are worthwhile.

Dissolved oxygen, Eh, pH, and temperature

These parameters, taken from column simulator experiments, are shown together in Fig. 6; all have time as common abscissa

Sediment oxygen demand (SOD) is a useful index for trophic classification of lakes. Lucas and Thomas¹⁰ obtained SOD values in Lake Erie's central basin by relating the changes in DO and time (t) with the area (A) above which their test boxes lie: $SOD = d(DO)/Adt$. According to Burns (N.M. Burns, pers. commun.) our DO values at 2.7 and 3.6 metres deep (both in the hypolimnion) being essentially identical, might be used along with the dimensions of hypolimnion to calculate the demand (Fig. 6 stratified, CS₁₁₂). Integrated SOD for 17 days from the day of sediment dumping to the end of experiment is calculated to be $1.1 \text{ gm } O_2 \text{ m}^{-2} \text{ day}^{-1}$. For the last 5 days of experiment, SOD is $1.5 \text{ gm } O_2 \text{ m}^{-2} \text{ day}^{-1}$ in both stratified cases. Note that there is an inspection window of one meter high and 0.1 meter wide in the hypolimnion, thereby allowing penetration of light, which in turn may assist O_2 production by photosynthetic reaction. In spite of this, the above SOD values are certainly indicative of eutrophic conditions and with time, an anoxic regeneration state would be reached. (Note: In a more recent personal communication when this report is practically finished, Burns suggests that our values of 1.1 and 1.5 $\text{gm } O_2 \text{ m}^{-2} \text{ day}^{-1}$ may not be true values of sediment oxygen demand but rather are representative of hypolimnion oxygen demand. One has to perform the type of experiments using test boxes as Lucas and Thomas did to arrive at true SOD values. On the other hand, our values are well within the expected range of sediment oxygen demand. Detailed

discussions and derivations for true SOD are beyond the scope of this report)

The DO behaviour at the top of the stratified column apparently indicates active competition between DO consuming and DO producing reactions as well illustrated by the zig-zag on Fig. 6. (Indeed, heavy growth of algae and other life forms was observed.) On the other hand, the mixed column (CS₂₅, CS₄₅) indicate practically no change in DO level in the entire column and very little algal activity was seen. But, as soon as the mixing in one of the 2 columns was stopped, the DO behaviour, coupled with increasing algal growth, immediately became similar to that of CS₁₁₂ stratified column (Fig. 6, solid circles).

The lesson is that the condition of low resulting concentration alone is insufficient to ensure a non-eutrophic simulator response; some mixing conditions -- to satisfy DO demand -- must be present in the system. Therefore, it seems that in an actual open water disposal, the factor which governs these two conditions is the rate of dilution of dumped materials as this rate is associated with the water mass involved and its natural mixing processes (such as currents and diffusion). Intrinsically then, the rate has two built-in subfactors: dilution and natural mixing processes, which help supply and maintain resistance to DO depletion. The ideal rate of dilution (or high

rate of dilution) would be realized if the natural mixing processes at the disposal site favour small effective sediment-water ratio and sufficient DO supply.

During the summer, these processes are particularly critical for Lake Erie as its DO "reserves" are rather limited compared to those of greater and deeper Lakes Huron, Superior and Ontario¹². Obviously then, it would be unwise to dispose dredged spoils (whether or not polluted) into Lake Erie during the summer months. On the other hand, even during this stratified period, the enormous mass of water and DO "reserves" for the other Great Lakes should favor the high rate of dilution, hence the open lakes disposal could be effected.

The E_h drop immediately after dumping is well illustrated in Fig. 6, which probably corresponds to chemical oxygen demand (COD). In a day or so, E_h return to original values and surprisingly increases further at days 14-18 before dropping again to correspond to low DO and low pH in the hypolimnion at day 21. These conditions (low DO, pH and E_h) correspond to conditions in which one would expect to see the beginning of regeneration of heavy metals and related components such as P. It is, therefore, desirable to further refine the experiments and continue for time periods beyond the three weeks duration of the completed tests.

CONCLUSIONS AND COMMENTS

1. The X tests, using 30 minutes shaking and one hour settling time, are preferred over the V tests because of the more repeatable results.
2. Disposal of "polluted" dredged sediments in water can result in large releases of Mn, P, Zn, organic matter and possibly Fe, even in oxic condition with pH 7-8. However, disposal in the Great Lakes corresponds to the case of X_N where N is very large and the resulting concentration tends towards that before dumping. This can be further illustrated by the recent field work^{5b} regarding the dramatic decrease of orthophosphate 15 minutes after dump, apparently primarily due to dilution effect as most phosphate would not precipitate out¹¹ and the disposal site was well mixed.
3. However, disposal in stratified or stagnant water conditions may cause a localized decrease in dissolved oxygen and may further influence trophic states.
4. It appears that the primary factor governing the disposal of polluted dredged sediments into the Great Lakes is the rate of dilution of available materials. The ideal rate of dilution would produce high degree of dilution and high resistance to DO depletion.

5. If X tests are to be applied to Great Lakes' waters as an effective elutriate assessment, the test envelope for water /sediment mixture ratios should at least characterize both the dredge site conditions and the receiving water conditions.
6. Oxidation reaction is probably responsible for the low concentration of Fe in the shaking tests as compared to that of P and Mn. Extensive experiments under oxic and anoxic conditions are desirable for further understanding of the relations involving DO, Fe, Mn, P and organic matter in sediments, interstitial water and elutriate.
7. It appears feasible, using XAD-2 columns, to prepare appropriate "zero" complexing capacity solutions which may allow one to make accurate measurements of conditional stability constant.

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ACKNOWLEDGEMENT

The authors would like to thank Drs. J.D.H. Williams, A.L.W. Kemp, J.O. Nriagu, R.L. Thomas and N.M. Burns for many fruitful discussions and criticisms; Dr. Y.K. Chau and K. Lum-Shue-Chan for measuring complexing capacity and providing use of the Hydrolab Surveyor; Mrs. A. Mudroch and H. Saitoh for technical assistance; Water Quality Branch (CCIW) in particular F. Philbert and his staff for the analyses of many chemical constituents.

