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A PROTOTYPE SYSTEM FOR MONITORING OFF-SHORE MARINE POLLUTION

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Abstract

A labour-efficient scheme for monitoring marine pollutants is described. Suspended particulate matter and biological indicators are suggested as being the most suitable sample parameters. The water phase is considered too variable and bottom sediments too insensitive for pollution monitoring purposes.

Equipment designs (with non-metallic components) and field trials were planned more specifically for trace metal rather than for organic pollutants. Samples were analysed for phosphorus, cadmium, copper, iron, lead, mercury and zinc.

Suspended particulate matter is collected and filtered from water samples using a RIMCO-CSIRO sampler. Short trials off Port Hacking (N.S.W.), Rottnest Is. (W.A.) and Spencer Gulf (S.A.) indicated statistically significant higher levels of most trace metals in particulates off Port Hacking. The S.A. values were lowest and W.A. intermediate, except for mercury for which S.A. had the highest and N.S.W. the lowest relative concentrations.

All sites showed high variability in particulate elemental levels. Tests off Port Hacking suggest that, given the natural variability and the present standard of analytical precision, significant trace metal differences would not be detected within 5 km of a sampling site. This implies that, in the absence of gross point sources of pollution, a minimum spacing of 10 km between coastal monitoring stations would be adequate.

A short time series study at one site indicated that the suggested techniques are sensitive enough to yield useful and subtle information on trace metal fluxes.

Particulates which are sinking through the water column are collected in a mid-water detritus trap. To minimize contamination and sample loss both before and after site exposure, a novel trap design was developed to open and close on command from an electronic timer. Total mass collected and concentration levels of trace metals in this type of material are higher than for suspended particulates collected in RIMCO samplers. Analytical precision is consequently higher. No comprehensive study of this marine sample fraction was made.

Mussels are shown to be excellent indicators of local environmental differences. The technique for using mussels as pollution indicators is improved by equilibrating animals (either natural or imported stock) at a reference site and then translocating these to the chosen monitoring sites. Site differences in trace metal levels are reflected in mussel tissue differences in less than one month. Animals are suspended in polypropylene mesh pockets, which afford protection and a means of individual identification by position in the mesh

array and also allow even exposure to the environment. Water temperature and food supply are the two main variables affecting rate of mussel metabolic activity. Mussel condition is more closely correlated with food supply (and hence particulate pollutants) in off-shore regions where food is more frequently a limiting growth parameter than it is in near-shore environments. Water temperature is recorded on a specially developed data logger. Mussel tissue sample preparation and analysis are straight forward operations.

A prototype submersing-reel assembly was built to enable the detritus trap, temperature recorder and mussel exposure frame to be set at intermediate water depths without floats on the surface. The assembly and associated apparatus is unreeled to the surface for pick-up after accelerated corrosion and fracture of a steel pin connected to a battery and presetable timing circuit. The equipment remains attached to the mooring block.

Further development work on the mid-water trap and the submersing-reel system is necessary. Compact, light-weight designs in polycarbonate plastic and fibre-glass are required. A multiple-depth version of the RIMCO-type sampler also would be useful. Results obtained with the prototypes suggest that such work would be worthwhile. Without refinement the equipment would not be used for long because of its awkwardness. Well-designed equipment usually soon finds wider use; such evolutionary progression has already happened in the case of the temperature data logger.

Possible extension of the monitoring scheme to include organic parameters - oil and synthetic chemicals - could be investigated. The marginal increase in program costs would be relatively small since most sampling times and station site maintenance would be in common with trace metal monitoring. Only the chemical analyses would be separate extra work.

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INTRODUCTION

At present there is no routine monitoring of potential pollutants in open seawater around the Australian coast. The only significant routine of chemical analysis in open water has been restricted to measuring nutrients such as nitrate and phosphate. Although these can be pollutants in large concentrations, the main uses of this information have been for tagging water masses and for estimating the nutrient status of the water.

In studies more directly associated with pollution, some bottom sediments from the continental shelf have been analysed for heavy metals (e.g. Harrison and Dix 1973, Davies 1974, de Forest *et al.* 1978).

Where the water column itself was sampled and analysed, the results must be considered unreliable because of inexperience and poor techniques used in determining the very low levels of pollutants which exist in this phase.

