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# IMPROVING THE ELUTRIATION TECHNIQUE FOR TESTING THE BIOAVAILABILITY OF CONTAMINANTS IN SEDIMENTS

by

Shirland A. Daniels

Research and Applications Branch National Water Research Institute Canada Centre for Inland Waters 867 Lakeshore Road, P.O. Box 5050 Burlington, Ontario, Canada, L7R 4A6

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#### MANAGEMENT PERSPECTIVE

The ability to make meaningful estimates of the capacity of contaminated sediments to exert detrimental effects on aquatic biota, and generally on water quality is vital to the effective management of fresh water resources.

An examination of the elutriate method of sediment assessment suggests that the standard approaches are somewhat at variance with the dynamics of natural aquatic systems. Hence, the extent to which data thus produced actualy reflects the bioavailability of sediment-bound contaminants is questionable. By operating a rotary tumbler in a low-frequency cycle (4 r.p.m.), more realistic data can be obtained. Moreover, the extrapolation of data between studies can be greatly facilitated by expressing results on a sediment dry-weight-equivalent basis.

Dr. J. Lawrence Director Research and Applications Branch

#### PERSPECTIVE-GESTION

Pour que la gestion des eaux douces soit efficace, il est essentiel qu'on puisse avoir une bonne idée du pouvoir délétère des sédiments contaminés sur le biote des milieux aquatiques et sur la qualité de l'eau en général.

En examinant l'évaluation des sédiments que permet de faire la technique d'élutriation, on constate que les méthodes standard s'éloignent quelque peu de la dynamique des milieux aquatiques naturels. On peut donc se demander jusqu'à quel point les données recueillies par ces procédés nous renseignent sur la biodisponibilité des contaminants retenus dans les sédiments. On peut faire une évaluation plus réaliste au moyen d'un tambour rotatif tournant lentement (4 tours par min.). En outre, l'extrapolation à partir de différentes études se trouve considérablement facilitée du fait que les résultats de l'analyse des sédiments s'expriment en équivalents de poids à l'état sec.

D<sup>r</sup> J. Lawrence Directeur Direction de la recherche et des applications SUMMARY

An improved method is proposed for the preparation of sediment elutriates which permits more realistic determination of bioavailable contaminants. This approach advocates the use of a rotary tumbler in a cycle of 3-4 rpm to achieve sediment-water chemical emphasize gross mixing. Às other methods undertaken comparing characterization, experiments were compressed air, the wrist-action shaker along with the reciprocal shaker, and the rotary tumbler as modes of agitation. Sediment to water ratios (S:W) of 0:1, 1:20, 1:10, and 1:4 were tested over 0.5, 1.0, 24, and 48-h extraction periods. Elutriate evaluations were based on determinations of pH, specific conductance, totaldissolved solids and volatile solids (loss on ignition, LOI), trace metals, organics, and <sup>14</sup>C-assimilation bioassays using phytoplankter Chlorella laboratory-grown cultures of the vulgaris. The data indicated that the rotary tumbling method produced the most consistent data, which was supported by bioassay results. The wrist-action and the reciprocal shakers represented harsh agitation methods capable of fracturing sediment particles, while the air-bubbling method was found to be unsuitable for uniform agitation of 1-L samples of 1:4 sediment to water sediment mixtures. Coincidentally, the tumbler proved to be comparatively more efficient particularly when used for 1.0 h with the 1:4 S:W mixture.

ii.

RESUME

On propose une méthode améliorée servant à la préparation des sEdiments par Elutriation avec laquelle le dosage des contaminants biodisponibles est plus réaliste. Suivant cette méthode, on utilise un tambour rotatif tournant à raison de 3 ou 4 tours par minute pour mélanger les sédiments à l'eau. Etant donné qu'avec les autres techniques l'analyse chimique est grossière, on a fait des expériences pour comparer divers modes d'agitation : barbotage, agitateur oscillant, agitateur à mouvement alternatif et tambour rotatif. On a analyse des échantillons constitués de sédiments et d'eau dans des rapports (S/E) de 0/1, 1/20, 1/10 et 1/4 avec extraction en 0.5, 1.0, 24 et 48 h. L'évaluation des préparations après élutriation était fondée sur les mesures suivantes : pH, conductance spécifique, matières totales dissoutes, perte au feu, métaux à l'état de traces et composés organiques; on a aussi fait des épreuves biologiques d'assimilation de C 14 avec l'organisme phytoplanctonique Chlorella vulgaris cultivé en laboratoire. On a constate que la méthode au tambour rotatif donne les résultats les plus constants, ce que les épreuves biologiques ont confirmé. Les méthodes à agitateur oscillant et à mouvement alternatif sont vigoureuses et, de ce fait, on risque de fracturer les particules sédimentaires; par ailleurs, le barbotage ne donne pas une agitation uniforme avec les échantillons de l L de rapport S/E de 1/4. On a aussi observe que le tambour est comparativement plus efficace surtout avec les échantillons de rapport S/E de 1/4 agités pendant 1 h.

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#### **1.0** INTRODUCTION

The role of aquatic sediments in garnering large quantities of contaminants has triggered great interest and scientific investigation (Lee et al., 1975; Shuba et al., 1977; Jones and Lee, 1978; Engler, 1979; Bahnick et al., 1981; Munawar et al., 1983, 1985, 1986; Brannon et al., 1986). Contaminants of interest are those which are subject to release from the adsorbing sediment particles mechanical by normal and physicochemical forces operating in the aquatic ecosystem. In addition, some of these substances possess the ability to penetrate the plasma membrane of aquatic organisms (Boudou et al., 1983). Hence, much research activity has been focussed on the circumstances and influences affecting the release of toxicants and their biotic effects (Mac et al., 1984; Seeley and Mac, 1984).

The Elutriate Test was developed as a leaching procedure primarily to determine the "solubility" of contaminants subject to release when dredged sediments were deposited in open water (Keely and Engler, 1974). The method was subsequently formalized and promulgated as the Standard Elutriate Test (Brannon and Engler, 1977). It advocated mixing sediment and site water by mechanical shaker at a rate of 100 excursions per minute, or by bubbling with compressed air accompanied by periodic stirring for 30 minutes. Côté and Constable (1982) examined a number of options in studies of leaching techniques

for evaluating the contamination potential of solid waste targeted for disposal.

The thrust of this study was the development of a procedure to: a) produce bioassay-compatible elutriates providing meaningful data about the bioavailability of sediment-linked contaminants; and b) approximate the natural leaching conditions of the aquatic system, without altering the physical integrity of sediment particles as this would tend to skew resulting data. Procedures based on rotary tumbling were adapted by the author, and compared to the two mixing methods widely applied in elutriate preparation (Brannon and Engler, 1977).

#### 2.0 METHODS AND MATERIALS

Eight studies were conducted which investigated sediment/water combinations with ratios of 1:20, 1:10, 1:4 and a control of 0:1, agitated initially for periods of 1.0 h and 48 h (Table 1). Since the overall goal concerned the pattern of contaminant removal, distilled water was used as the liquid phase in most of the preliminary studies.

The 48 h mixing period was eventually dropped and the 0.5 h mixing period included since it had been recommended and applied (Keely and Engler, 1974; Brannon and Engler, 1977; Munawar <u>et al</u>., 1985.

#### Sample Collection

2.1

Sediment used in the preliminary studies was collected from Triangle Pond, a settling basin on Toronto Harbour's East Headland (Fig. 1). Later sampling was conducted in west Toronto Harbour (Fig. 2) using a Ponar grab sampler. Sediment samples were immediately subsampled for chemical characterization, and stored briefly in teflon-lined containers at 4°C until used in elutriate preparation (usually within 72 h). Collection and handling of sediment was generally consistent with the guidelines defined by Brannon and Engler (1977).

Glass-distilled water (DW) was used to prepare elutriates in studies I, II, IV, V and VI; while site water collected at Triangle Pond provided dilution water in study III. The leaching medium used in studies VII and VIII was water collected in Lake Ontario at Toronto Harbour. Site water was settled for four hours, decanted and was then stored at 4C until used.