The authors gratefully acknowledge the use of the Chemex report prepared for EPS and DPW, as a source for E_h , pH, D.O. and temperature data. The availability of this data has been made possible by the kind assistance of I. Serman (EPS) and E. Douglas (DPW).

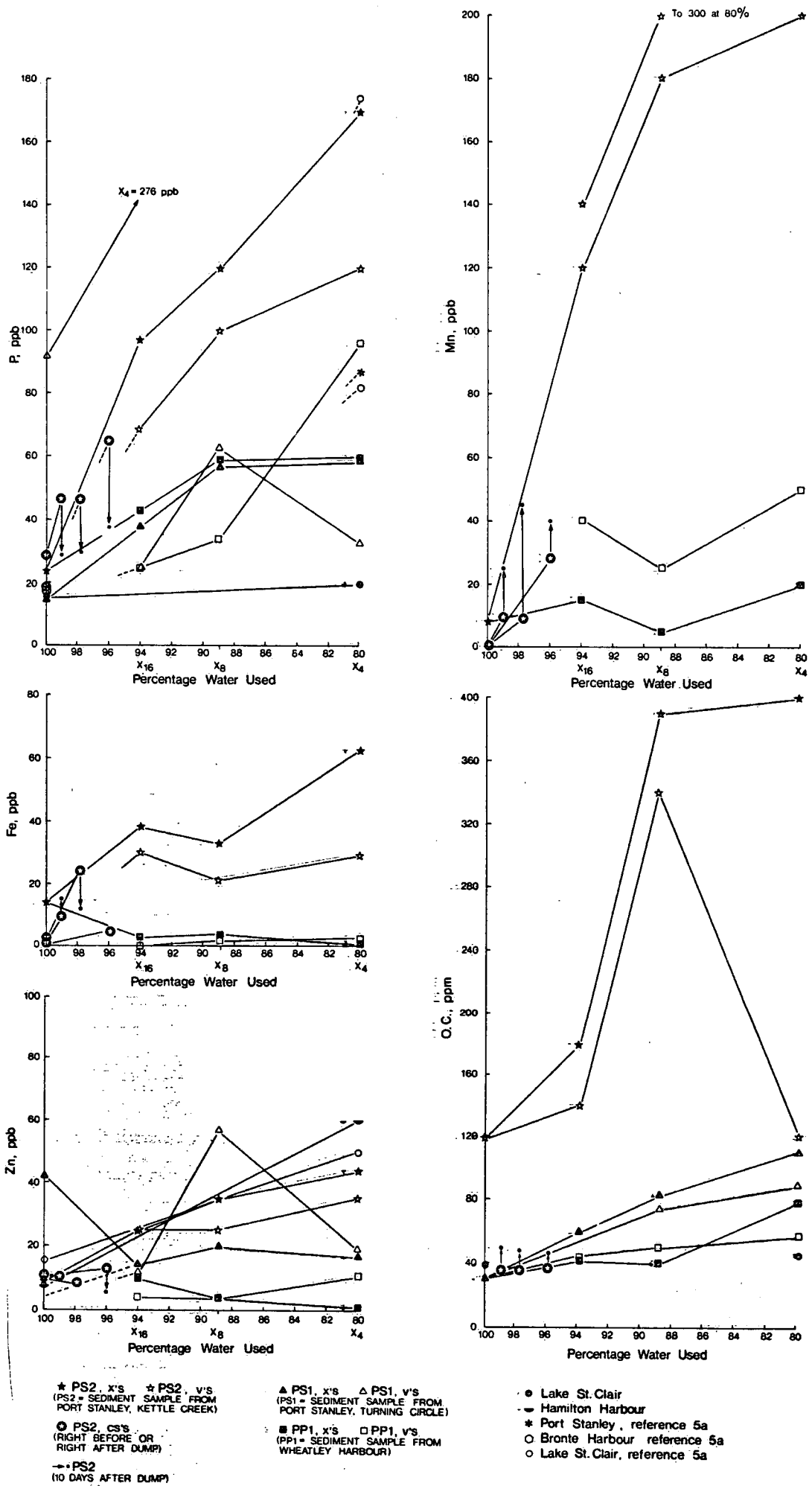


