

PROCEDURE FOR SAMPLING THE SEA-SURFACE MICROLAYER

Unesco 1985



14 AOUT 1985

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PREFACE

This report was prepared by the Intergovernmental Oceanographic Commission (IOC) with the collaboration of a Consultant, Mr. W.D. Garrett of the Naval Research Laboratory, Environmental Sciences Division, Washington D.C., USA.

The methods described have been discussed and approved by the IOC Group of Experts on Methods, Standards and Intercalibration (GEMSI) at the fifth Session, Paris, 14-17 June 1983, subject to the provision that as more information becomes available through experience gained in intercalibration exercises, the proposed methods will be amended accordingly.

The IOC Manuals and Guides N° 15 contributes to the Marine Pollution Monitoring Programme for Petroleum (MARPOLMON-P) and complements IOC Manuals and Guides 13 "Manual for Monitoring Oil and Dissolved/Dispersed Petroleum Hydrocarbons in Marine Waters and on Beaches."

1. INTRODUCTION

The sea-surface microlayer is a thin layer of seawater, a few of tenths of a millimeter in thickness at the boundary between the atmosphere and the ocean. In recent years there has been an increasing interest in the chemistry, biology and physics of the surface microlayer, a boundary layer which plays an important role in pollutant transfer and concentration processes (GESAMP, 1980). Pollutants are accumulated by various physico-chemical and biological processes in the surface microlayer, pollutants are enriched in this zone, and certain polluting substances such as oil films modify the physical properties of the air-sea boundary in ways that alter the interfacial flux of other pollutants.

Because of these important aspects of the sea-surface microlayer a GEMSI ad hoc Working Group was requested to select an appropriate microlayer sampler for use in monitoring programmes; the first instance being the IOC Marine Pollution Monitoring Programme for Petroleum (MARPOLMON-P). In its report (IOC, 1981), the Working Group recommended the screen sampler (Garret, 1965) for the collection of microlayer samples in MARPOLMON-P to be used for the determination of dissolved/dispersed petroleum hydrocarbons. The selection of the screen sampler was based not only on its simplicity and ease of operation, but also on its ability to collect a sample of exact thickness from a measurable seasurface area. In addition, it does not alter the concentration or chemical nature of the constituents collected from the ocean surface.

IOC Manuals and Guides N° 15 describes methodology tested and shown to be appropriate for the sampling of the sea-surface microlayer. It is not the intention to suggest that the collection and analysis of sea-surface microlayer for such components as petroleum hydrocarbons should constitute a monitoring programme. The transient nature of films and slicks in space and time detract from the utility of this phase for trend monitoring purposes.

The sampling and analysis of the sea-surface microlayer can, in the context of studying bio-geochemical cycles of selected pollutants, be important for studying a range of processes, e.g. photo oxidation and other modes of decomposition which have direct bearing on the levels and identity of the transformed products of environmental contaminants.

2. THE SCREEN SEA-SURFACE MICROLAYER SAMPLER

2.1 DESCRIPTION

This method of surface sampling involves the withdrawal of a wire mesh (screen) from beneath the surface of the water through the air-water interface while maintaining the screen horizontal and parallel to the sea-surface. As the screen is raised through the water below the surface, sea-water merely flows between the wires. When passing through the surface, however, thin segment (on the order of a few tenths of a millimeter) of the surface layer between the wires are removed. This technique collects all of the dissolved and dispersed constituents within the layer removed by the screen.

The screen sampler (figure 1) consists of the screen, two handles, and a framework which supports the screen and handles. The screen has 16 wires per inch (2.54 cm) and is stainless steel or other alloy resistant to seawater corrosion. The screen portion of the sampler which is contacted to the water horizontally measures 50 x 65 cm. Other screen size may also be used as long as the dimensions are known. If the frame and handles are constructed from metals different from that of the screen, the sampler should be rinsed with salt-free water after use to prevent corrosion. The metal screen is primarily intended to be used for sampling of dissolved/dispersed petroleum hydrocarbons in the sea-surface microlayer in the framework of MARPOLMON-P. It is possible that plastic screen may be used for the collection of samples to be analyzed for non-organic pollutants in a future development of the Marine Pollution Monitoring Programme.