## 2.2 Elutriate Preparation

Volume:volume sediment/water combinations were prepared using the method of volumetric displacement (Brannon and Engler, 1977). Studies I, II, III, and IV were restricted to the evaluation of the "ferris-wheel" type rotary tumbler, Rugged Rotator, model RD 250 (Kraft Apparatus Inc., Mineola, N.Y.). It was modified by the addition of six retort arms to each of which was attached a metal clamp capable of accomodating a 1.0-L

Nalgene polypropylene wide-mouth bottle to ensure secure attachment of each vessel (Fig. 3). The device was operated at a rate of 4 rpm, and sediment/water combinations and agitation periods previously detailed. This device was employed by Côté and Constable (1982). In study IV, the pH of the elutriation mixtures was adjusted to 6.0 before mixing.

Study V evaluated the air-agitation method advocated by Brannon and Engler (1977). The system consisted of a water-trap assembly through which compressed air was saturated before its delivery through fritted-glass air diffusers to the sample mixtures (Fig. 4b). Study VI concentrated on the Burrel wristaction shaker (Fig. 4a), used at a rate of approximately 100 excursions per minute. Studies VII and VIII compared all options by including the three methods of agitation, the sediment/water combinations detailed above, and mixing periods of 1.0 h and 24 h in study VII; and 0.5 h, 1.0 h and 24 h in study VIII. The Eberbach reciprocal shaker was substituted for the wrist-action shaker in studies VII and VIII, to accomodate 1.0-L containers.

After agitation, treatment mixtures were settled for a minimum period of 6.0 h at 4°C before the liquid phase was removed by aspiration. The supernatant was partitioned by spinning in a Sorvall RCB2-B automatic refrigerated ultracentrifuge at 10,000 rpm for 30 min before filtration through pre-washed  $0.45-\mu$ m Millipore HA 47-mm membrane filters. Resulting filtrates represented the elutriate end product.

Elutriate sub-samples for trace metal, nutrient-major

ions, and trace organic determinations were conducted immediately after elutriate preparation using standard procedures. The remaining portion of each elutriate was reserved for use in bioasays. All samples were then stored at 4°C in the dark (for no more than 72 h) until used in bioassays or chemical analysis.

2.3

#### Physical and Chemical Assessment

The pH of sediments and elutriates was monitored using a Corning 125 single-probe digital meter. Measurements of the specific conductance (conductivity) were carried out using a Radiometer CDM 83 conductivity meter, expressed in units of  $\mu$ S cm<sup>-1</sup>. Gravimetric determinations of total dissolved solids (TDS), volatile solids, VS (loss on ignition), and moisture content were performed using a Mettler digital analytical balance. Sediments and elutriates were analyzed to determine concentrations of eight trace metals using inductively-coupled argon plasma emission spectrometry. All analyses were conducted using the procedures and methods of the National Water Quality Laboratory.

Organic parameters were estimated by gas chromatography and included organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs). A Varian Vista 6000 gas chromatograph equipped with a Vista 8000 autosampler, splitless capillary injector, and a J&W DB5-30N 0.5-mm ID fused silica column. Sediment samples received pre-treatment on an Autoprep 1200A gel permeation chromatograph (Analytical Biochemical Laboratories Inc., Columbia, Mo.) prior to chromatographic analysis. All analyses

were carried out at the Canada Centre for Inland Waters using the procedures and methods of the Water Quality National Laboratories (1985).

2.4

#### Phytoplankton Culture Preparation

Axenic cultures of <u>Chlorella vulgaris</u> Bayerinck were acquired from Carolina Biological Supply Co., (Burlington, NC) and grown aseptically at a constant temperature of 20°C in Chu 10 medium (Nichols, 1973) and at a light regime of 16 hours light and 8 hours dark. When appropriate densities were achieved (usually about 5 x 10<sup>6</sup> cells ml<sup>-1</sup>), cultures were diluted, while still in the log phase of replication. The diluent consisted of  $0.45-\mu$ m filtered water collected 1.0 km offshore in Lake Ontario. This incubation mixture was in each instance allowed to equilibrate at 20°C for 24 h, before use in bioassays.

#### 2.5 Bioassessment Procedures

The bioassays conducted in these studies involved a series of well defined procedures as follows:

1. Polycarbonate Erlenmeyer bottles, 100 ml capacity, were thoroughly cleaned by washing with detergent, and 10% HNO3 followed by multiple DW rinses.

2. Four replicate bottles for each treatment were each charged with 50 mL of the incubation mixture. Two sets of replicates, untreated with elutriates, were used as controls - one set being

exposed to light during incubation (light control; LC), and the other incubated in the dark (dark control, DC). The dark control monitored the level of any heterotrophic carbon assimilation which occurred during incubation, and values resulting from this treatment were used to correct data from all light-incubated samples.

3. Elutriates were spiked into incubation mixtures at the level of 5% and 25%. These were computed using the following equation:

X = Y (50 + X) (Eq.1)

where X = the volume (ml) of elutriate to be added,

Y = the desired level of elutriate addition,

50 = volume of the incubation mixture.

Therefore, the 5% addition was computed as follows:

X = 0.05 (50 + X) = 2.5 + 0.05X = 2.5/0.95 = 2.63 mL.

Similarly, the 25% addition level was 16.7 mL.

4. After elutriate addition each bottle was treated with 2  $\mu$ Ci 14C as NaHCO<sub>3</sub> (Arlington Heights, Illinois) using Eppendorf microdispensers. Incubation mixtures were well mixed and incubated for 4 h at 20°C in a Conviron E7 Plant Growth Chamber (Winnipeg, Manitoba) with CMP 3000 microprocessor control system, providing constant light at 252.5  $\mu$ E m<sup>2</sup> sec<sup>-1</sup>. Because of the large number of treatment units in Study VIII, a series of nine

separate bioassays were performed with samples grouped on the basis of time and method of shaking.

Thus, the first bioassay comprised treatments that were agitated by aeration for 0.5 h (A/0.5); and the second, those mixed by Eberbach reciprocal shaker for 0.5 h (E/0.5). Samples prepared using the rotary tumbler (R/0.5) were used in the third bioassay. Similarly, bioassays of samples agitated by the three methods for 1.0 h and also for 24 h were conducted (Table 2). Each experiment included a light and a dark control.

5. At the end of the incubation period the temperature was automatically lowered to  $4^{\circ}$ C and the lights extinguished. Before sample filtration (0.45  $\mu$ m Millipore HA filters) to collect phytoplankton cells, a 1.0-ml sub-sample was removed from each bottle for estimation of total available activity. These were each placed in separate scintillation vials and preserved with monoethanolamine. Filters with collected phytoplankton cells were washed under negative pressure not exceeding 17kPa with 0.1N HCl to remove surface residue of 14C-NaHCO<sub>3</sub>. Each filter was placed in a separate scintillation vial and subsequently treated with 10 mL of the scintillation fluor PCSII (Amersham Corp.) after all filtration was completed. Samples were vortex-mixed and decays per minute (dpm) measured using an LBK Wallac 1211 Rackbeta automatic liquid scintillation counter.

#### 2.6

# Data Handling and Analysis

Data acquired from scintillation counting were

corrected to reflect dark control readings, and assimilation coefficients (Assim Coeff) were computed. This is a unit which expresses the efficiency of carbon assimilation by phytoplankton and has been devised to minimize the effect of variation between experiments. Assim.Coeff. is defined as follows:

## Assim Coeff = 100 (dpm Assim/dpm Avail) (Eq.2)

where, dpm  $A_{ssim}$  = the level of <sup>14</sup>C-uptake by the plankton cells dpm  $A_{vail}$  = the level of <sup>14</sup>C available for assimilation (Total Activity).