Fig. 1 - Dependence of elutriate concentration on percentage water used

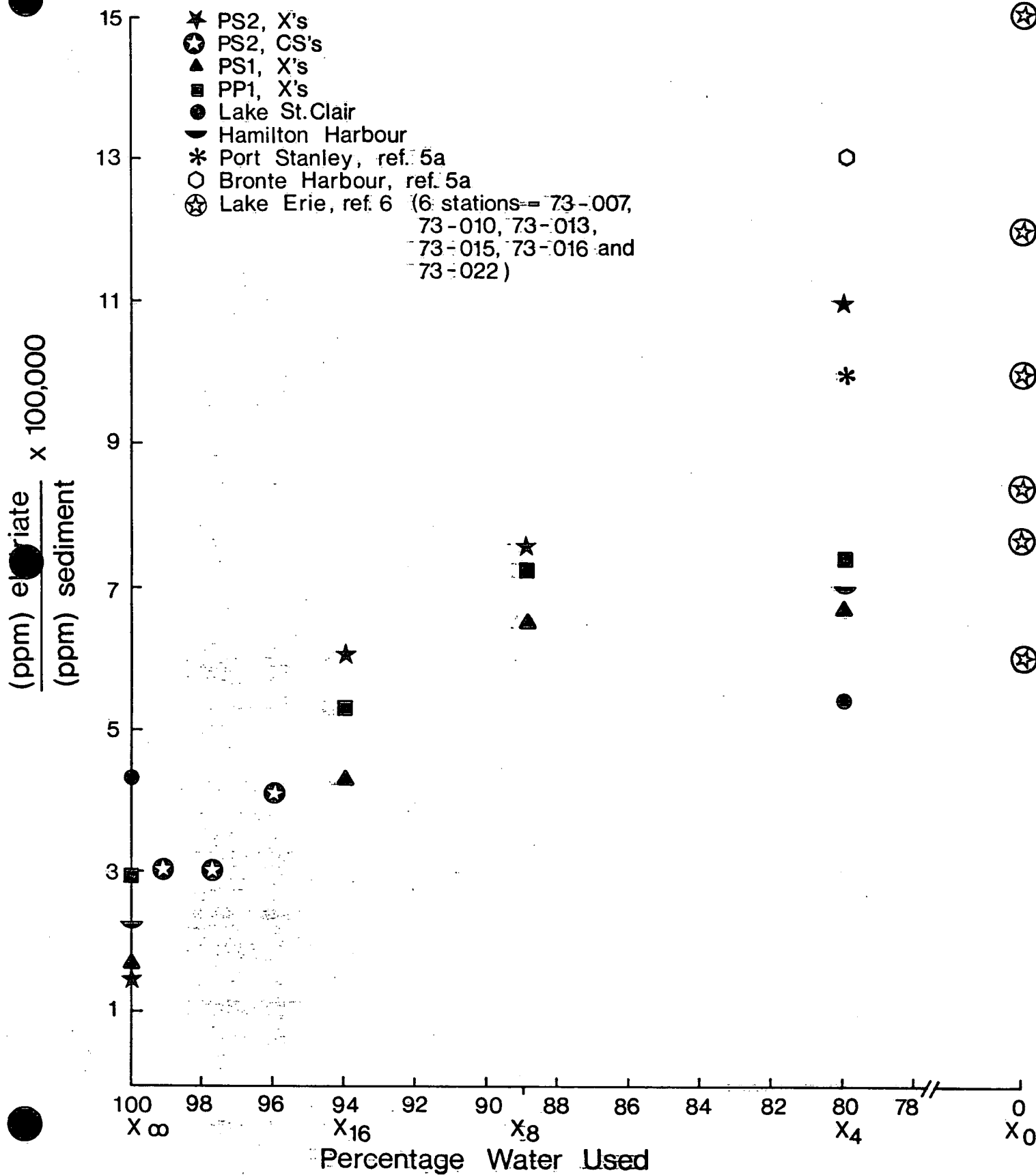


Fig. 2 - Dependence of P concentration ratio (elutriate/sediment) on percentage water used.

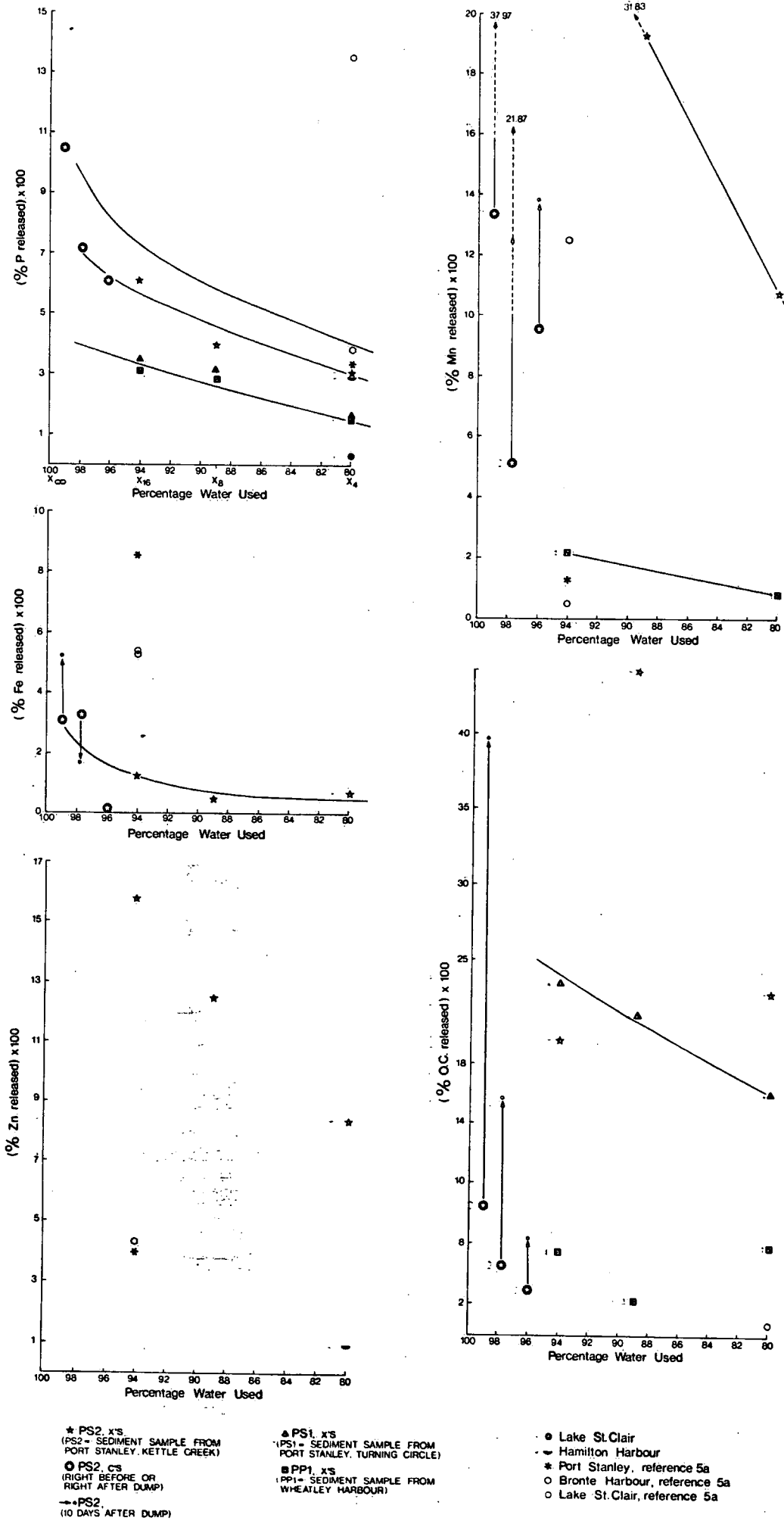


Fig. 3 - Percentage constituent released as a function of percentage water used.