Another possible screen sampler configuration (figure 2) may be used for surface sampling from the bow of a slowly moving ship, thereby eliminating the need to sample from a small boat. This triangular screen is lowered and raised through the sea-surface from the ship's bow with a line connected through a bridle to a three-point attachment to the corners of the screen frame. Surface sampling from a slowly moving ship should only be conducted when it is not possible to make collections from a small boat or fixed platform.

2.2 CLEANING AND PROTECTING THE SAMPLER

New samplers should be thoroughly degreased with clean methylene chloride or other suitable hydrocarbon-free solvent. After cleaning, a blank determination for dissolved/dispersed hydrocarbons should be conducted on a microlayer sample taken from hydrocarbon-free water, to assure that interfering substances were removed from the new sampler. The screen portion of the cleaned sampler should be covered with clean aluminum foil or a thin PTFE sheet to protect the screen from contamination during storage and transportation.

Following sampling the screen, frame and handles should be rinsed with clean, salt-free water and allowed to dry prior to recovering. Do not touch the screen with bare hands at any time during any cleaning, handling, or sampling operations. Care should be taken to protect the screen against damage, so that it is not torn and remains as flat as possible.

3. SAMPLING PLATFORM AND SITE SELECTION

3.1 PLATFORMS

The rectangular screen sampler with handles (figure 1) is normally used from a small boat. Sampling should be performed from the bow with the craft moving slowly forward. Boat propulsion may be with oars or a battery-powered electric motor. If possible engines fueled with petroleum products should be avoided when sampling for dissolved and dispersed petroleum hydrocarbons. It has been demonstrated that the triangular sampler (figure 2) can be used successfully for dissolved/dispersed petroleum hydrocarbon sampling from the bow of a ship which is moving slowly on a straight path through waters which meet the site selection criteria (section 3.2). This sampler cannot be used from a ship with a bulbous bow.

Screen sampling is also possible from fixed research platforms as long as there are no unwanted interfering pollutants in the surrounding waters. For example, dissolved/dispersed petroleum hydrocarbon sampling should not be conducted in the vicinity of a natural seep of petroleum. Platform sampling should be performed from the upcurrent corner or edge, so that ambient water is constantly flowing past the sampling site and contamination from the platform can be avoided.

3.2 SAMPLING SITE SELECTION

The selection of sampling sites should take into account the following guidelines to avoid unwanted sources of the pollutant being studied and other interfering substances:

- (a) Do not select an area for study with strong natural sources of the pollutant under analysis.
- (b) Avoid sampling in floating debris or sea life, such as refuse, kelp, etc., as these extraneous materials will be lifted from the sea-surface by the screen and possibly modify the analytical results.
- (c) Avoid contamination from the sampling platform by following the procedures outlined in section 3.1. In general, the sampler should be placed into ambient water which is flowing directly toward the source of potential contamination. For example, sampling operations would be conducted from the bow of a vessel moving forward, and not from the stern.
- (d) This method is presently intended for samples to be analyzed for dissolved/dispersed petroleum hydrocarbons in MARPOLMON-P. Surface sampling of an oil spill should be avoided, because extremely high hydrocarbon concentrations would be obtained. This is due to the fact that the thickness of the oil on the water is often a sizeable fraction of the thickness collected by the screen sampler. Surface sampling in the same general area, but not directly in the oil film would be desirable, however, to determine the impact of the pollution on petroleum hydrocarbon concentrations in the adjacent surface waters. Also, sampling in natural, biogenic sea slicks should not be avoided. To distinguish between natural slicks and petroleum films use the guidelines detailed in Annex I and published in IOC Manuals and Guides N° 13 (1984).