The experimental design applied was a 2x3x3x4 factorial involving the two levels of elutriate addition, three methods of agitation, the three time periods and the four sediment/water ratios, as described above. Analysis of variance was utilized in the analysis of data from studies VII and VIII employing the Ftest as a test of significance. Data assessment was focussed on interactions between level of addition (L) and ratio of sediment and water (R), because conclusions and interpretations regarding the other variables had already been facilitated by studies I to VI. Student's t-test comparisons were also applied to data enabling other intra-experimental evaluations. Data were then tabulated and respective levels of significance indicated.

3.0 RESULTS

#### pH Changes

In studies I and II where rotary tumbling and distilled water were used, only small changes were observed when samples mixed for 24 h were compared with those treated for only 1.0 h (Table 3). A pH reduction of 0.16 was noted in the elutriate control (0:1), while all other treatments increased by 0.14-0.23. Similarly, a pH decrease of 0.29 in the control occurred with 48h agitation. All other 48-h treatments also experienced reductions with mean differences of 0.04 for the 1:4 mixture, and 0.07 for the 1:20 soil-water mixture (Table 3).

By adjusting the pH to 6.0 prior to tumbling, the pH increased in most 24-h samples compared to 1-h agitated samples. The sole exception was the 1:10 combination which showed a 0.04 pH reduction (Table 4). The 48 h treatment caused an overall reduction in pH, but its reading of 7.46 was reduced compared to the 24-h 1:4 sample. Eluriates prepared by tumbling with site water produced pH changes between the 1.0 h and the 24 h samples which showed no great differences compared to the DW sample treatments (Table 5).

Other methods of mixing produced reduced pH readings for both the 24 h- and 48-h treated samples compared to the respective 1.0 h-treatments (Tables 6 and 7).

#### 3.2

#### Changes in Conductivity

Conductivity values of rotary-tumbled elutriate controls prepared with DW, showed values which were greatly

10

3.1

reduced, 62.5% for the 24-h control and 76% for the 48-h control (Table 8). Other treatment values increased several orders of magnitude, with differences generally greater with longer periods of agitation (Table 8). When the pH of elutriate mixtures was adjusted to 6.0 before agitation, the same general changes in conductivity were observed (Table 9): the controls showed reduced conductivity values, while the treatments generally increased with increased agitation periods.

Table 10 presents data showing the effects of rotary tumbling and duration of exposure on the specific conductance of elutriates prepared with site water. It is evident that increased  $\mu$ S cm<sup>-1</sup> values resulted when sample mixing was carried out for 24 h compared to 1.0 h (Table 10). The same pattern was observed when distilled was used in elutriate preparation with airdiffuser agitation (Table 11) and also with the wrist-action shaking (Table 12).

#### 3.3

#### Changes in Dissolved Solids

Rotary-tumbled elutriates with unamended pH produced volatile solid results which differed statistically (P<0.05-P<0.001) from their respective controls (Table 13). Generally, the greater the sed:water and the period of agitation, the greater were the volatile solids measured. The analysis of total dissolved solids generally showed a significant and increasing trend as the treatment period increased. The exception was the 1:4 sediment-water mixture, where a 7% reduction was observed

when agitation was carried out for 24 h. The 1.0 h agitation produced TDS values which showed a progressive and significant increase as the sediment component of the treatments was increased, but this was not true for the 24-h and 48-h treatments. The 1:10 combinations failed to show significant changes. In fact, significant decreases were observed for both treatment periods as the sediment component increased (Table 13).

When the pH was adjusted to 6.0 prior to agitation, no change was observed in the values of volatile-solids controls (Table 14). Moreover, the huge differences (83% to 2200%) observed in the absence of pH modification were significantly reduced (-31% to 85%) after this adjustment had been applied. The total dissolved solids observed in Table 13 increased by orders of magnitude ranging from 3 to 13 (Table 14) after pH modification.

The use of site water in the preparation of rotary tumbled elutriates produced radically different volatile solids 24-h measurements were (Table 15), in results that most significantly reduced relative to their respective 1.0-h agitated elutriates. In addition, values between sediment-water treatments for the 1.0-h samples showed no statistical differences compared to the control, while the 1:10 and the 1:4 treatments demonstrated significant differences (P<0.05) among the 24-h agitated samples. Data for total dissolved solids (Table 15) indicated that the controls underwent no significant changes whether mixed for 1.0 h or for 24 h. There was no overall trend

since the 1:20/24-h treatment showed a 24% decline compared to the 1.0-h sample. The 1:10 treatment produced a 35% increase, and a 14% reduction occurred when the 1:4 mixture was examined. The inter-treatment data within the 1.0-h exposure period revealed that the 1:4 sediment-water treatment produced the only data significantly different (P<0.05) to the control.

Air-diffuser produced volatile solids data (Table 16) did not differ statistically when samples mixed for 24-h were compared to those mixed for 1.0 h. The 48-h agitation period generated volatile solid values representing an increase compared to the respective 1.0-h agitated samples. Moreover, these volatile solid values did not statistically differ from their respective controls except the 1:4 treatments (P<0.05 - P<0.01).

Total dissolved solids (TDS) data produced by airdiffuser treatment (Table 16) were generally significantly different to their respective controls. The only exception to this was the 1:20/1-h treatment. Note that the concentrations of total dissolved solids in the sediment-water combinations generally increased with increasing treatment period. Exceptions to this were 24-h treated samples involving the control and the 1:10, treatments.

The Burrell wrist-action shaker generated volatile solids data (Table 17) which, in general, showed few statistical differences between treatment periods. Total dissolved solids were significantly increased over their controls (Table 17). All concentrations of volatile solids generally increased as the

sediment component increased, except for the 1:4/48-h treatment. The treatments showed two principal trends with time: the TDS of the controls declined progressively as the treatment period increased, but the 1:20, 1:10 and 1:4 treatments showed a consistent increase after 24 h, followed by reductions of 23% to 31% after 48 h.

In studies VII and VIII where elutriates were prepared from Toronto Harbour sediment and site water by all three methods of agitation, there were only small differences in volatile solids values between treatment periods. Within a given mixing period, however, a different trend was observed (Table 18). Generally, there were small elutriate volatile-solids differences between 1:20 and 1:10 treatments with both mixtures showing greater disparity compared to their respective 1:4 treatments, and to their controls in each case. The 1:4 sed:water treatments were invariably significantly increased compared to their controls. This was true for, both treatment periods. Note that rotary treatment produced values which progressively increased as the sediment constituent in the treatment combination increased.

Total dissolved solids in comparative studies (Table 18) indicated that mixing by air diffuser produced increases as the time of mixing and sediment content of mixtures increased. Use of the reciprocal shaker generated values showing no significant change between 1.0-h and 24-h controls, but showed a 9.0% reduction in the 1:20/24-h treatment. The 1:10 and 1:4 treatments increased significantly after mixing for 24 h. Rotary-

tumbling produced results indicating that, except for an 8.0% reduction in the 24-h control, all treatments increased as the mixing period increased. Moreover, concentrations of total dissolved solids were significantly increased in all treatments compared to respective controls.

## 3.4 Trace Metal Analysis

Comparative studies of elutriation methodologies produced mean trace-metal concentrations for the 0.5-h treatment which showed no great differences between the three methods of mixing. Values generally increased as sediment level increased (Table 19). There were instances (usually involving 1:10 treatments) where the trend was disrupted by some marked decreases. Mn values produced by rotary tumbling increased 200%-300% over corresponding data from the other two forms of mixing.

When agitation continued for 1.0 h, there were small changes in Cu concentrations where the 1:4 treatment values usually increased particularly when mixed by reciprocal and rotary shaking (Table 20). Whereas 0.5-h mixing produced erratic data for Zn with reciprocal and rotary agitation, values from 1.0-h mixing, though not necessarily greater, demonstrated more logical progression with increasing sediment content. Fe and Mn data also showed stabilized values which generally increased. This was especially noticeable in Mn data from reciprocal mixing, though air-diffuser generated values were approximately 50% reduced.