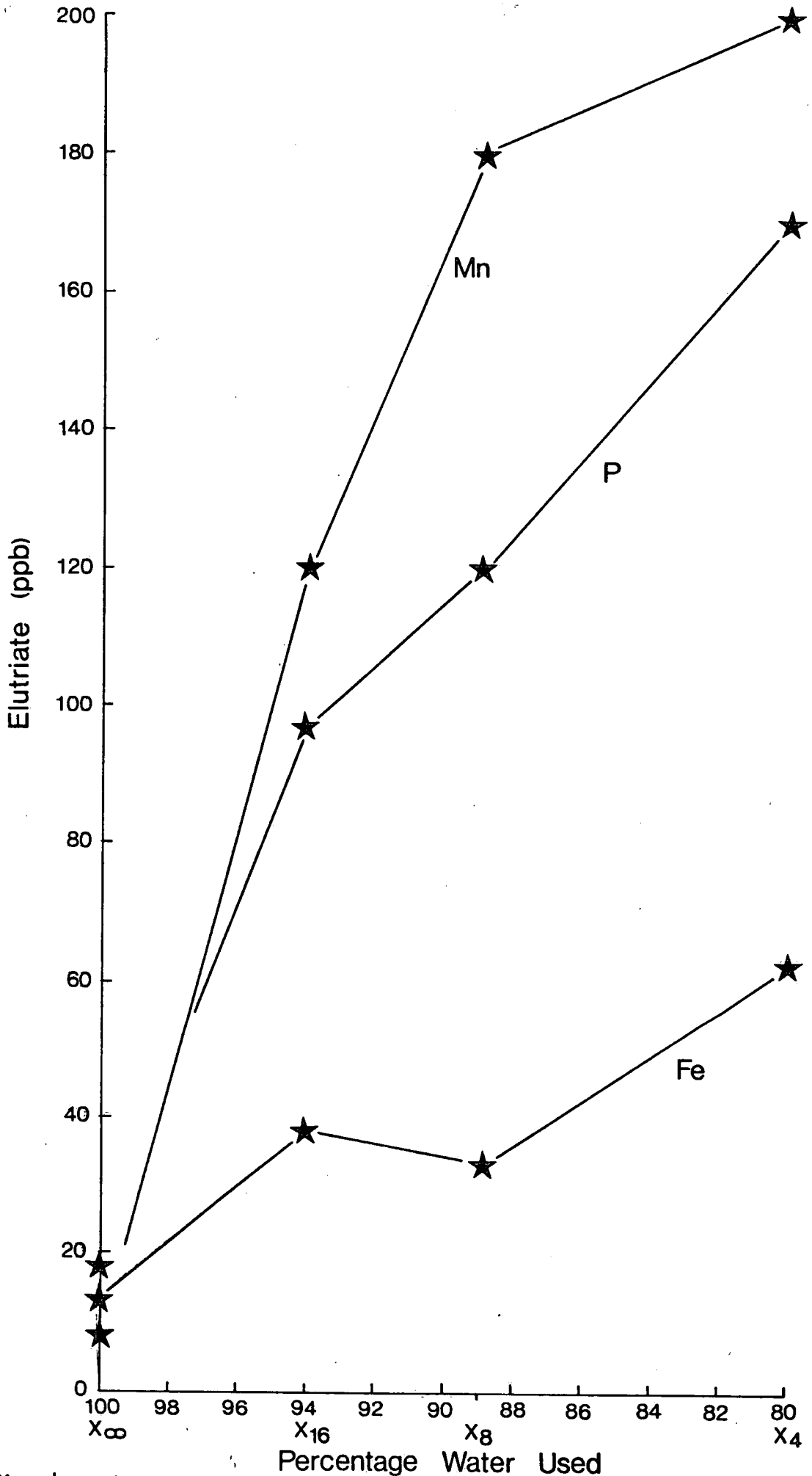


Fig. 4 - Concentration of Mn, P and Fe in elutriates from (Port Stanley, Kettle Creek sediments - Lake Ontario water) mixtures.