4. MICROLAYER SAMPLING TECHNIQUE

4.1 Remove the screen sampler from its protective covering, taking care not to touch the screen mesh with bare fingers or hands. Place the sampler into the water with the screen in a horizontal position parallel to the sea surface. After about 5 seconds with the screen still parallel to the surface, withdraw the sampler from the water, then replace it into the water. Do this several times before each sample is taken to condition the screen wires to the chemical substances in the water. This is an important step which improves the accuracy and effectiveness of the actual sampling process.

4.2 The surface sampling proceeds as in 4.1, except that after withdrawal of the sampler, it is immediately tilted toward one of the rear corners of the frame, so that the collected surface water can drain into an appropriate sample collection container.

The screen will drain almost completely in 45-60 seconds. Nearly complete draining is recommended, especially when 10 or fewer screen dips are required to collect sufficient water for a particular analytical procedure. The quantity of sample collected and the size and composition of the collection container will be determined by the pollutant being determined and the analytical methodologies to be applied.

4.3 The number of surface contacts (dips) required for a particular analytical procedure depends upon the volume of seawater needed for analysis. The volume collected per dip is a function of the screen wire diameter and mesh number (wires per unit length). The volume per screen contact with the water must be measured for each different sampler by draining collected water into a graduated cylinder. The water from ten surface contacts should be collected in the cylinder, and the total volume of water collected divided by ten in order to obtain the volume per dip.

A screen which measures 50 x 65 cm has a surface area of 3250 cm². If the screen removes a 0.03-cm-thick surface layer, then 3250 cm² x 0.03 cm = 97.5 cm³ of water is collected per surface contact. Even though the volume collected per dip can be estimated from the dimensions of the screen by calculation, it is essential to actually measure the volume in order to accurately determine the layer thickness sampled and to compare the performance of one sampler with another.

5. RECORDING THE SAMPLING-OPERATION

5.1 DRAFT FORM FOR RECORDING THE SAMPLING-OPERATION

A draft form for recording the sampling-operation is included as Annex II. Code tables with explanations are found in Annex I of IOC Manuals and Guides N° 13 for the Marine Pollution Monitoring (Petroleum) Programme. In addition to the usual information to be recorded on Date, Time, Position, Environmental Information (wind, waves, temperature), Station, Sample Number, etc., the following data pertaining to surface sampling are required.

5.2 DESCRIPTION OF SCREEN 'SURFACE MICROLAYER SAMPLER

- (a) Type: Enter name of metal alloy, e.g. stainless steel, or plastic, e.g. nylon, from which the screen is constructed. Following this enter (T) only if the triangular screen configuration was used.
- (b) Mesh: Enter number of wires per inch.
- (c) Area: Enter area of screen in square centimeters.
- (d) Wire diameter: Enter diameter of screen wire in millimeters

5.3 SAMPLING-PARAMETERS

Enter the following information:

- (a) Number of dips per sample.
- (b) Average drainage time in seconds.
- (c) Average volume collected per dip in milliliters.

5.4 SEA-SURFACE OBSERVATIONAL CODES

There is a scientific interest in the enrichment of certain pollutants in natural as well as pollutant sea slicks (oil spills, films from municipal dump sites, etc.). Consequently, item 1 (i-iv) of Annex I of IOC Manuals and Guides N° 13 (1983), has been modified slightly to include the existence of natural slicks. Under item 1 (i), "Status of observation", add number 3, "Natural sea slicks observed". The other codes will remain unaffected. For example, if one observes natural slicks in lines over one-fourth of the sea surface, the observational codes will be as follows :

$$\begin{array}{cccc} A & B & C & D \\ \frac{A}{3} & - & \frac{C}{3} & \frac{D}{2} \end{array}$$

If both thin oil films and natural slicks are observed in patches over one-half of the sea surface the codes should read:

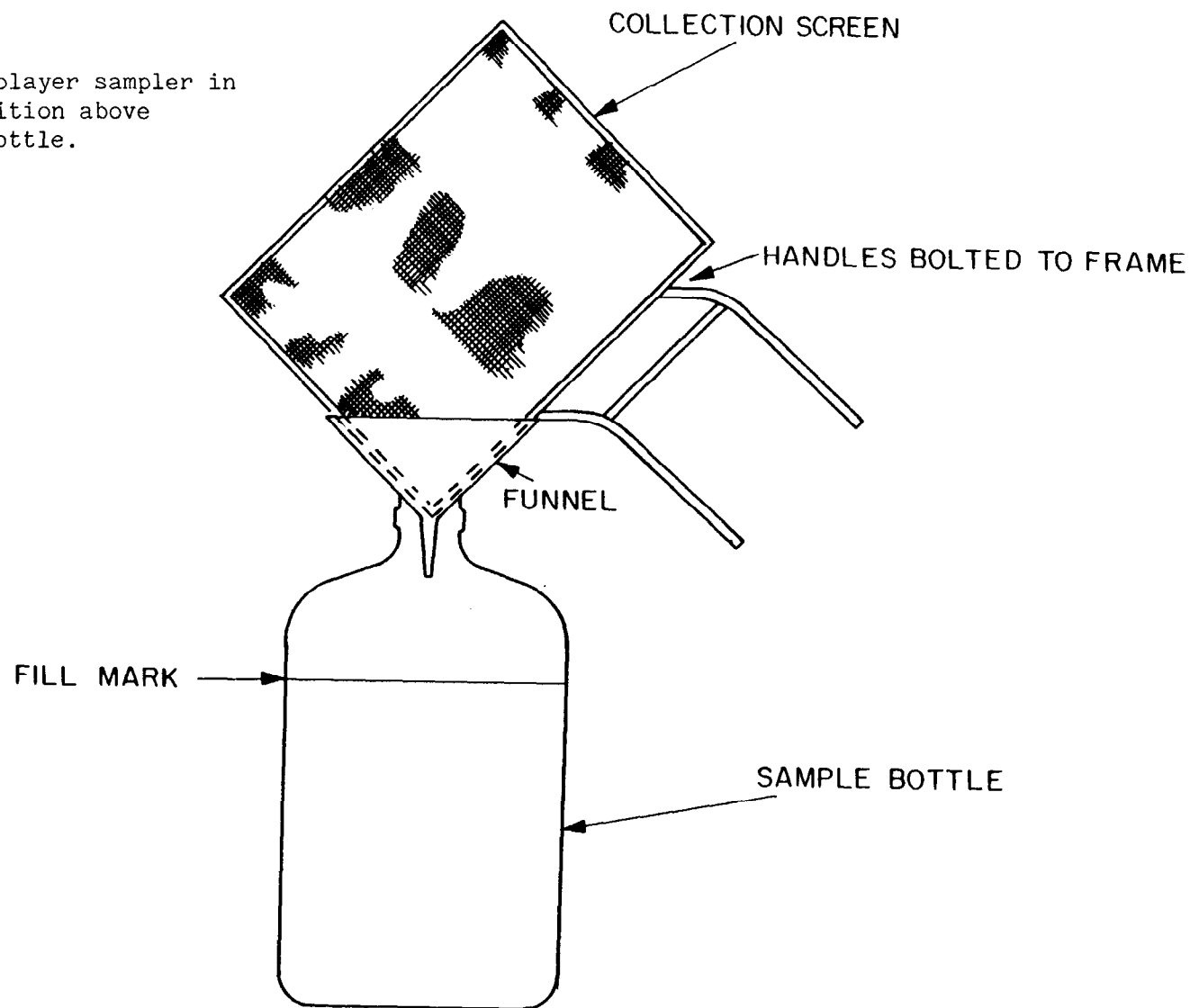
$$\begin{array}{cccc} A & B & C & D \\ \frac{A}{2,3} & \frac{B}{1} & \frac{C}{2} & \frac{D}{4} \end{array}$$

The relative coverage of oil films versus natural slicks should be specified in the last column (additional information).