Twenty-four hour mixing produced no consequential changes in Cu values regardless of agitation method. There were small increases in Fe concentrations with air-diffuser and rotary agitation; but the values from reciprocal shaking were increased by a factor of 2 to 4 (Table 21). Mn levels were somewhat increased in air-mixed samples. Increases were even greater with reciprocal mixing, and virtually doubled with rotary agitation. Zinc concentrations were generally unchanged, but somewhat erratic, with reciprocal and rotary treatments. Trace metal concentrations of sediment used to prepare elutriates (Table 19) indicated that only very small quantities of the total constituents were actually partitioned by the various mixing procedures.

#### 3.5 Organic Analysis

The only organic parameter of note was the total PCB concentration. Traces of  $\alpha$ -BHC were detected when all three mixing methods were applied for 0.5 h and 1.0 h, and with rotary agitation for 24 h (Tables 22, 23, & 24). PCBs were released after 0.5 h only with reciprocal shaking (Table 22); but 1.0-h shaking generated greatly increased PCB partitioning with all methods (Table 23). The reciprocal and air-diffuser methods produced similar PCB values, but concentrations produced by the former increased as the sediment content increased in the treatment mixtures used in elutriates production. Significantly increased concentrations resulted from 1:4 rotary mixing. Twenty-

four-h mixing also produced PCB partitioning by all methods at greatly reduced levels (Table 24). It was noted that HCB,  $\alpha$ - and  $\gamma$ -Chlordane, Heptachlor Epoxide, Aldrin, and three other organochlorine parameters were also monitored, but were not detected in elutriates.

3.6

#### **Biological Assessment**

Bioassays performed with air-mixed 0.5 h (A/0.5) elutriates produced values with no statistical differences to bioassay control (LC) or elutriate control (0:1), except for the 1:20/25% treatment (Table 25). Neverless, significant differences (P<0.01) were noted between sediment-water ratios (R), but not between elutriate addition levels (L) nor the RxL interaction. Reciprocal shaking caused significant reductions in carbon uptake especially at 25% elutriate addition level. These lowered values were significant compared to those of both experimental controls (Table 25). Moreover, the variables R, L, as well as the RxL interaction were statistically significant (P<0.001).

When rotary treatment applied for was 0.5 h, significant carbon assimilation was noted compared to bioassay controls (LC); and also compared to the elutriate control (0:1), only in 1:4 treatments. The levels of significance were P<0.05 and P<0.01 compared to LC, and P<0.01 and P<0.01 compared to the 0:1 controls for 5.0% and the 25% elutriate additions, respectively. It was noted that significant interactions (P<0.001) were recorded between sedediment-water ratios.

The air-mixing method produced no significant  $14C-CO_{2-}$ assimilation changes with the 5.0% elutriate addition, whether treatment was for 1.0 h (Table 26) or 24 h (Table 27). Little differences were observed when 1-h mixed elutriate was added to the incubation mixture at a level of 25%, but significant interactions between addition levels (P<0.01), and also in interactions between ratios and levels (P<0.05) were evident. However, the 25% addition of 1:4 24-h air-mixed elutriates promoted significant enhancement (P<0.01) of carbon assimilation, compared to bioassay control, and to elutriate control (0:1). The only other case of significant air-diffuser influenced Cassimilation was the 1:20/24-h treatment (Table 27). In this instance. the assimilation coefficient was significantly different (increased) compared only to elutriate control. Only interactions between ratios showed any significance (P<0.01) among the interacting variables.

The 5% addition of 1.0-h reciprocally-shaken elutriate produced enhanced carbon uptake, while the 25% addition significantly inhibited all carbon assimilation. The 24-h 1:10 and 1:4 treatments were the only ones showing significant differences. The inhibition of  $^{14}$ C-CO<sub>2</sub> assimilation tended to be the normal pattern. Statistical significance occurred between ratios, between levels and the R-L interaction, with 1.0-h mixing. No such significance was recorded with 24-h mixing.

**Rotary mixing** generally reflected significant inhibition of <sup>14</sup>C-CO<sub>2</sub> uptake by <u>Chlorella</u> <u>vulgaris</u> with the 1.0-h

and the 24-h treatments. This was particularly evident with the 25% elutriate addition. Samples receiving a 5.0% spike of 1.0-h rotary mixed elutriate showed some comparative significant differences, and no change in 24-h samples. Ratio (R), level (L), and R-L interactions were also highly significant (P<0.001) with 1.0-h mixing; but while significant differences occurred among ratios and among levels in 24-h treatments, there was no significance in RxL relationships (Table 27).

#### 4.0 DISCUSSIONS AND CONCLUSIONS

The use of distilled water as the leaching medium enabled the achievement of experimental conditions which permitted discrimination of treatment effects without complications from the influence of dissolved salts, buffering capacity, etc. Therefore, the pronounced elevated pH trend of elutriates as exposure-time and sediment volume increased was evidently due to the calcareous nature of Triangle Pond sediment (Munawar et al., 1986). It may be recalled that the alkaline effect was reduced when the pH had been previously adjusted to 6.0 (Table 4), and that this measurement was generally similar to the initial pH of the leaching distilled water. The large buffering capacity of the sediment required excess H<sup>+</sup> to achieve the pH adjustment to 6.0. Therefore, ions were then available to neutralize some of the alkaline influences of the sediment thereby resisting great pH increases.

The reduced pH gradient of air-mixed samples (Table 6) was likely caused largely by oxidation of  $Ca^{2+}$ - and  $Mg^{2+}$ producing insoluble oxides and carbonates. In addition, the fact that the air diffuser was not found to be very effective in creating sustained general turbulance when sediment volume exceeded 150 mL, would explain the observed relative resistance to pH increase. The insignificant pH changes observed with the use of site-water (Table 5) was due to the absence of an effective pH gradient between the alkaline dilution water and the sediment.

The pH increases tended to be less incremental with longer mixing periods and increasing sediment volume because of a well recognized phenomenon. High biological and chemical activity in these sediments demonstrated a sequence of oxygen consuming events during which nitrate and sulphate reduction occurs, accompanied by eventual CH<sub>4</sub> production (Förstner <u>et al.</u>, 1984). In addition, Calmano <u>et al.</u> (1983) reported observing pHdecreases and bacterial leaching of metals under conditions of this kind. Adams <u>et al</u>. (1982) reviewed this phenomenon and pointed out that <u>in situ</u> oxygen demand (OD) is comprised of a water oxygen demand (WOD) and sediment oxygen demand (SOD).

The reduced SOD would have been the principal contributor to OD, since distilled water was used in most instances. Reduced species such as  $Fe^2_+$ , Mn<sup>+</sup> and H<sub>2</sub>S undergo rapid oxidation resulting in reduced availability of such metals. Thus, with prolonged mixing the pH dropped as anoxic conditions

developed, and as the 48-h data indicated, the pH of elutriates either stabilized or actually decreased in some instances (Tables 4, 5).

Generally, the specific conductance was influenced by the same factors as the pH since it (specific conductance) indicates the level of ionic activity in a sample. Thus, the trends in conductivity values generally paralleled those for pH where values actually declined (Tables 8 and 10). Nevertheless, the 20% increase in the pH-adjusted elutriate (Table 9), and the 403 uS cm<sup>-1</sup> increase as treatment combinations increased in the air-mixed samples (Table 11) should not be overlooked. The scope of this project did not permit the pursuit of a definitive explanation, but it is reasonable to conclude that the buffering systems in both cases must have had the capacity to facilitate the release of more solids. The significance of their rather similar pH measurements (7.46 and 7.43 respectively) cannot be merely co-incidental.

Volatile solids (loss on ignition, LOI) provides a crude collective measurement of the organic constituent of a sample. Ideally, this parameter should show direct proportionality with values for total dissolved solids. This was gererally so, with the few inconsistencies most likely resulting from the fact that the sample size was only 30 mL. Increased replication may have been instrumental in minimizing this flaw. In addition to the stability of trend being greater in the 1.0 hmixed samples and more so in samples prepared with site water

(Tables 15 and 18), the rotary tumbler showed greater efficiency. This was evidently due to the ability of the rotary tumbler to promote complete sediment-water interaction, by permitting the non-colloidal sediment particles to completely traverse and become dispersed in the entire water column during each cycle.