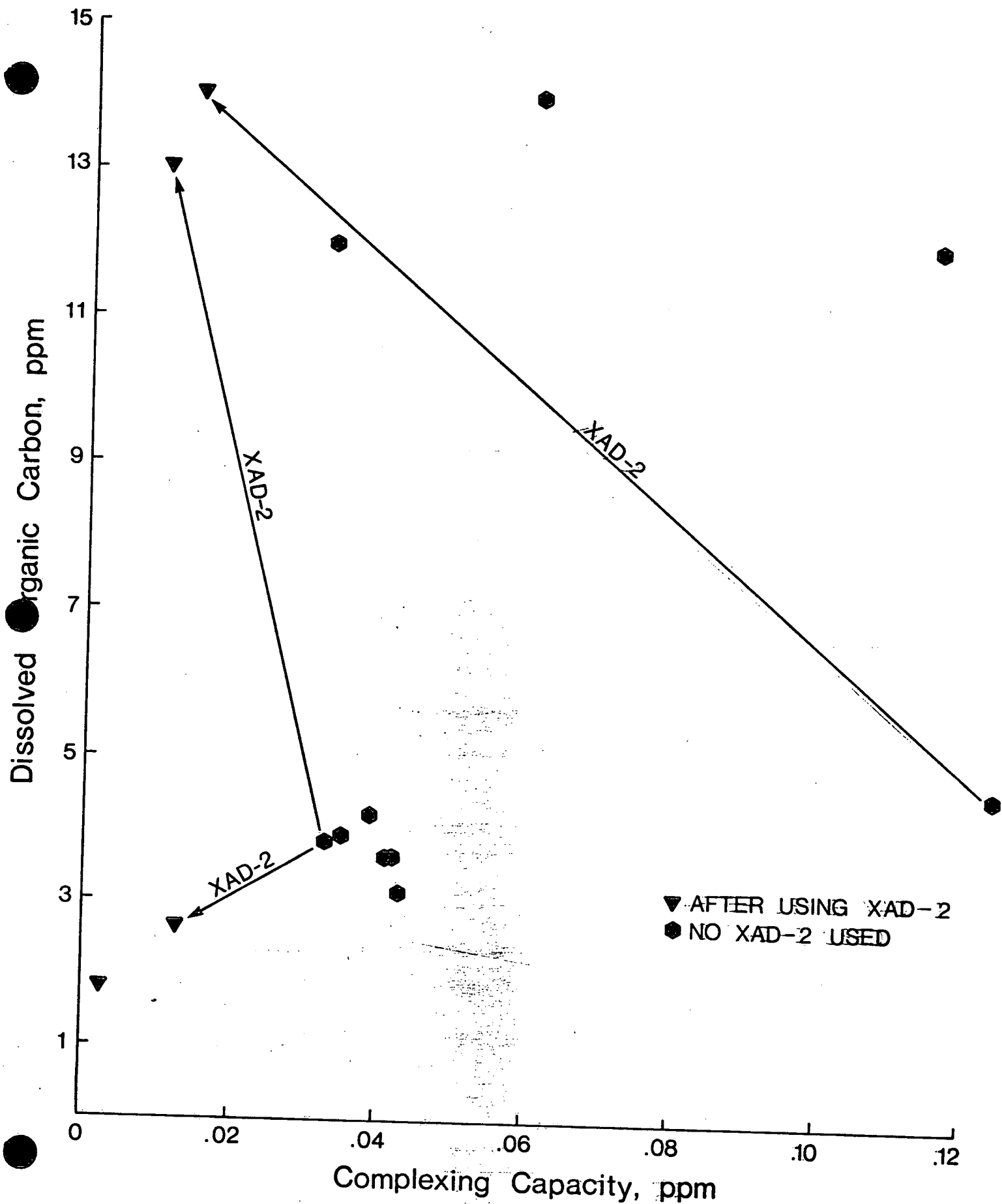
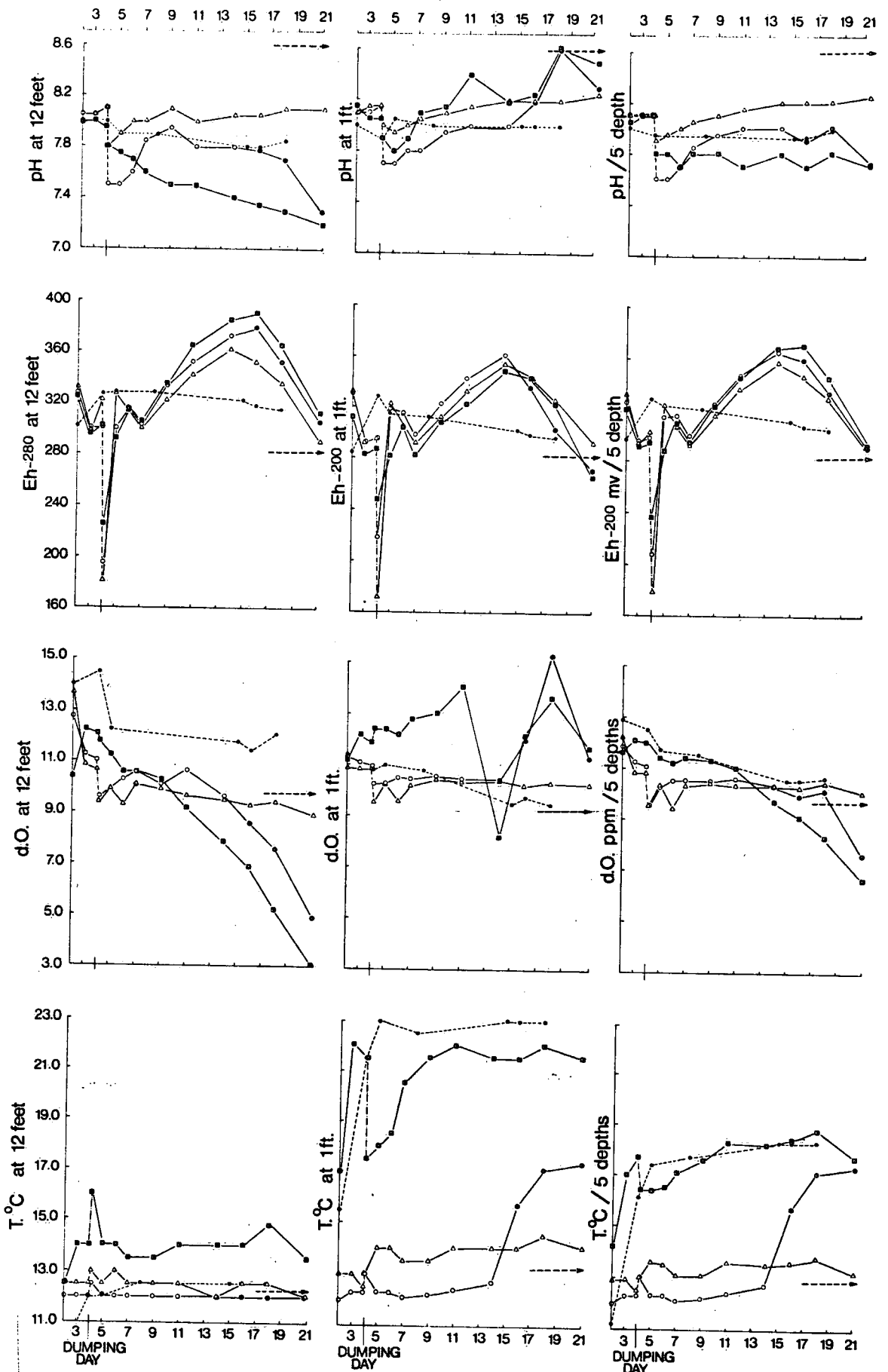


Fig. 5 - Complexing capacity dependence of dissolved organic carbon.



NO. DAYS COLUMNS HAVE BEEN FILLED

- KEY:
- | | |
|---------------|---------------|
| STRATIFIED | MIXED |
| Control | ----- Control |
| ● 360 lbs | △ 200 lbs |
| ■ 80 lbs | ○ 360 lbs |

Fig. 6 - DO, E_h, pH and T°C variations after sediment dumping in lake column simulators. 12 feet, 1ft, 5 depths.