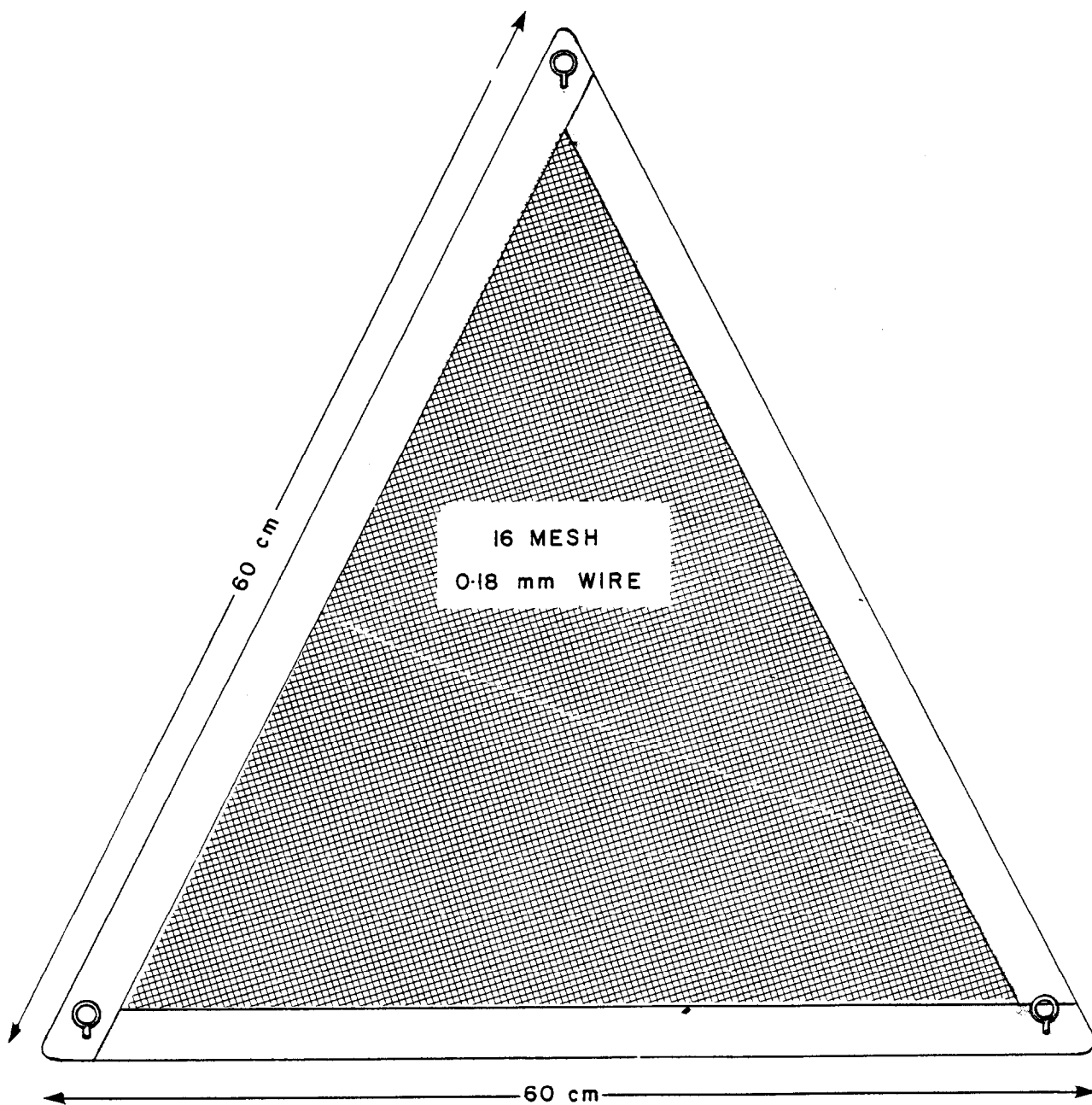
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Figure 1. Surface microlayer sampler in draining position above collection bottle.