A program was started in 1978 by CSIRO with financial support from the Marine Protection Branch of the former Department of Science and the Environment, to design a system for collecting samples from open ocean sites around the Australian coast and analysing them for selected heavy metals, oil, and organic pollutants. This work, if carried out on a continuing basis, would establish base-line concentrations and long-term trends, and would detect localized discharges of contaminating chemicals.

Two sample parameters were chosen for the proposed monitoring program; suspended particulate matter (seston) and a biological accumulator organism - mussels in the first instance.

Several new types of field equipment were needed for the program:- a mussel exposure frame, an automatic detritus trap which opens and closes on command, a recoverable moored submerged buoy system, associated timing mechanism, and a temperature recorder. Prototypes of these items have been made. This report describes their construction and field tests in detail.

The results of some field trials show that the system should succeed in its objective of providing satisfactory reference data on pollutants in seawater. However, its successful implementation will depend on the availability of multiple units produced on a semi-commercial basis. Some modification of the prototype equipment will be required to make it easier to manufacture and operate.

Principles of Monitoring Ocean Pollution

The design of the proposed monitoring system compromises five interrelated criteria:

1. relevant sample parameters,
2. reliable sample collecting methods,
3. economical sampling methods,
4. standard analytical techniques, and
5. adequate work satisfaction.

1. Relevant sample parameters. Of the four possible sample parameters - *suspended solids, biological specimens, bottom sediment* and *water*, - only two, suspended solids and biological indicators, were considered suitable for a long term monitoring program.

The *water* phase was rejected because concentrations of potential trace pollutants in open seawater are very low, and the handling of samples taken for analysis needs such high standards of care and cleanliness to minimize contamination, that it cannot realistically be expected to be maintained throughout years of routine work. There are also analytical problems, including doubts about preservation techniques, large errors when operating near the detection limits of some methods, and unresolved questions about the significance of chemical speciation in deducing a pollution threat from simple analytical chemical data.

The *bottom sediment* phase was rejected because it is impossible to separate "resident" sediment from recently transported or precipitated material, and only poor estimates of the proportions of each in a sample can be made from presently available methods such as grain-size, core slice and organic carbon analyses. This is a serious deficiency because the relatively high and variable levels of trace metals in resident sediments mask the evidence of all but gross inputs of polluting metals, thus making analysis of bottom sediments an insensitive means of monitoring pollutants.

Suspended solids are good sample parameters because a significant fraction of trace metals which may have been initially in the aqueous phase soon transfers to a solid phase by adsorption, precipitation, or plankton ingestion. There is usually

ample time for metals discharged in solution at the shoreline to establish an equilibrium between solid and aqueous phases before being sampled further offshore. If suspended solids are analysed then the additional analysis of surrounding water is redundant. Suspended solids not only concentrate pollutants from the surrounding water but they act as time-integrating samplers reflecting average environmental conditions over a period of days or weeks. Pollutant concentrations in a grab sample of water are more transitory in both time and space dimensions.

Two types of suspended solids samplers have been suggested for this project: the RIMCO sampler which filters particulate matter from an integrated water sample taken between the surface and 20m depth, and a mid-water detritus trap. Which is the more relevant to pollution surveillance will not be known until both have been used and compared over a long period of time.

Biological indicator organisms are necessary components of an adequate pollution monitoring system, with a role equivalent to their use in pharmacology. Bio-accumulators discriminate between biologically available (and potentially toxic) and non-available forms of a contaminant, a distinction which is difficult and expensive if not impossible to determine by chemical or physical means alone. (Estimating the relative proportions of 3-(toxic) and 5-(non-toxic) valent forms of arsenic is one example). If an organism neither accumulated nor was physiologically stressed by an environmental contaminant, then the potential pollutant would be demonstrably harmless whether or not concentration fluxes were detected chemically. Of course, as in pharmacology, the careful selection of appropriately sensitive bio-accumulators is critical to a successful program. Ideally, more than one type of organism should be used.

Rates of bio-accumulation and saturation capacities vary in individual animals, with physical environmental conditions, and with seasons. Such differences may be mitigated by suitable program design. The effect of variations between individual animals can be minimized through using samples each with total wet weights approximately the same and of more than 25 individuals. The most important physical parameter affecting metabolic accumulation rate is water temperature, and this can easily be monitored continuously. The effect of seasonal variations can be determined and overcome by sampling each site at, say, monthly intervals.

The most practical advantages of using bio-accumulators are that they concentrate contaminants to easily measured levels thereby allowing more laboratories and analysts to participate in a monitoring program - an important consideration in a national program - and that they offer a means of averaging out short-term variations in environmental concentration fluctuations and thus afford easier recognition of long-term trends.

