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THE NWRI MICROLAYER SAMPLER MARK II

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#### EXECUTIVE SUMMARY

The NWRI Microlayer Sampler Mark II

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The present NWRI Surface Microlayer Sampler Mk-II is a scaled-down version of the previous model to make it more portable and more convenient to use in the field. It is smaller in size, lighter in weight, and can be motor or manualy operated. The unit is side-mounted on a Boston Whaler, and can be transported, installed and operated by one person. It has been field-tested in the St. Clair and St. Lawrence Rivers in our alkyllead studies. Its overall performance is considered superior than the earlier model.

## RÉSUMÉ À L'INTENTION DE LA DIRECTION

L'échantillonneur de micro-couche Mark II de l'INRE

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La version actuelle de l'échantillonneur de micro-couche en surface MK II de l'INRE est un modèle réduit par rapport au précédent, ce qui le rend plus transportable et plus facile à utiliser sur le terrain. Il est de plus petite taille, plus léger et peut être motorisé ou actionné manuellement. Il est monté sur la coque d'une baleinière Boston et peut être transporté, installé et utilisé par une seule personne. On en a fait l'essai dans la rivière Ste-Claire et le fleuve Saint-Laurent dans le cadre de nos études sur les dérivés alcoylés du plomb. Son rendement global est supérieur à celui de l'ancien modèle.

#### THE NWRI MICROLAYER SAMPLER MARK II

#### INTRODUCTION

The Surface microlayer is a hydrophobic thin film where water and air meet. It is a boundary between the two phases. Metals as well as hydrophobic organic materials, including high molecular weight hydrocarbons such as plant waxes, can be accumulated in this layer from atmospheric inputs (Owen and Meyers, 1984). Indeed, enrichments of copper and lead have been consistently observed in the surface microlayer of the ocean (Lion and Leckie, 1981). Accumulation of alkyllead compounds has been found in microlayer samples from the St. Clair River although they were absent in the underlying waters (Chau et al. 1985). Once in the microlayer, these compounds can be further concentrated into aerosol particles, by bursting of bubbles, or into sinking particles by compression of the surface film. Thus, this thin layer can act as a vehicle in the transport of pollutants between water and the atmosphere and between water and suspended particulate material.

Various ingenious devices have been designed to sample the surface microlayer. The simplest one is the dipping glass plate method (Harvey and Burzell, 1972). All methods, unfortunately, are operationally defined by the samplers, with variable sample thicknesses, ranging from ca.  $10^{-2}$  um to more than  $10^{2}$  um. The uncertainty in sample thickness, and hence its volume, makes it

very difficult to evaluate the actual concentration of any substances in the layer, and hence their significance. Before a method is available to measure the true thickness of the microlayer being sampled, at least a uniform and reproducible layer should be sampled in order to be able to evaluate data on a comparative basis.

The rotating drum sampler originally described by Harvey (1966), modified by Platford et al. (1984), called the NWRI Microlayer Sampler, seems to be the unit of choice for surface microlayer studies. The present NWRI Microlayer Sampler Mk II is a scaled-down version of the previous model to make it more portable and more convenient to use. It is smaller in size, lighter in weight, and can be motor or manually operated. The unit is side-mounted on a Boston Whaler, and can be transported, installed and operated by one person. It has been field-tested in St. Clair and St. Lawrence Rivers in alkyllead studies. Its overall performance is considered superior to the earlier model.

#### CONSTRUCTION

The rotating cylinder is 50 cm in length, 32 cm in diameter, giving a total area of  $5027 \text{ cm}^2$ , which, if running at 5 rpm, will sample an area of 25135 cm<sup>2</sup> per minute. The depth of immerson in water is kept at 2-3 cm by adjusting the floats. All the adjustments can be controlled by personnel sitting in the boat during operation. The rotation of the cylinder is powered by a gear-reduction motor which is operated by a 12 volt storage battery, at 4-5 rpm. In case of

power failure, a hand crank can be attached to drive the cylinder under unusual circumstances. The adhered surface microfilm carried by the cylinder is scraped off by a teflon and neoprene blade (supplied by Tridon Limited, Burlington, Ontario) and guided into a 4-L sample bottle. The gross weight of the sampler is 30.8 kg. The whole device is self-floating and self-adjusting as guided by two parallel vertical poles mounted on a side frame attached to the Boston Whaler, so that it is independent of any vertical movements caused by the boat or by waves. Figure 1 is a photograph of the device. A detailed blue-print, specifications, and descriptiono of parts are given in Appendix 1. A bracket for a 4-L sample bottle has since been added.