This argument acquires greater credence when the pattern of trace metal partitioning is critically evaluated (Tables 19, 20 and 21). The consistent and efficient performance of the tumbler is indisputable as indicated by the values for Cu, Fe, Mn and Zn. Moreover, even the inconsistent trend observed for Zn at the 0.5 and 24 h-treatment periods was absent in 1.0-htreated samples. In addition, organic analysis did not dispute this contention (Tables 22, 23 and 24).

It is important to note that the indications that trace metals, PCBs and other constituents inhibited phytoplankton  $^{14}$ C-CO<sub>2</sub> uptake was supported by the bioassay results. Given then, that the strong partitioning capabilities of reciprocal (and wrist-action) shaking as conventionally as conventionally practised, it was not surprising that significant inhibition of carbon uptake was observed for all mixing periods. It is also useful to reiterate at this point that the levels of contaminants partitioned in this manner do not necessarily have any meaningful relationship to the levels partitioned under normal lacustrine conditions.

Compare this with rotary tumbling where the 1:4 rotary treatment at 0.5 h promoted enhanced  $14C-CO_2$  uptake, while the

1.0-h and 24 h mixings resulted in inhibited C-uptake. Given the short exposure time, the enhanced uptake with the 0.5 h tumbling likely resulted primarily from nutrient release. Longer periods generally permit more effective release of toxic contaminants, having the ability to negate the enhancing effects of nutrient enrichment. When these observations are combined with the fact that 1.0 h rotary tumbling was the only treatment which produced extreme statistically significant interaction (P<0.001) among sediment-water ratios (R), among spiking levels (L), and also between the interactions of ratios and addition levels (RxL) in an analysis of variance.

Thus, given that the air-mixing method is inappropriate, and that the reciprocal and wrist-action methods of mixing (at 100 rpm) tend to produce over-estimates of bioavailable contaminant levels, rotary tumbling would seem to be the most preferable approach to sediment-water mixing to estimate biologically available contaminant content.

Therefore, it is recommended that a method of elutriate preparation be adopted which utilizes a rotary tumbler, with a 1:4 sediment-site water mixture agitated in cycles of approximately 4 rpm for 1.0 h. Moreover, it is suggested that elutriates prepared in this manner would provide superior data for the assessment of contaminant bioavailability in polluted sediments (Fig. 5). The resulting elutriate is bioassaycompatible since site water is utilized with no chemical adjustments. Moreover, the gentle cycle of the "ferris-wheel"

type rotary tumbler, by more closely mimicking the natural dynamics of lacustrine sediment-water interations, coincidentally allows more efficient leaching by promoting more complete and thorough interaction between sediment particles and dilution water. The gentleness of the mixing process also maintains the structural characteristics of the sediment particles, thereby minimizing the likelihood of particle damage.

The recommended approach thus achieved the targeted objectives of this study, which focussed on the elaboration of a method for evaluating the effects of normally available contaminants in sediments. Therefore, the author believes that this approach can be used to generate more meaningful data in the assessment of contaminated aquatic sediments than some methods traditionally practised.

Finally, it is suggested that a more accurate approach to the preparation of wet sediment-water mixtures would be to compute the sediment component using dry weight calculations, rather than the wet weight volume:volume relationships currently in vogue. By basing calculations on the dry weight equivalent of the sediment, more accurate extrapolation of data would then be possible. During the conduct of this study, aquatic sediment was encountered which varied in moisture content from 55% to 70%. Without a dry-weight correction therefore, great variation may occur from experiment to experiment, where different sediments are used. An idea of the levels and kinds of variation that one might expect may be had by viewing the examples presented below:

Moisture	·····	Sediment:Wat	er
(%)	1:20 (48mL:952mL)	1:10 (91mL:909mL)	1:4 (200mL:800mL)
55	21.6g	40.9g	90g
60	19.2g	36.4g	80g
65	16.8g	31.8g	70g
70	14.4g	27.3g	60g

It is evident, then, that the quantity of sediment actually assessed in a 1:4 sediment:water elutriate may vary from 60 g to 90 g, depending on the moisture content. Hence, the author advocates that a more uniform approach be brought to this method of sediment assessment by the adoption of a dry-weight oriented procedure.

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Summary of Treatments and Procedures Used in Elutriation Studies

Study	Elutriate Preparation and Treatments
I	<ul> <li>-Agitation by ferris-wheel type rotary tumbler operated at speed of 4 rpm: Evaluation of the procedure;</li> <li>-S:W ratios, 0:1, 1:20, 1:10, &amp; 1:4; Triangle Pond sed.;</li> <li>-Dilution water: distilled water;</li> <li>-Periods of agitation of 1.0 h and 48 h;</li> <li>-Conductivity, pH, volatile &amp; total solids monitored.</li> </ul>
II	-Agitation by rotary tumbler at a rate of 4 rpm; -S:W ratios, 0:1, 1:20, 1:10, & 1:4; Triangle Pond sed.; -Dilution water: distilled water; -Periods of agitation of 1.0 h, 24 h, & 48 h; -Conductivity, pH, volatile and total solids monitored;
III	-Agitation by rotary tumbler at a rate of 4 rpm; -S:W ratios, 0:1, 1:20, 1:10, & 1:4; Triangle Pond sed.; -Dilution water: Triangle Pond site water; -Periods of agitation of 1.0 h, & 24 h; -Conductivity, pH, volatile and total solids monitored.
IV	-Agtation by rotary tumbler at rate of 4 rpm; -S:W ratios, 0:1, 1:20, 1:10, & 1:4; Triangle Pond sed.; -Dilution water: distilled water; -Periods of agitation of 1.0 h, 24 h, & 48 h; -pH of elutriation mixture adjusted to 6.0 with acetic acid prior to agitation.
V	-Agitation by air-diffuser system; -S:W ratios, 0:1, 1:20, 1:10, & 1:4; Triangle Pond sed.; -Dilution water, distilled water; -Periods of agitation of 1.0 h, 24 h, & 48 h; -Conductivity, pH, volatile and total solids monitored.
VI	-Agitation by wrist-action shaker at rate, 100 cycles/h; -S:W ratios, 0:1, 1:20, 1:10, & 1:4; Triangle Pond sed.; -Dilution water, distilled water; -Periods of agitation of 1.0 h, 24 h, & 48 h; -Conductivity, pH, volatile and total solids monitored.
VII, VIII	<ul> <li>-Comparison of three methods of agitation with the reciprocal shaker substituted for wrist-action shaker;</li> <li>-S:W ratios, periods of agitation, and bioassay levels detailed in Table 4; Toronto Harbour water &amp; sediment;</li> <li>-Volatile and total solids, chemical, and biological parameters monitored.</li> </ul>

TAB	LE	2
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Summary of Experiments and Treatments in Comparative Studies