TABLE 1 - WORKING DEFINITIONS

Elutriate		Volume Ratio of Sediment:Water	Mixing Time	Settling Time	Centrifugation Time	% Water used = $\frac{\text{vol. water}}{\text{vol. sed.} + \text{vol. water}} \times 100$
X	X _∞	disposal site water	0	0	0	100
	X ₁₆	1:16	30 minutes	1 hour	~ 1 hour	94
	X ₈	1:8	"	"	"	88.9
	X ₄	1:4	"	"	"	80
X'	X' ₄ (X' _∞ = distilled water)*	1:4 (distilled water) ^{5a}	2 minutes	0	0	80
V	V _∞	disposal site water	0	0	0	100
	V ₁₆	1:16	5 minutes	5 minutes	~ 1 hour	94
	V ₈	1:8	"	"	"	88.9
	V ₄	1:4	"	"	"	80
Y	Y _∞	dredging site water	0	0	0	80
	Y ₄	1:4	30 minutes	1 hour	0 (see Cheam et al.)	80
Z	Z _∞	50-50 mixture of X _∞ and Y _∞	0	0	0	88.9
	Z ₈	1:4:4	30 minutes	1 hour	0 (see Cheam et al.)	88.9
CS	Col. simulator (CS)					
	CS _∞	disposal site water	0	3 days (at least)	0	100
	CS ₁₁₂ (stratified)*	1:112	about 60 minutes	"	0	99
	CS ₄₅ (mixed)*	1:45	"	"	0	97.8
	CS ₂₅ (mixed)*	1:25	"	"	0	96.0

* 40 kg. sediment was used to obtain CS₁₁₂; 100 kg. for CS₄₅; 180 kg. for CS₂₅. Mixing was effectively realized by simply bubbling air about 0.3 m below the thermocline at a rate fast enough to produce visible movement of water body at the top of each column.

+ see note on bottom page 3

Table 2. Concentrations in ppm of some constituents in different elutriates: Port Stanley sediment (Kettle Creek, PS2) - Lake Ontario water system. Values in [] are those of unfiltered samples.

Chemical constituent (in solutions)	X _∞ 100% W	X ₁₆ 94% W	X ₈ 88.9%	X ₄ 80% W	V ₁₆ 94% W	V ₈ 88.9% W	V ₄ 80% W
Volatile solids	20[38]	52[90]	43[99]	43[150]	40[100]	42[124]	52[90]
Oil & Grease	1[1]	2[1]	2[2]	2[1]	1[1]	1[3]	1[1]
Mercury	<.00005[<.00005]	<.00005[-]	.00005[-]	.00009[-]	<.00005[-]	<.00005[+]	<.00005[-]
Lead	<.001[<.001]	<.001[.27]	<.001[<.001]	<.001[<.001]	<.001[.11]	<.001[.30]	<.001[<.001]
Zinc	.008[.007]	.025[.50]	.035[.016]	.044[.07]	.026[.20]	.025[.45]	.035[.01]
Cadmium	<.0002[.0005]	<.0002[.011]	<.0002[.0032]	<.0002[.0016]	<.0002[.0002]	<.0002[<.0002]	<.0002[<.0002]
Iron	.014[.016]	.038[13]	.033[.20]	.063[.75]	.030[20]	.021[30]	.029[.25]
Manganese	.008[.008]	.15[3.4]	.18[2.2]	.20[1.8]	.14[1.2]	.20[2.9]	.30[1.2]
Total phosphorus (P)	.024[.017]	.097[6.0]	.12[.079]	.17[.14]	.069[4.7]	.10[.069]	.12[.066]
Total inorganic phosphate (P)	.020[.013]	.041[6.0]	.04[.058]	.061[.11]	.031[4.7]	.048[.054]	.047[.049]
Dissolved organic carbon (C)	12 [8.8]	18 [14]	39[14]	40[35]	14[17]	34[10]	12[13]
Complexing Capacity	.116				.061	.069	.033

Table 3. Concentrations in ppm of some constituents in different elutriates: Port Stanley sediment (Turning circle PS1) - Lake Ontario water system. Values in [] are those of unfiltered samples.

Chemical constituent (in solutions)	X _∞ 100%	X ₁₆ 94%	X ₈ 88.9%	X ₄ 80%	V ₁₆	V ₈	V ₄
Volatile solids	28[24]	34[62]	41[58]	40[59]	30[]	110[66]	40[70]
Oil & Grease	<1 [2]	20 [2]	<1 [2]	2 [1]	<1	<1 [2]	1 [1]
Mercury	<.00005[<.002]*	<.00005[.002]*	<.00005[<.002]*	<.00005[.016]*	<.00005	<.00005[.016]*	<.00005[.006]*
Lead	.003 [<.001]	<.001 [.044]	<.001 [.027]	<.001[<.001]	<.001	<.001[<.001]	<.001[<.001]
Zinc	.042 [.040]	.014[<.001]	.020[.003]	.017[.012]	.012	.057[.012]	.019[.031]
Cadmium	<.0002[<.0002]	<.0002[.0002]	<.0002[.0006]	.0004[.0006]	.0002	<.0002[.0004]	<.0002[.0002]
Total phosphorus (P)	.015[.018]	.038[4.49]	.057[2.63]	.059[.033]	.025	.063[6.18]	.033[.022]
Total inorganic phosphate (P)	.012[.010]	.021[3.89]	.019[2.39]	.018[.013]	.017	.022[5.86]	.014[.010]
Dissolved organic carbon (C)	3.1 [2.7]	6.0 [6.3]	8.3 [9.9]	11 [29]	5.0	7.4 [10]	8.9 [15]

* Total mercury in mixture water-sediment

Table 4. Concentrations in ppm of some constituents in different elutriates: Wheatley Harbor sediment (PP1) - Lake Ontario water system. Values in [] are those of unfiltered samples.