Mussels and oysters are excellent animals with which to begin such a national program.

2. Reliable sample collecting methods. Two sources of unreliability can arise at the point of sampling. One is due to operator variability. This is minimized if procedures and equipment are unambiguously understood and easily operated by sea-going personnel. Equipment should be designed for simple deployment and retrieval without recourse to dangerous or awkward manoeuvres. Fulfilling these requirements introduces a dilemma common to developmental stages of work: attempts to simplify or substitute manual operations with automatically-operated equipment often complicate the apparatus and increase its cost.

The second source of unreliability comes from loss or damage of equipment which, in turn, results in temporal gaps in data records. Unattended field stations at sea are exposed to loss or damage from storms, surface shipping, vandalism, theft, fishing operations, and where mussels or oysters are used, poaching. Equipment should be designed to withstand or avoid these hazards. Since these hazards (except being snagged in fishing nets) are significantly reduced if the field apparatus is set below the surface, a system which permits instruments and continuous sample collectors to be submerged and recovered without needing a surface marker-buoy offers advantages in security and reduced exposure to structural stress. Submerged marker-buoys with acoustic recall are now being introduced into the fishing industry for similar reasons.

However, there is an increased risk of such equipment being inadvertently caught in a trawl net, since fishermen have no visual indication of submerged gear which they might otherwise avoid.

3. Economical sampling methods. The field work necessary in collecting samples is usually the most costly component of a monitoring program and it is important that every effort be made to minimize this cost.

Ships of opportunity - that is, vessels engaged primarily in other tasks - can be used incidentally in the sample-collecting program with much more cost effectiveness than specifically dedicated research vessels - provided the reliability of samples taken can be maintained.

Sampling operations from such vessels should require a minimum of time, structural conversion, or special deck equipment which might interfere with the primary function of the ship. To ensure maximum sample integrity, procedures should be simple enough for relatively untrained and unmotivated personnel to manage competently.

To these ends, gear should be as light as possible and retrievable rather than expendable. Mooring blocks, once in place on the sea-bed, should be used repeatedly. They should not have to be hauled to the surface or replaced with another block on every visit to a monitoring station. Sample preservation techniques should be relatively simple and safe. For example, the use of acids or organic solvents is potentially dangerous and should not be required: simple freezing, bagging or drying is all that non-specialist technicians should be expected to do.

Finally, the collection of too many samples through superfluous replication, too frequent sampling, or the inclusion of unimportant parameters needlessly adds to costs, and smothers interest by imposing excessive or repetitious work loads.

4. Standard analytical techniques. Ideally, a monitoring program, from sampling methods through to chemical analysis, should be based on standard techniques. Pioneering techniques, no matter how superficially attractive, are usually subject to frequent modification. Such techniques are often in active stages of evolution, which make early data difficult to compare with data generated later in the same program and with data from programs elsewhere. In some cases unsuspected deficiencies may become evident with time and the technique abandoned completely. On the other hand it is pointless to adopt standard oceanographic techniques which are obviously inadequate for new situations.

Adequate field techniques did not appear to be available for open ocean pollution monitoring, so developmental work was needed in that area.

Sample parameters which could be analysed by fairly standard methods were chosen - particulates and bio-accumulators. Exceptionally high standards of skill or cleanliness are not required. Results of trace pollutants in solid phases are more readily accepted and their significance not questioned to the same extent as are water analyses for the same contaminants. These latter are at present surrounded by controversy about chemical speciation and analytical quality control.

The question of legal admissibility of data has also to be kept in mind should it subsequently be required in prosecution or other litigation proceedings. In general only officially approved standard methods have any weight in legal proceedings.

5. Adequate work satisfaction. This factor is, of course, desirable in most work programs but it is particularly important in long-term studies where subtle trends could be obscured by unnecessarily large variability in data arising from technical indifference.

While some intrinsic research interest may be associated with the task of interpreting data, such interest is beyond the critical practical steps upon which the quality of the data is based. Conscientiously executed routines in sample collection and chemical analysis are the essence of success in monitoring programs. There is little academic content in such work and technicians - or others - soon become disenchanted with work which is too repetitive or too demanding. Fatigue and a sense of futility soon become evident in analytical work if environmental concentrations are consistently near or less than the detection limit of the method used. A high rate of staff turnover further increases the non-environmental variability of results.