SEA-SURFACE COLLECTION ASSEMBLY
IN DRAINING POSITION

FIGURE 2

Drawing of a triangular surface microlayer sampler for use from the bow of a slowly moving ship.

ANNEX I

DISTINGUISHING BETWEEN OIL SLICKS AND NATURAL FILMS

1. A large spill of crude oil or a residual fuel is obvious to the eye. If it has not weathered to tar-like residues, there will be central zones which are brown or black in colour and represent thick oil layers. These will be surrounded by thinner films, sometimes showing iridescence or sheen (various coloured bands due to light interference effects). At the outer edges of the petroleum slick, even thinner films may be present with no obvious colours, but which are visible because of their damping action on the capillary ripples. Subsequent weathering of these heavy petroleum products will lead to tar residues within the oil slick, usually at the downwind end.

2. Description of Different Surface Films

It is sometimes difficult to distinguish natural sea slicks from the films formed by some types of petroleum products. Such problems may arise when the spilled oil is a distillate product (diesel oil, lubricating fluid or fuel oil), which has spread into a thin film with little colour. Since an oil film of this type eliminates capillary ripples as does a natural sea slick, the following guides should assist the observer in making a correct distinction between petroleum oils and natural films.

(a) When winds are greater than 8 knots (4.1 m sec.^{-1}), natural slicks are readily dispersed by air-sea dynamic forces. Under these conditions visible natural surface slicks will be rare, and visible films should be assumed to be oil pollution. However, a long, narrow, isolated band of slick, sometimes containing seaweed and ship's refuse, should not be considered an oil slick.

(b) Under relatively calm wind conditions a considerable percentage of the sea-surface can become covered with a natural surface film as evidenced by extensive areas of ripple-damped water. Pollutant slicks may be confused with natural films under such low-wind conditions. The following rules of judgment would be applied in such a case.

If the conditions in section 1 (above) are observed (layer of dark oil and/or tar residues) or if an oily odour is evident, the slick should be considered of petroleum origin.

When the sea is relatively calm and if the slick is not obviously petroleum, it should be considered to be a natural film. When it is not possible to distinguish between a natural slick and an oil film, the quantity of pollutant oil would be extremely small and the slick should not be considered a spill.

3. Description of a Natural Slick

A visible sea-surface pattern in which capillary ripples are absent. It is a film of recent biologically produced organic material, generally too thin to be seen except by its ability to damp and to resist the formation of wind-generated ripples. The ripple-damping property produces a light reflection pattern which renders the slick visibly different from the surrounding rippled water. The slick is usually lighter in appearance than the rippled water, but may be seen as a darker zone when viewed toward the sun. In the absence of wind (no ripples) the entire sea-surface appears to be slicked, however, there is generally no evidence of film colour, oily odor or of thick films unless pollutant oils are present.

IOC MARINE POLLUTION MONITORING PROGRAMME
LOG FORM FOR
SURFACE MICROLAYER SAMPLING

PLATFORM/SHIP		COUNTRY	INSTITUTE	CRUISE No.	SCREEN MICROLAYER SAMPLER			
TYPE	NAME				TYPE	MESH	AREA	WIRE DIAMETER

[illegible]

**IOC MARINE POLLUTION MONITORING PROGRAMME
LOG FORM FOR
SURFACE MICROLAYER SAMPLING**

SAMPLE NUMBER	POSITION										ENVIRONMENTAL INFORMATION												ADDITIONAL INFORMATION				
	QUAD	LATITUDE				LONGITUDE				UNIT	WIND				WAVE				TEMPERATURE °C								
		DEG.		MIN.		DEG.		MIN.			SPEED		DIR.		PERIOD		HEIGHT		AIR			WATER					
		Q _c	L _a	L _a	L _a	L _a	L _o	L _o	L _o		L _o	L _o	f	f	d	d	P _w	P _w	H _w	H _w	±	T		T	T	T _w	T _w