	Treat	ment	
Experiment	Level of Elu	triate Addition	Replicates
·	5%	25%	-
I	A 0:1 /0.5	A 0:1 /0.5	4
I	A 1:20/0.5	A 1:20/0.5	4
I	A 1:10/0.5	A 1:10/0.5	4
I	A 1:4 /0.5	A 1:4 /0.5	4
II	E 0:1 /0.5	E 0:1 /0.5	4
II	E 1:20/0.5	E 1:20/0.5	4
ÍI .	E 1:10/0.5	E 1:10/0.5	4
II	E 1:4 /0.5	E 1:4 /0.5	4
III	R 0:1 /0.5	R 0:1 /0.5	4
ĨĨĨ	R 1:20/0.5	R 1:20/0.5	4
III	R 1:10/0.5	R 1:10/0.5	4
III	R 1:4 /0.5	R 1:4 /0.5	4
•			
IV	A 0:1 /1.0	A 0:1 /1.0	4
IV	A 1:20/1.0	A 1:20/1.0	4
IV	A 1:10/1.0	A 1:10/1.0	4
· IV	A 1:4 /1.0	A 1:4 /1.0	4
V	E 0:1 /1.0	E 0:1 /1.0	4
v	E 1:20/1.0	E 1:20/1.0	4
v	E 1:10/1.0	E 1:10/1.0	4
v	E 1:4 /1.0	E 1:4 /1.0	4
VI	R 0:1 /1.0	R 0:1 /1.0	4
VI	R 1:20/1.0	R 1:20/1.0	4
VI	R 1:10/1.0	R 1:10/1.0	4
VI	R 1:4 /1.0	R 1:4 /1.0	4
VII	A 0:1 /24	A 0:1 /24	4
VII	A 1:20/24	A 1:20/24	4
VII	A 1:10/24	A 1:10/24	4
VII	A 1:4 /24	A 1:4 /24	4
VIII	E 0:1 /24	E 0:1 /24	4
VIII	E 1:20/24	E 1:20/24	4
VIII	E 1:10/24	E 1:10/24	4
VIII	E 1:4 /24	E 1:4 /24	4
IX	R U:1 /24	R 0:1 /24	4
IX	R 1:20/24	R 1:20/24	4
IX	R 1:10/24	R 1:10/24	4
<u> </u>	<u>R 1:4 /24</u>	R 1:4 /24	4
A = Air Diffuser;	E = Reciprocal	Shaker; R = Rota	ry Tumbler

.

Treatment	Period Of Agitation		
(S:W)	<u>1h</u>	24h	48h
0:1	6.71	6.55	6.42
1:20	8.07	8.30	8.00
1:10	8.11	8.25	8.06
1:4	8.22	8.39	8.18

Mean pH Values of Elutriates Prepared from DW Triangle Pond Sediment by Rotary Tumbling

#### TABLE 4

pH of Elutriates Prepared from DW and Triangle Pond Sediment - pH-Adjusted to 6.0 Prior ro Rotary Tumbling

Treatment	Period of Agitation				
(S:W)	lh	24h	48h		
0:1	6.33 <u>+</u> .10	6.37 <u>+</u> .02	6.27 <u>+</u> .01		
1:20	7.56 <u>+</u> .03**	7.61 <u>+</u> .03***	7.28 <u>+</u> .08**		
1:10	7.62 <u>+</u> .011**	7.58 <u>+</u> .20*	7.12 <u>+</u> .05**		
1:4	7.38 <u>+</u> .06**	7.56 <u>+</u> .01***	7.46 <u>+</u> .03***		

\*....Statistically significant at the 95% probability level compared to control.

\*\*...Statistically significant at the 99% probability
 level compared to control.

\*\*\*...Statistically significant at the 99.9% probability level compared to control.

pH of Elutriates	
Prepared from Triangle Pond Sediment	and
Sampling-Site Dilution Water -	
Agitation by Rotary Tumbling	

Treatment	Period of Agitation	
(S:W)	lh	24h
0:1	8.09	8.28
1:20	8.19	8.23
1:10	8.17	8.08
1:4	8.24	8.22

# TABLE 6

# pH of Elutriates Prepared from DW and Triangle Pond Sediment - Agitation by Air Diffuser

freatment	Pe:	riod Of Agita	tion
(S:W)	lh	24h	48h
0:1	6.15	5.08	6.45
1:20	7.66	7.55	7.47
1:10	7.73	7.70	7.55
1:4	7.90	7.76	7.43

Treatment	Pe	riod of Agi	tation
(S:W)	1h	24h	48h
0:1	6.44	6.30	6.00
1:20	7.93	7.81	7.69
1:10	8.00	7.68	7.81
1:4	8.10	7.78	7.91

pH of Elutriates Prepared from DW and Triangle Pond Sediment -Agitation by Wrist-Action Shaker

#### TABLE 8

Mean Conductivity of Elutriates Produced from DW and Triangle Pond Sediment - Rotary Tumbling

		·	
Treatment (S:W)		Specific Conduc (µS cm <sup>-1</sup> )	tance
	<b>1</b> h	24h	48h
0:1	9	3	2
1:20	387	734	674
1:10	495	739	848
1:4	369	636	701

Treatment (S:W)	Spe	Specific Conductance $(\mu \text{S cm}^{-1})$				
	lh	24h	48h			
0:1	3	2	1			
1:20	1152	1096	1560			
1:10	906	1370	1585			
1:4	1292	1578	1911			

# Conductivity of Elutriates Prepared from DW and Triangle Pond Sediment with pH Adjusted to 6.0 Prior to Rotary Mixing

## TABLE 10

# Conductivity of Elutriates Prepared from Triangle Pond Site Water and Sediment -Rotary Tumbling

Treatment	Specific C (µS c	$m^{-1}$ )	
(S:W)	lh	24h	
0:1	997	1022	
1:20	1022	1101	
1:10	1018	1345	
1:4	1010	1171	

reatment	Spe	cific Conducta (µS cm <sup>-1</sup> )	nce
(S:W)	1h	24h	48h
0:1	3	2	5
1:20	248	420	426
1:10	427	537	617
1:4	547	696	1020

Conductivity of Elutriates Prepared from DW and Triangle Pond Sediment - Agitation by Air Diffuser

### TABLE 12

# Conductivity of Elutriates Prepared from DW and Triangle Pond Sediment -Wrist-Action Shaker

Treatment	Specific Conductance (µS cm <sup>-1</sup> )						
(S:W)	lh	24h	48h				
0:1	3	2	2				
1:20	183	338	347				
1:10	235	461	383				
1:4	371	486	496				

reatment	Vola	atile :	Solids	Total D	issolved Sol	ids
(S:W)	1h	24h	48h	1h	24h	48h
0:1	1	6	23	70 <u>+</u> 01	107 <u>+</u> 12	135 <u>+</u> 7
1:20	11	39	30	146 <u>+</u> 11*	506 <u>+</u> 06**	595 <u>+</u> 12***
1.10	20	37	77	268 <u>+</u> 05***	500 <u>+</u> 07**	601 <u>+</u> 08***
1:4	35	58	76	396 <u>+</u> 03***	368 + 03**	428 + 02***

## Mean Values of Dissolved Solids of Elutriates Prepared from Distilled Water and Triangle Pond Sediment -Rotary Tumbling (mg/L)

\*...Statistically significant at the 95% probability level compared to control.

\*\*..Statistically significant at the 99% probability level compared to the control.

\*\*\*.Statistically significant at the 99.9% probability level compared to the control.

Dissolved Solids Prepared from DW and pH Adjusted to 6.0 Prior to Rotary Tumbling (mg/L)

Treatment Volatile Solids					Tota.	l Dis	SO.	lved So	olids		
(S:W)	1h	n 241	n 48h	-	-	Lh		2	4h	481	1
0:1	0	0	0	5	±	02	18	+	04	22 <u>+</u>	03
1:20	917	636	1040	1903	<u>+</u>	04***	1652	<u>+</u>	150**	2606 +	11***
1:10	588	892	1090	1325	<u>+</u>	70**	2195	<u>.+</u>	03***	27 <u>2</u> 6 <u>+</u>	_ 38***
1:4	940	1028	1407	2069	<u>+</u>	131**	2200	<u>+</u>	20***	2959 <u>+</u>	- 30***

\*....Statistically significant at the 95% probability level compared to the control.

\*\*...Statistically significant at the 99% probability level compared to the control.

\*\*\*..Statistically significant at the 99.9% probability level compared to the control.

<b>Creatment</b>	Volatile	Solids	Total Dissol	ved Solids
(S:W)	1h	24h	1h	24h
0:1	69.5	26.5	609 <u>+</u> 0.5	612 <u>+</u> 1.2
1:20	74.0	25.5	616 <u>+</u> 5.3*	465 <u>+</u> 2.9***
1:10	59.0	53.5	530 <u>+</u> 57	715 <u>+</u> 8.0***
1:4	90.0	50.0	694 + 11.5*	595 + 3.2

Dissolved Solids of Elutriates Prepared from Triangle Pond Water and Sediment - Rotary Tumbling (mg/L)

\*....Statistically significant at the 95% probability level compared to the control.