Attention must therefore be paid to such traditional factors in planning a long term monitoring program. The prospect of a feed of mussels or oysters may relieve the routine at times!

Description of Field Equipment

1. RIMCO-CSIRO Particulate Matter Sampler

This apparatus is manufactured in Melbourne by Rauchfuss Instruments and is available through Selby's Scientific Ltd. (Major 1977). A simplified set of operating instructions is appended (Appendix 1).

The sampler is made of perspex and held within a protective stainless steel frame. It was designed to monitor trace metals in seawater, especially the particulate fraction, by permitting unskilled operators to collect and semi-automatically filter water samples free from contamination. It operates by collecting 5ℓ of water integrated through the upper 20m of the ocean. This water is then immediately filtered internally using the pressure of air trapped in the sampler.

2. Midwater Detritus Trap

Principle. Four requirements were considered essential in the design of a suitable trap. Most importantly, the trap should be capable of opening and closing automatically at pre-selected times to prevent extraneous particles being caught in the trap before deployment and to prevent loss of trapped material during recovery. Secondly, the exposed collecting surface area, when open, should catch sufficient detrital material in, say, one month to permit accurate chemical analysis. Thirdly, the trap should be easy to handle in the field, i.e. compact in design, light, and simple to manipulate. Finally, it should be easily flushed out in the laboratory (for particulates), and easily cleaned and prepared for further use.

Table 1. Detritus deposition rates in ocean, coastal and estuarine sites.

Site	Reference	Deposition Rate $g.m^{-2}.day^{-1}$	$0.1m^2$ Trap Set for 1 month $g.0.1m^{-2}.30\ days^{-1}$
Deep Sargasso Sea	Honjo (1978)	0.046	0.14
20 km off Californian coast	Souter *et al.* (1977)	1.3	3.9
S.W. Arm Port Hacking estuary	Bulleid (pers. comm.)	3.75	11

Few of these features appeared to be combined in the large range of devices hitherto described in the literature. One possible exception which may be worth evaluating is the unit described by Zeitzschel *et al.* (1978). Nevertheless, it was thought worthwhile to develop new apparatus. A prototype design has been built. It is suspected of being structurally weak in parts. Also, as yet, its collecting efficiency has not been evaluated. This would be needed for absolute sedimentation rate measurements, but not for obtaining concentrations of elements or compounds in collected samples, which is often the more relevant information in pollution studies.

Studies by Gardner (1980a,b) on sediment trap efficiency indicate that the baffled box shape has very little over- or under-trapping bias. His comprehensive studies were not known until after this work was completed. A modified version of his deep sea trap (Rowe and Gardner 1979) may be another suitable alternative.

Specification. The general features of the trap and its operation are evident from Figures 1-4. The reasons for its shape and size are less obvious and are explained here.

The trap consists of two symmetrical halves made up of polymethacrylate (perspex) sheeting. The halves are hinged at the centre and, except for the centrally located handle and more distant parts of the supporting frame, there is no obstruction directly over the opening to impede particles from falling or drifting in. The trap is of square cross-section, 220 mm x 220 mm, and when open presents two collecting surfaces with a combined area of approximately 0.1 m^2. Since 2g, dry weight, of material is a satisfactory quantity of sediment for chemical analysis, this size of trap should be ideal for use on continental shelf sites which could be visited at one monthly intervals. As indicated in Table 1, more than 2g of material would accumulate in this time at all but the most non-productive areas.

The trap has vertical sides and a depth to width ratio of 4:1 obtained by the internal grid of baffles which divides the trap into small tubes each of square cross-section with 30 mm sides and 120 mm depth. These features dampen internal turbulence and prevent significant loss of material through resuspension from the trap (Kirchner 1975). However, the effects of the pyramidal ends