During operation, the Boston Whaler was trolling at about one knot. The volume collected is ca. 300 ml per minute and the thickness of the microlayer is estimated to be ca. 100 um thick.

 $(1 \text{ um} = 1 \text{ micron} = 1 \times 10^{-6} \text{ m}).$ 

Under conditions of fast flowing water such as in a river, the boat can be anchored during sample collection.

#### ALKYLLEAD COMPOUNDS IN THE MICROLAYER

The sampler was used in the St.Lawrence and St.Clair Rivers to investigate the presence of alkyllead compounds in these areas. Four litres of sample were collected at each location and stored in amber bottles and kept in a cool room until analysis according to the method given by Chau et al. (1983).

Tetraalkyllead compounds are hydrophobic and considerable enhancement might be expected in the microlayer. Results indicated that alkyllead compounds (R= Me, Et), mainly triethyllead, diethyllead and lead(II) were found in the surface microlayer samples in the St. Lawrence River off Maitland, and in the St. Clair River near Corunna where alkyl lead plants are located. The absence of tetraalkyllead compounds in the the microlayer was likely due to the high vapor pressure of these compounds, causing them to evaporate into the atmosphere, or to photo-degrade by sunlight to the trialkyl- and dialkyllead species.

Tables 1 and 2 show the concentrations of alkyllead compounds detected in the microlayer. Their presence in the surface microlayer may well reflect the possibility of either atmospheric transport of these compounds which were trapped in this layer, or continuous extraction and partition of these compounds from the underlying water into this hydrophobic layer. Another reason for the existence of the triethyllead and diethyllead species in the microlaver is the photo-decomposition of the tetraethyllead originally trapped in this layer. The presence of inorganic lead(II) is either because it is the end product of degradation, or it could be concentrated in this layer by association with organic materials by complexation. The data presented only serve to illustrate the capability of the microlayer sampler. The distribution of the various species and their pathways will be presented elsewhere in other studies.

#### ACKNOWLEDGEMENT

The Sampler was designed by one of us (N.M.) and constructed by the Engineering Group of National Water Research Institute at Burlington. We wish to record our appreciation of the assistance of R. Tkacz and M. Comba in field testing. REFERENCES

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|             | Et3-Pb | Et2Pb | Pb(II)           |
|-------------|--------|-------|------------------|
| Sta 1       |        |       |                  |
| June        | nd     | nd    | 678              |
| July        | nd     | nd    | . 370            |
| Aug         | ñđ     | nd    | nđ               |
| Sept        | 71     | 30    | 660              |
| Sta 2       |        |       |                  |
| June        | nd     | nd    | 973              |
| July        | 75     | nd    | 675              |
| Aug         | 240    | nd    | 3327             |
| Sept        | 10     | nd    | 186              |
| Sta 3       |        |       |                  |
| June        | nd     | nd    | 260              |
| July        | nd     | nd    | 590 <sup>-</sup> |
| Aug         | nd     | nd    | 905              |
| Sept        | nd     | nd    | 186              |
| Control Sta | L      |       |                  |
| June        | nd     | nd    | 176              |
| July        | nd     | nd    | 480              |
| Aug         | nd     | nd    | 355              |
| Sept        | nd     | nd    | 231              |

Table 1. Alkyllead Compounds in the Surface Microlayer ofSt. Lawrence Rivers, Ontario. (1985)

Concentrations in ng/L as Pb; Sampling Stations are about 100m off shore. Sta 1, off Maitland; Sta 2 and Sta 3 are about 1000m and 2000m respectively downstream of Sta 1. Control Sta, about 20 km upstream of Sta 1. nd - not detectable.

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|             | Et3-Pb | Et2-Pb | Pb(II)     |
|-------------|--------|--------|------------|
| Sta 1       |        |        |            |
| June        | nd     | nđ     | nd         |
| July        | 233    | nd     | 744        |
| Aug         | 17     | 'nð    | 415        |
| Sept        | 35     | 20     | 125        |
| Sta 2       |        |        |            |
| June        | nd     | nd     | 425        |
| July        | 348    | nd     | 747        |
| Aug         | 23     | nd     | 223        |
| Sept        | 85     | 54     | 352        |
| Sta 3       |        |        |            |
| June        | nd     | nd     | nd         |
| July        | 214    | nđ     | 890        |
| Aug         | 12     | 9      | 561        |
| Sept        | 20     | 24     | 340        |
| Control Sta |        |        |            |
| June        | 'nđ    | nđ     | 185        |
| July        | nd     | nd     | 460        |
| Aug         | nd     | nd     | <b>191</b> |
| Sept        | nd     | nd     | 62         |
|             |        |        |            |

Table 2. Alkyllead Compounds in the Surface Microlayer of St.Clair River, Ontario. (1985)

Concentrations in ng/L as Pb; Sampling stations are about 50m off shore. Sta 1, off Corunna; Sta 2 and Sta 3 are about 700m and 1100m respectively downstream of Sta 1. Control Sta, about 12 km upstream of Sta 1. nd - not detectable.