\*\*\*...Statistically significant at the 99% probability level compared to the control.

Treatm	ent	Volat	ile So	lidsTot	al Dissolved	Solids
(S:W)	1h	24h	48h	1h	24h	48h
0:1	51	48	78	124 <u>+</u> 2	78 <u>+</u> 18	113 <u>+</u> 7
1:20	53	61	113	278 <u>+</u> 78	302 <u>+</u> 05**	396 <u>+</u> 16**
1:10	81	87	77	440 <u>+</u> 07**	** 385 <u>+</u> 58*	475 <u>+</u> 32**
1:4	103	117	150	470 <u>+</u> 00**	* 650 <u>+</u> 67*	825 <u>+</u> 135*

#### Dissolved Solids of Elutriates Prepared from DW and Triangle Pond Sediment - Air Diffuser Agitation (mg/L)

\*....Statistically significant at the 95% probability level compared to the control.

\*\*\*..Statistically significant at the 99.9% probability level compared to the control.

	ΓA	B	L	E	1	7
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### Dissolved Solids of Elutriates Prepared from DW and Triangle Pond Sediment - Wrist-Action Shaker (mg/L)

Treatmen	t <u>Vol</u>	atile	Solids	Total	Dissolved	Solids
(S:W)	ĺh	24h	48h	1h	24h	48h
0:1	52	43	43	176 <u>+</u> 3	156 <u>+</u> 13	100 <u>+</u> 7
1:20	61	48	63	206 <u>+</u> 6*	252 <u>+</u> 5*	246 <u>+</u> 5**
1:10	66	87	83	262 <u>+</u> 6**	438 <u>+</u> 50*	364 <u>+</u> 39*
1:4	104	102	75	421 <u>+</u> 6***	452 <u>+</u> 42*	320 <u>+</u> 14**

\*....Statistically significant at the 95% probability level compared to the control.

\*\*...Statistically significant at the 99% probability level compared to the control.

\*\*\*..Statistically significant at the 99.9% probability level compared to the control.

Treatment	Volati	<u>le Solids</u>	Total Dissolved Solids			
(S:W)	lh	24h	lh	24h		
A 0:1	39	53	97 + 3 127 + 13	108 + 2		
A 1:10	78	63	268 + 8**	275 ± 5**		
A 1:4	75	90	313 + 13**	455 + 75*		
Ê 0:1	53	53	100 + 3	100 + 0		
E 1:20	82	70	230 7**	210 + 7**		
E 1:10	83	. 88	255 + 15**	312 + 12**		
E 1:4	118	135	$403 \pm 13^{**}$	457 <u>+</u> 55*		
R 0:1	53	70	112 + 14	103 + 13		
R 1:20	77	87	207 + 3**	270 + 3**		
R 1:10	90	97	297 <del>+</del> 13*	327 + 3**		
R 1:4	122	147	430 + 57*	$492 + 42^*$		

#### Dissolved Solids Prepared from Toronto Harbour Sediment and Site Water by Three Methods of Agitation (mg/L)

\*....Statistically significant at the 95% probability level compared to the control.

\*\*...Statistically significant at the 99% probability level compared to the control.

\*\*\*..Statistically significant at the 99.9% probability level compared to the control.

A = Agitation by aeration.

E = Agitation by Eberhard reciprocal shaker.

R = Agitation by rotary tumbler.

								· · ·
Treatment	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Dry Sed.	5.8*	12*	151*	2.8**	_	44*	479*	480*
A 0:1 /0.5	<1	<1	<1	<1	<10	<1	<1	<1
A 1:20/0.5	<1	<1	5	17	78	2	1	9
A 1:10/0.5	<1	<1	4	36	87	2	1	15
A 1:4 /0.5	<1	<1	7	19	126	3	1	30
E 0:1 /0.5	<1	<1	<1	<1	<10	<1	<1	<1
E 1:20/0.5	<1	<1	6	10	91	2	<1	12
E 1:10/0.5	<1	<1	2	7	27	<1	<1	1
E 1:4 /0.5	<1	<1	5	23	136	3	<1	7
R 0:1 /0.5	<1	<1	<1	<1	<10	<1	<1	<1
R 1:20/0.5	<1	<1	4	18	148	2	<1	17
R 1:10/0.5	<1	. <1	.3	16	256	2	<1	3
R 1:4 /0.5	<1	<1	4	18	305	.3	<1	24

# Mean Values of Trace Metals: Elutriates Prepared from Toronto Harbour Dilution Water Using Three Methods of Agitation for 0.5 h (µg/L)

\*....Values expressed in units of mG/L.

\*\*...Value expressed in percent.

 $A \equiv$  Agitation by aeration.

E = Agitation by Eberhard reciprocal shaker. R = Agitation by rotary tumbler.

Mean Values of Trace Metals: Elutriates Prepared from Toronto Harbour Dilution Water Using Three Methods of Agitation for 1.0 h  $(\mu g/L)$ 

Treatment (S:W)	Cđ	Со	Cu	Fe	Mņ	Ni	Pb	Zn
A 0:1/1	<1	<1	<1	<1	<10	<1	·<1	<1
A 1:20/1	<1	<1	5	25	28	2	<1	7
A 1:10/1	<1	<1	8	24	36	2	<1	20
A 1:4 /1	<1	<1	6	44	64	3	<1	13
E 0:1 /1	<1	<1	<1	<1	<10	<1	<1	<1
E 1:20/1	<1	<1	4	15	162	2	<1	11
E 1:10/1	<1	<1	5	14	167	2	<1	15
E 1:4 /1	<1	<1	15	78	299	2	1	20
R 0:1 /1	<1	<1	<1	<1	<10	<1	<1	<1
R 1:20/1	<1	<1	8	11	178	2	<1	9
R 1:10/1	<1	<1	9	12	286	3	<1	14
R 1:4 /1	<1	<1	15	41	369	3	<1	24

A = Agitation by aeration.

E = Agitation by Eberhard reciprocal shaker.

R = Agitation by rotary tumbler.

#### Mean Values of Trace Metals: Values from Elutriates Prepared from Toronto Harbour Dilution Water and Sediment Using Three Methods of Agitation for 24 h

(µg/L)

Treatment	Cđ	Co	Cu	Fe	Mn	Ni	Pb	Zn
A 0:1 /24	<1	<1	<1	<1	<10	<1	<1	<1
A 1:20/24	<1	<1	8	37	53	2	<1	11
A 1:10/24	<1	<1	8	11	54	2	<1	20
A 1:4 /24	<1	<1	12	64	60	3	10	25
E 0:1 /24	<1	<1	<1	<1	<10	1	<1	<1
E 1:20/24	<1	<1	7	19	205	4	<1	11
E 1:10/24	<1	<1	9	100	251	3	<1	.9
E 1:4 /24	<1	<1	20	143	393	4	<1	12
R 0:1 /24	<1	<1	<1	<1	<10	<1	<1	<1
R 1:20/24	<1	<1	6	17	205	4	<1	14
R 1:10/24	<1	<1	8	69	335	2	2	7
R 1:4 /24	<1	<1	15	71	770	3	<1	13

A = Agitation by aeration.

E = Agitation by Eberhard reciprocal shaker.

R = Agitation by rotary tumbler.