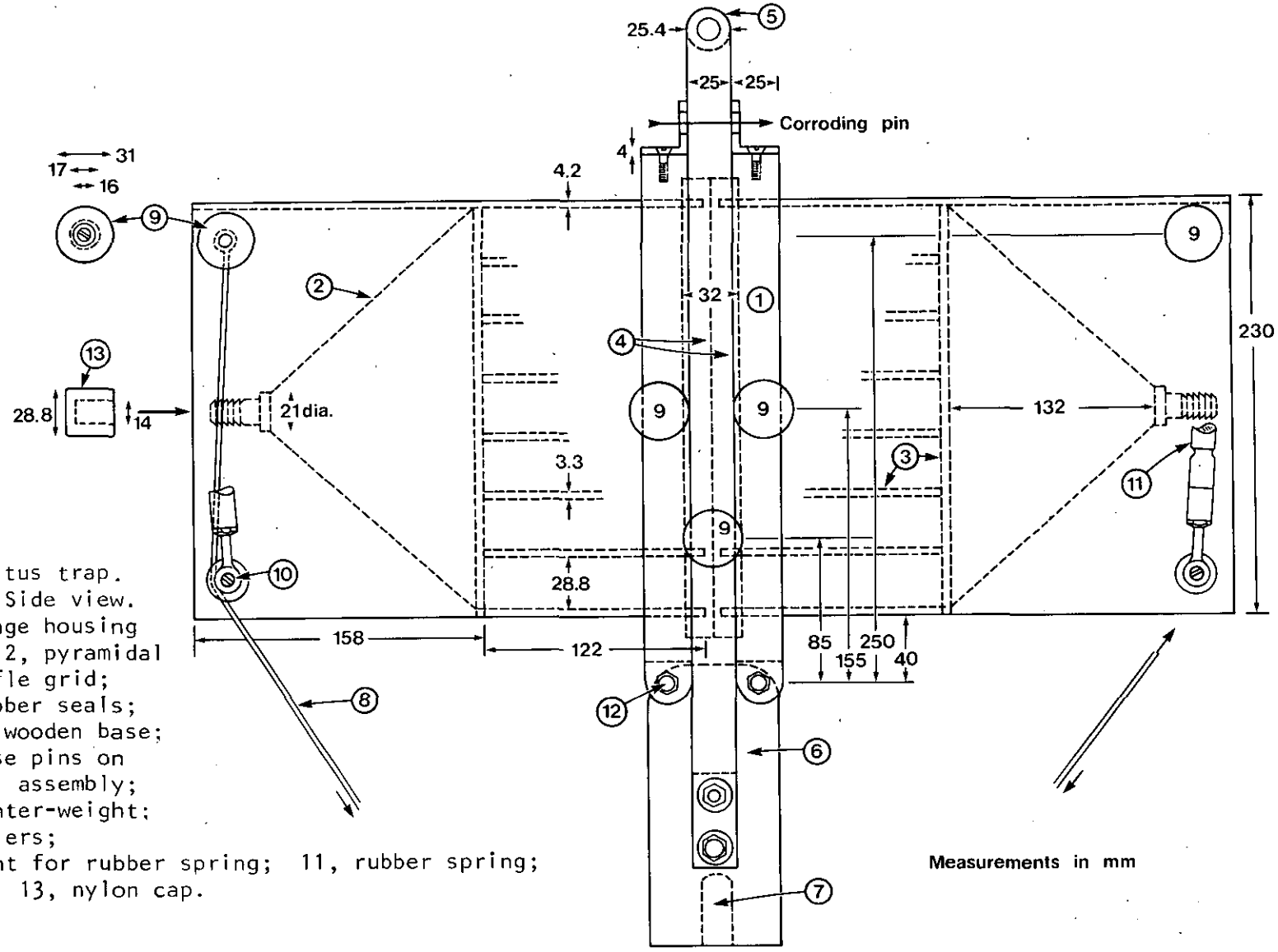


Fig. 1a Mid-water detritus trap. Specification. Side view. 1, perspex flange housing rubber seals; 2, pyramidal sides; 3, baffle grid; 4, silicone rubber seals; 5, handle; 6, wooden base; 7, hole to house pins on submersing-reel assembly; 8, cord to counter-weight; 9, grooved rollers; 10, anchor point for rubber spring; 11, rubber spring; 12, hinge pin; 13, nylon cap.