Chemical Constituent (in solutions)	X _∞	X ₁₆	X ₈	X ₄	V ₁₆	V ₈	V ₄
Volatile solids	28 [24]	9 [67]	30 [78]	37 [81]	64 [66]	50 [59]	25 [69]
Oil & Grease	<1 [2]	<1 [<1]	<1 [2]	<1 [4]	<1 [1]	<1 [1]	<1 [1]
Mercury	<.00005 [<.00005]	.00016 [int.]	.00008 [int.]	.00010 [int.]	<.00005 [int.]	<.00005 [int.]	.00011 [int.]
Lead	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]
Zinc	.008 [.007]	.010 [.0020]	.0040 [.0010]	.0010 [.0010]	.0040 [.0010]	.0040 [.0010]	.012 [.0010]
Cadmium	<.0002 [.0005]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]
Iron	.014 [.016]	.0030 [.0060]	.0040 [.0060]	.0010 [.063]	.0005 [.012]	.0020 [.057]	.0030 [.12]
Manganese	.008 [.008]	.015 [.045]	.0050 [.040]	.020 [.095]	.040 [.030]	.025 [.080]	.050 [.15]
Total Phosphorus (P)	.024 [.017]	.043 [3.0]	.059 [6.7]	.060 [22]	.025 [8.8]	.034 [7.8]	.096 [6.2]
Total inorganic phosphate (P)	.012 [.010]	.015 [3.0]	.033 [6.7]	.051 [22]	.011 [8.8]	.022 [7.8]	.016 [6.2]
Dissolved organic carbon (C)	3.1 [2.7]	4.2 [5.0]	4.0 [9.1]	7.8 [11]	4.4 [7.0]	5.0 [7.7]	5.7 [13]

Table 5. Concentrations in ppm of some constituents in different elutriates: Hamilton Harbor sediment (near Dofasco) - Lake Ontario water system. Values in [] are those of unfiltered samples.

Chemical Constituent (in solutions)	X _∞	X ₄	Y _∞	Y ₄	Z _∞	Z ₈
Volatile solids	- [53]	- [61]	- [80]	- [99]	93 [-]	- [101]
Oil & Grease	- [1.0]	- [1.0]	- [1.0]	- [1.0]	2.0 [-]	- [2.0]
Mercury	.00017 [.00013]	.00017	.00018 [.00022]	.00015	.00017	.00018
Lead	<.0005 [.002]	<.0005	<.0005 [.002]	<.0005	<.0005	<.0005
Zinc	.008 [.012]	.060	.032 [.060]	.060	.012	.010
Cadmium	<.0002 [<.0002]	<.0002	<.0002 [<.0002]	<.0005	<.0002	<.0002
Total phosphorus (P)	.092 [.153]	.276 [6.750]	.153 [.400]	.275 [9.200]	.092	.430 [5.200]
Complexing capacity	.055	.124	.200	.207	.095	.168
DDT	<.000005	<.000005	<.000005	<.000005	<.000005	<.000005
PCB	.0001	<.0001	<.0001	<.0001	<.0001	.0002
Total dissolved solids	- [226]	- [205]	- [369]	- [337]	289	- [297]

Table 6. Concentrations in ppm of some constituents in different elutriates:
 X_4 = Lake St. Clair sediment (dredging site for filling Bays B and C, 1974) - Lake Ontario water system.
 Y_4 (act.) = elutriate coming directly out of the pipe of hydraulic dredge filling bays B and C of the Pilot Island, Mitchell Bay (1974).
 Values in [] are those of unfiltered samples.

Chemical Constituent (in solutions)	X_{∞}	X_4	Y_{∞}	Y_4 (act.)
Volatile Solids	43	54	26	29 [33]
Oil & Grease	3	6	<1	<1 [<1]
Mercury	.00021	.0018	<.00005	<.00005 [.00026]
Lead	<.050	<.050	<.001	.001 [.035]
Zinc	.015	.050	.016	.020 [.190]
Cadmium	<.005	<.005	.0003	.0002 [.0005]
Total Phosphorus (P)	.016	.020	.0091	.0086 [2.160]
Total inorganic phosphate (P)	.0078	.0063	.0018	.0027 [1.155]
Dissolved Organic Carbon (C)	3.9 (X_{AD-2} 2.6)	4.5 (X_{AD-2} 14)	2.0 (X_{AD-2} 1.8)	3.8 [4.1] (X_{AD-2} 13)
Complexing Capacity	.002 (.035)*	.021 (.124)*	<0 \equiv 0	.0327
Complexing Capacity (XAD-2)	.0125	.0145	.0024	.0105
DDT			<.000005	<.000005
PCB			<.0001	<.0001 [<.0001]
Total dissolved solids				

* measured by Ken Lum-Shue-Chan

Table 7. Concentrations in ppm of some constituents in different elutriates obtained from lake column simulators. Port Stanely sediment (Kettle Creek, PS2) - Lake Ontario water system. Values in [] are those for unfiltered samples.