#### Appendix 1. SPECIFICATIONS

Weight: 30.8 kg Wt. of boat clamp: 7.7 kg Dimensions, length: 74 cm width : 94 cm height: 46 cm Drum dia.: 32 cm

Motor: Pittman Gearmotor c/w Tach 38.3 to 1 reduction. Model No. GMT9414E279 No load rpm: 7370 Final reduction: 9.86 to 1 Gear: 138T Pinion: 14T Total reduction: 378 to 1 Drum rpm: 5- 14

Drum : Low Carbon Sheet Steel Cylinder, baked-on vitreous enamel finish, PVC ends, Delrin bushings.

Depth of Drum Immersion: ca. 2.5 cm

Floats: Polyurethane closed cell foam with fibreglass/polyester resin coatings

Drum Manufacturer: Clark Porcelain Ltd., 2440 Cawthra Road, Mississauga, Ontario , L5A 2X1

Float Manufacturer: FA210 Fiberglass Ltd., 23 Robinson Street, P.O.Box 357, Fort Erie, Ontario, L2A 5N1

Sample scraping blade: Neoprene. Maker: Tridon Ltd., 2190 South Service Road, Oakville, Ontario, L6L 5T8

### DESCRIPTION OF PARTS

| ITEM | DVG. No.   | DESCRIPTION                         | QTY. |
|------|------------|-------------------------------------|------|
| l    | ME-5257-6  | DRUM                                | 1    |
| 2    | ME-5257-2  | DRUM HUB                            | 1    |
| 3    | ME-5257-3  | DRUM HUB & GEAR BLANK               | 1    |
| 4    |            | 'D' RING CORD 1/4"                  | 7 F  |
| 5    | ME-5257-4  | FRAME                               | 1    |
| 6    | ME-5257-5  | FRAME PIVOT BRACKET                 | .4   |
| 7    |            | HEX. HEAD BOLT 1/4-20UNC X .75 S.S. | 8    |
| 8    |            | SHAFT 3/8' DIA. X 24.625 L. SS      | 1    |
| 9    |            | SPACER                              | 1    |
| 10   |            | TROUGH ASSEMBLY                     | 1    |
|      | ME-5257-16 | TROUGH                              |      |
|      | ME-5257-8  | TROUGH PIVOT ARM                    |      |
|      | ME-5257-17 | WIPER HOLDER                        |      |
|      | ME-5257-15 | OVERFLOW RETAINER                   |      |
| 11   |            | SPROCKET GEAR .25P 14T 303SS        | 1    |
| 15   |            |                                     |      |
| 13   |            | GEARMOTOR C/W TACH. 38.3 TO 1 RED.  | 1    |
|      |            | 7370 RPM N.L. 12VDC P.M. SERVO      |      |
| 14   | ME-5257-9  | MOTOR CAN                           | 1    |

| ITEM | DWG. No.   | DESCRIPTION                       | QTY. |
|------|------------|-----------------------------------|------|
| 15   |            | WATERTIGHT ELECT. CONNECT.        | 1    |
| .17  | ME-5257-11 | FLOAT                             | 2    |
| 18   |            | HEX. HEAD BOLT 1/4-20UNC X 1.5 SS | 2    |
| 19   |            | LOCKNUT & FL. WASHER 1/4-20UNC SS | 2    |
| 5)   | ME-5257-12 | SHAFT CLAMP BLOCKS                | 4    |
| 51   |            | HEX. HEAD BOLT 1/4-20UNC X 2 SS   | 4    |
| 22   |            | LOCKNUT & FL. WASHER 1/4-20UNC SS | 4    |
| 23   |            | GEAR COVER                        | 1    |
| 24   |            | CLEVIS PIN 1/4 X .75 SS           | 4    |
| 25   |            | PIN RETAINER SS                   | 4    |
| 56   |            | TURNBUCKLE SS                     | 2    |
| 27   |            | SLOT. HEAD SCREV #10-32UNF        | 3    |
| 5B   | ME-5257-10 | MANUAL DRIVE DETAILS              | 1    |
| 29   | ME-5257-14 | BUAT BRACKET                      | 1    |
|      |            |                                   |      |
|      |            |                                   |      |
|      |            |                                   |      |
|      |            |                                   |      |
|      |            |                                   |      |



# Figure 1. The NWRI Microlayer Sampler Mark-II.

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