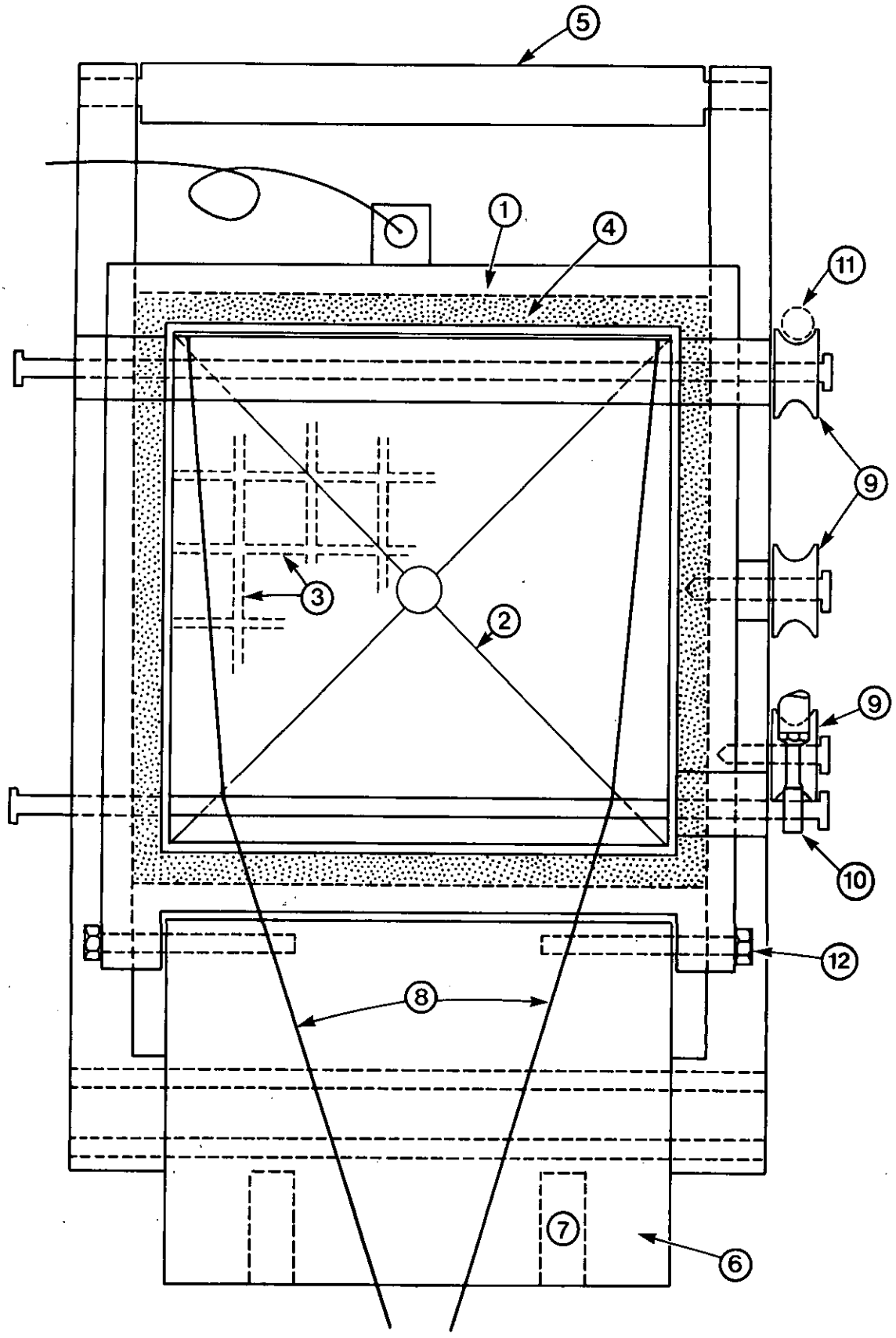


Fig. 1b Mid-water detritus trap. Specification. End view.
1, perspex flange housing rubber seals; 2, pyramidal sides; 3, baffle grid; 4, silicone rubber seals; 5, handle; 6, wooden base; 7, hole to house pins on submerging-reel assembly; 8, cord to counter-weight; 9, grooved rollers; 10, anchor point for rubber spring; 11, rubber spring; 12, hinge pin; 13, nylon cap.