Chemical Constituent (in solutions)	CS _{4.5} (97.8%W)			CS ₂₅ (96%W)			CS ₁₁₂ (99%W)			
	0.3 m	1.8 m	3.6 m	0.3 m	1.8 m	3.6 m	0.3 m	1.8 m	3.6 m	
	1'	6'	12'	1'	6'	12'	1'	6'	12'	
Volatile Solids	Before	38 [27]	39 [32]	44 [32]	43 [21]	40 [32]	36 [24]	38 [35]	39 [35]	42 [40]
	After	32 [45]	40 [38]	42 [35]	34 [34]	44 [67]	41 [69]	41 [48]	42 [58]	40 [52]
	10 Days After	28 [37]	25 [33]	44 [33]	24 [51]	62 [55]	66 [56]	58 [48]	58 [47]	58 [15]
Oil & Grease	Before	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [1]	<1 [1]
	After	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	1 [<1]	1 [<1]
	10 Days After	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]	<1 [<1]
Mercury	Before	<00005 [<00005]	<00005 [<00005]	<00005 [<00005]	<00005 [<00005]	<00005 [<00005]	<00005 [<00005]	<00005 [<00005]	<00005 [<00005]	<00005 [<00005]
	After	" "	" "	" "	" "	" "	" "	" "	" "	" "
	10 Days After	" "	" "	" "	" "	" "	" "	" "	" "	" "
Lead	Before	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]
	After	<.001 [.015]	<.001 [.018]	<.001 [.032]	<.001 [.035]	<.001 [.032]	<.001 [.073]	<.001 [.023]	<.001 [.024]	<.001 [.048]
	10 Days After	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]	<.001 [<.001]
Zinc	Before	.010 [.012]	.0090 [.011]	.078 [.11]	.013 [.012]	.011 [.0080]	.0090 [.0090]	.011 [.0050]	.0080 [.0070]	.010 [.0090]
	After	.0080 [.080]	.0070 [.13]	.011 [.14]	.012 [.14]	.017 [.12]	.0090 [.28]	.0050 [.090]	.010 [.10]	.014 [.19]
	10 Days After	.0070 [.0060]	.0060 [.0060]	.011 [.010]	.008 [.060]	.006 [.006]	.008 [.013]	.003 [.0020]	.011 [.0060]	.015 [.014]
Cadmium	Before	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]
	After	<.0002 [.0010]	<.0002 [.0020]	<.0002 [.0030]	<.0002 [.0030]	<.0002 [.0020]	<.0002 [.0060]	<.0002 [.0020]	<.0002 [.0020]	<.0002 [.0040]
	10 Days After	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]	<.0002 [<.0002]
Iron	Before	.0040 [.021]	<.0005 [.022]	<.0005 [.023]	.0020 [.042]	.0044* [.039]	.0020 [.040]	.0025 [.0090]	<.0005 [.013]	.0020 [.019]
	After	.063 [2.8]	.0040 [4.67]	.0040 [5.8]	.0070 [6.6]	.0075 [6.0]	.0020 [10]	.0075 [4.2]	.0025 [4.6]	.019 [7.4]
	10 Days After	.031 [.061]	.003 [.051]	.003 [.077]	.0035 [.13]	.004 [.13]	.008 [.26]	.0035 [.072]	.037 [.067]	.005 [.14]
Manganese	Before	.0005 [.0080]	<.0002 [.0024]	<.0002 [.0024]	.0002 [.0010]	.0010 [.0015]	<.0002 [.0026]	.0020 [.0010]	<.0002 [.0010]	<.0002 [.0049]
	After	.0076 [.23]	.0050 [.36]	.013 [.42]	.021 [.47]	.016 [.42]	.046 [.86]	.0070 [.30]	.010 [.34]	.011 [.54]
	10 days After	.030 [.030]	.030 [.020]	.045 [.035]	.040 [.050]	.035 [.040]	.045 [.060]	.010 [.010]	.015 [.030]	.050 [.060]
Total Phosphorus (P)	Before	.014 [.019]	.017 [.019]	.018 [.020]	.017 [.018]	.018 [.017]	.021 [.024]	.018 [.020]	.049 [.018]	.020 [.020]
	After	.040 [.55]	.039 [.50]	.062 [.94]	.065 [.78]	.089 [.75]	.042 [1.4]	.041 [.49]	.041 [.53]	.059 [.86]
	10 Days After	.034 [.10]	.024 [.037]	.034 [.037]	.041 [.044]	.028 [.042]	.040 [.044]	.011 [.029]	.044 [.048]	.032 [.050]
Total Inorganic Phosphate (P)	Before	.0085 [.014]	.0085 [.014]	.0094 [.016]	.0076 [.013]	.0078 [.014]	.0081 [.019]	.0046 [.014]	.039 [.013]	.0096 [.015]
	After	.024 [.54]	.026 [.49]	.035 [.93]	.029 [.74]	.033 [.73]	.026 [1.3]	.026 [.45]	.020 [.51]	.035 [.85]
	10 Days After	.017 [.029]	.017 [.029]	.021 [.032]	.023 [.036]	.021 [.034]	.022 [.035]	.0054 [.018]	.027 [.037]	.027 [.046]

Dissolved	Before	3.1	[3.0]	3.1	[3.0]	3.0	[3.2]	3.1	[3.0]	3.2	[3.4]	3.2	[3.2]	3.4	[3.1]	3.1	[3.1]	3.2	[3.2]
Organic	After	3.5	[3.4]	3.6	[3.0]	3.6	[3.0]	3.6	[3.5]	4.2	[3.4]	3.5	[3.5]	3.6	[3.2]	3.6	[3.2]	3.6	[3.3]
Carbon(C)	10 days after	4.7	[4.9]	4.8	[5.2]	4.8	[4.9]	4.2	[4.7]	4.7	[4.5]	4.9	[4.8]	4.8	[4.7]	4.8	[4.5]	5.3	[4.6]
Complexing	Before	0.43																	
Capacity	After			.042						.039						.041			
Total	10 Days After																		
Dissolved	Before	189	[193]	187	[198]	202	[200]	200	[168]	184	[196]	194	[192]	193	[194]	193	[190]	194	[204]
Solids	10 Days After	198	[196]	197	[200]	209	[205]	196	[222]	204	[213]	200	[236]	196	[194]	178	[204]	194	[222]

† Before, 60 minutes and 10 days after dump of sediment.

* Instead of .044

Table 8. Concentrations in ppm of some constituents in different sediment samples (per dry weight basis)

Chemical Constituent (in Sediment)	EPA's "Criteria" for determining acceptability of dredged spoil disposal to the nations waters (1971)	Wheatley Harbor PP 1	Port Stanley Turning Circle PS 1	Port Stanley Kettle Creek PS 2	Port Stanley ^{5a}	Bronte ^{5a} Harbor ^{5a}	Lake St. Clair ^{5a}	Hamilton Harbor 9
Volatile solids (loss on ignition at 550°C)	60000	49000	22000	33000	28000			
Oil and Grease	1500	1085	699	2787				
Mercury	1	.07	.07	.07				5.3
Lead	50	173	1	286				1100
Zinc	50	87	106	143	68.5	87.6	15.5	4160
Cadmium		8.7	19.2	9.5				15
Iron		18200	28900	23800	23423	18913	19447	40500
Manganese		450	578	590	668	568	320	1600
Total Phosphorus(P)	1000 (in Canada) [†]	814	880	1580	852	621	370	4000
% Organic Carbon		2.684	1.634	4.048			2.21	4.97
% Inorganic Carbon		2.614	2.804	1.852				
% Water Content		30.7*	30.7*	30.7*	30.7	25	25	55.8
% Sand:Silt:Clay		3.03:60.61:36.36	2.48:51.49:46.04	2.99:51.74:45.27				

* % water content assumed to be the same as that of Port Stanley.^{5a}

† R.L. Walker & Partners. 1974 March. "Identification of pollution potential from dredging operations in the Great Lakes".
Prepared for EPS, Department of Environment, Canada.

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