MEAN	<b>VAI</b>	UES	OF	ORGA	JU T (	S:	ELUTRI	ATES	PREI	PAREL	FROM
TORON	OTV	HAR	BOUR	DII	ί <b>Ū</b> Τ]	ION	WATER	AND	SEDI	MENT	USING
	THI	REE	METH(	ODS	ÔF	AG]	TATION	FOR	0.5	h	
					( í	hġ/I	5)				

Treatment (S:W)	α−BHC	γ−BHC	Total PCB
A 0:1 /0.5	<0.4	<0.4	< 4
A 1:20/0.5	1.5	<0.4	< 4
A 1:10/0.5	1.2	0.4	< 4
A 1:4 /0.5	1.3	<0.4	<4
E 0:1 /0.5	<0.4	<0.4	<4
E 1:20/0.5	<0.4	<0.4	122
E 1:10/0.5	<0.4	<0.4	138
E 1:4 /0.5	<0.4	< 0.4	267
R 0:1 /0.5	<0.4	<0.4	<4
R 1:20/0.5	0.6	<0.4	< 4
R 1:10/0.5	0.7	0.4	< 4
R 1:4 /0.5	<0.4	<0.4	< 4

A = Agitation by aeration.

E = Agitation by Eberhard reciprocal shaker.

R = Agitation by rotary tumbler.

Treatment (S:W)	α-BHC	ү-ВНС	Total PCB
A 0:1 /1	<0.4	<0.4	<4
A 1:20/1	21.6	<0.4	381
A 1:10/1	<0.4	<0.4	277
A 1:4 /1	13.1	6.5	496
E 0:1 /1	<0.4	<0.4	< 4
E 1:20/1	4.3	9.8	307
E 1:10/1	10.8	4.3	334
E 1:4 /1	8.6	<0.4	459
R 0:1 /1	1.6	0.5	< 4
R 1:20/1	1.4	<0.4	276
R 1:10/1	0.9	<0.4	302
R 1:4 /1	<0.4	<0.4	507

### Mean Values of Organics: Elutriates Prepared from Toronto Harbour Dilution Water and Sediment Using Three Methods of Agitation for 1.0 h (ng/L)

A = Agitation by aeration.

E = Agitation by Eberhard reciprocal shaker.

R = Agitation by rotary tumbler.

	Mean Val	ues of O	)rganics:	Elutriat	es Prepar	red
from	Toronto Ha	arbour Di	lution Wa	ater and	Sediment	Using
	Three	Methods	of Agita	tion for	24 h	
		(	ng/L)			

Treatment (S:W)	α-BHC	ү-ВНС	Total PCB
A 0:1 /24	<0.4	<0.4	<4
A 1:20/24	<0.4	<0.4	145
A 1:10/24	<0.4	<0.4	272
A 1:4 /24	<0.4	<0.4	354
E 0:1 /24	<0.4	<0.4	< 4
E 1:20/24	<0.4	<0.4	108
E 1:10/24	<0.4	<0.4	242
E 1:4 /24	15.5	<0.4	433
R 0:1 /24	<0.4	<0.4	<4
R 1:20/24	<0.4	<0.4	136
R 1:10/24	0.9	<0.4	222
R 1:4 /24	<0.4	<0.4	143

A = Agitation by aeration.

E = Agitation by Eberhard reciprocal shaker.

R = Agitation by rotary tumbler.

Tı	eatment	Assim. Co	eff.	Probabil	ity > F
	(S:W)	5% Amended	25% Amended	R	L ææ <sub>RxL</sub>
	LC	0.539 <u>+</u> .042	0.539 <u>+</u> .042		
A	0:1 /0.5	0.508 <u>+</u> .033	0.508 <u>+</u> .007		
À	1:20/0.5	0.633 <u>+</u> .040	0.699 <u>+</u> .056+	.01	.69 .34
A	1:10/0.5	0.570 <u>+</u> .055	0.574 <u>+</u> .037		
A	1:4 /0.5	0.631 <u>+</u> .070	0.503 <u>+</u> .045		
	LC	0.674 <u>+</u> .04	0.674 <u>+</u> .045		
Ē	0:1 /0.5	$0.512 \pm .016^{*}$	0.512 <u>+</u> .033		
Ē	1:20/0.5	0.521 <u>+</u> .040	0.332 <u>+</u> .011**	++ .0001	.0001 .001
E	1:10/0.5	0.486 <u>+</u> .041*	$0.311 \pm .014^{**}$	+	۰.
E	1:4 /0.5	0.452 <u>+</u> .011**+	0.250 <u>+</u> .013**	*++	
	LC	0.805 <u>+</u> .073	0.805 <u>+</u> .073		
R	0:1 /0.5	0.693 <u>+</u> .038	0.693 <u>+</u> .045		
R	1:20/0.5	0.624 <u>+</u> .067	0.626 <u>+</u> .083	.0001	.71 .94
R	1:10/0.5	0.710 <u>+</u> .055			
R	1:4 /0.5	$1.534 \pm .127^{**++}$	1.442 <u>+</u> .167*+	• <b>+</b> .	
*	Statistic control ( respectiv	cally significant c LC): *, **, ***9 vely.	ompared to untr 5%, 99%, and 99	eated phy .9% sign:	ytoplankton Ificance
+	Statistic +, ++9	ally significant c	ompared to elut e respectively.	riate com	ntrol (0:1)

TABLE 25Mean Bioassay Values of ElutriatesPrepared from Toronto Harbour Dilution Water and SedimentUsing Three Methods of Agitation for 0.5 h

A = Air diffuser; E = Reciprocal shaker; R = Rotary tumbler.

ææ..Interaction between ratio (R) of sed. to water, and level
 (L) of elutriate addition.

Tı	reatment	Assim. C	oeff.	Probab	ility :	> F
	(S:W)	5% Amended	25% Amended	R	L æ	eRxL
	LC	0.141 <u>+</u> .014	0.141 <u>+</u> .014			
Ą	0:1 /1.0	0.141 <u>+</u> .018	0.141 <u>+</u> .011			
A	1:20/1.0	0.156 <u>+</u> .007	0.118 <u>+</u> .003	.30	.003	.03
A	1:10/1.0	0.146 <u>+</u> .009	0.109 <u>+</u> .003+			
A	1:4 /1.0	0.158 <u>+</u> .003				
	LC	0.150 <u>+</u> .004	0.150 <u>+</u> .004			· · · · · · · · · · · · · · · · · · ·
E	0:1 /1.0	0.156 <u>+</u> .011	0.156 <u>+</u> .007			
E	1:20/1.0	0.180 <u>+</u> .005**	0.112 <u>+</u> .003**	+ •014	.0001	.001
E	1:10/1.0	0.177 <u>+</u> .006*	0.115 <u>+</u> .002**	++		
Ē	1:4 /1.0	0.187 <u>+</u> .007*	0.096 <u>+</u> .002**	*+++		
	LC	0.248 <u>+</u> .014	0.248 <u>+</u> .014	· · · · ·	tanan arta san	
R	0:1 /1.0	0.272 <u>+</u> .006	0.272 <u>+</u> .010			
R	1:20/1.0	0.255 <u>+</u> .005	0.208 <u>+</u> .002*+	+ .0001	.0001	.0002
R	1:10/1.0	0.262 <u>+</u> .190*++	0.190 <u>+</u> .000*+	•+		
R	1:4 /1.0	0.239 <u>+</u> .006+	0.211 <u>+</u> .004++			
*	Statistic phytoplar significa	ally significant akton control (LC) ance respectively.	compared to untr : *,**,***95%,	eated 99%, 9	9.9%	
+	Statistic +,++,+++	cally significant .95%, 99%, 99.9%	compared to elut significance res	riate c pective	control	(0:1)

# TABLE 26Mean Bioassay Values of ElutriatesPrepared from Toronto Harbour Dilution Water and SedimentUsing Three Methods of Agitation for 1.0 h

# Fig. 1: Toronto Harbour East Headland showing:

• Triangle Pond



Fig. 2: Map of Toronto Harbour Front depicting:

- Sediment sampling site
- Relative Position of the Eastern Headland

to the Inner and Outer Harbours.



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# Fig. 4a: Burrell Wrist-action Shaker

# 4b: Aeration System of Agitation



# Fig. 5: Schematic Representation of the Sediment Elutriate Bioassessment Procedure.