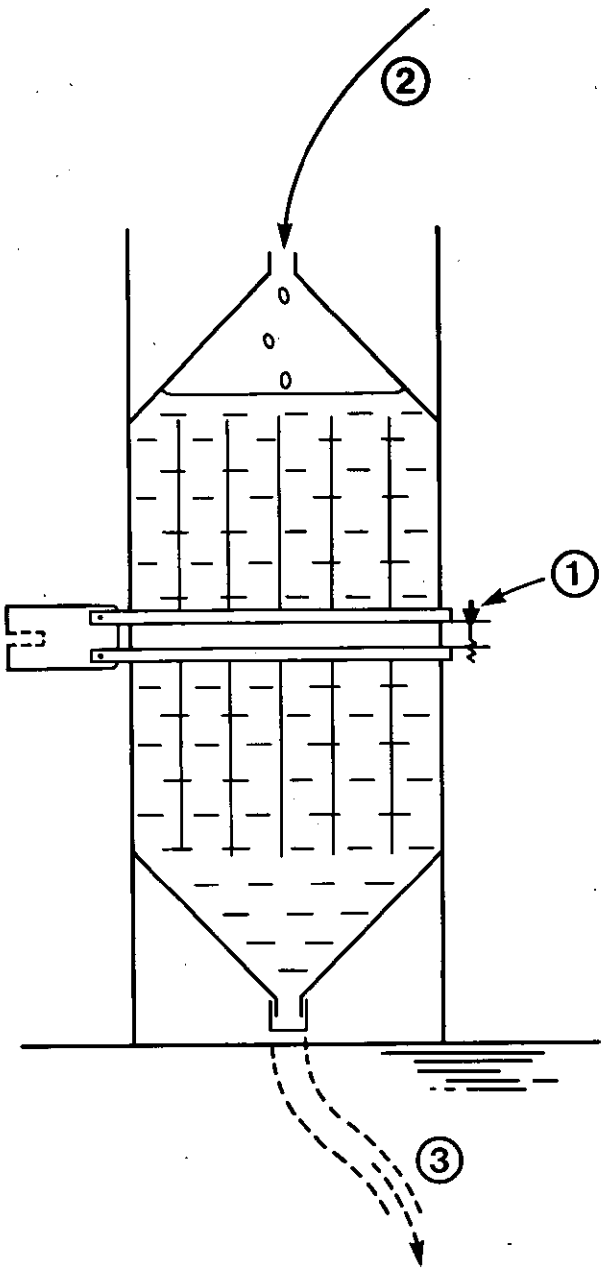


Fig. 2 Mid-water detritus trap. Preparation and sample removal.

1. Clamp shut with electro-corrosive pin.
2. Fill with particle-free water.
3. After sampling period, drain contents into collecting bucket.

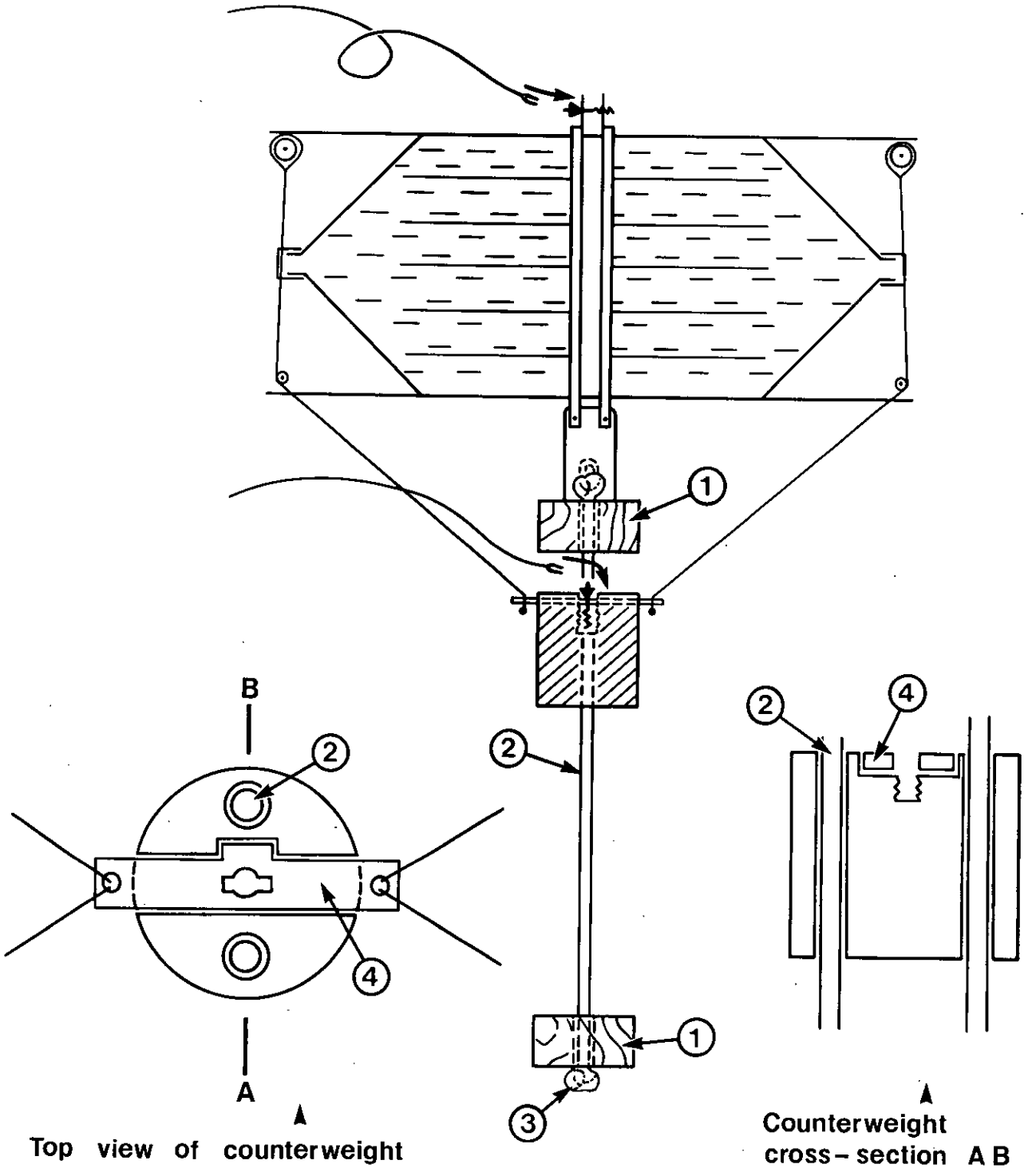


Fig. 3 Mid-water detritus trap. Deployment.

1. submersing-reel frame,
2. 12 mm polypropylene guide rope,
3. knot, e.g. monkey fist,
4. stainless steel plate.

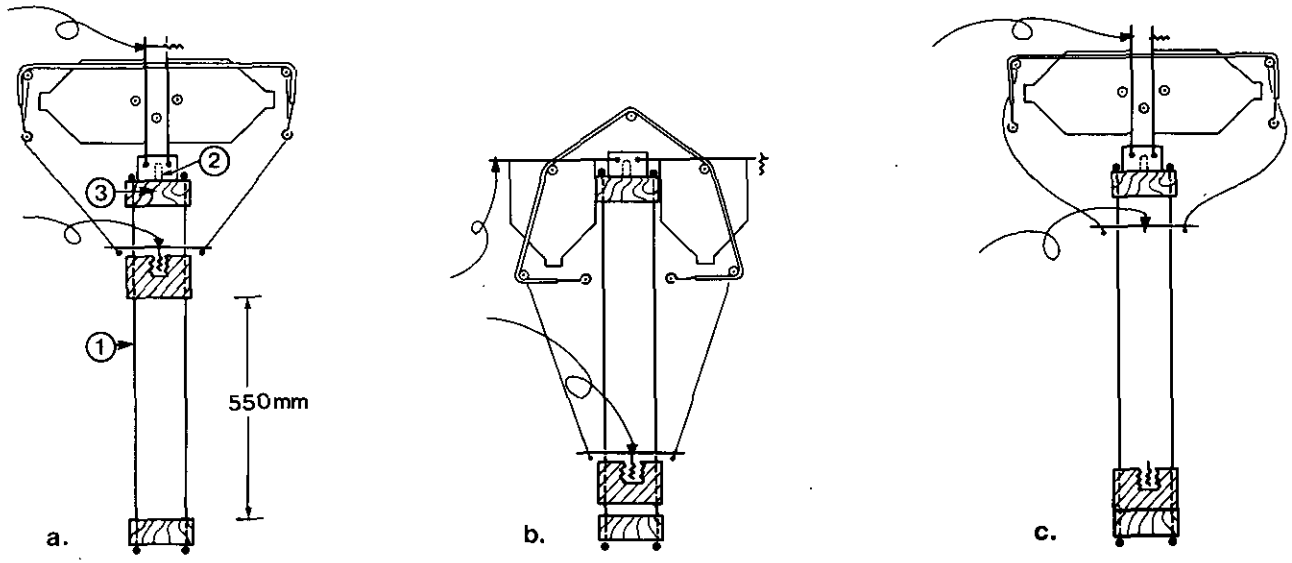


Fig. 4 Mid-water detritus trap. Opening and closing sequence.

(a) before opening
(b) open position
(c) after closing

1. Counter-weight guide ropes (here shown 90° out of position for clarity - see figure 3 for correct orientation);
2. bayonet fitting of trap on to deployment frame;
3. deployment frame.

which were incorporated to aid flushing and cleaning, together with the square cross-section, and the wide rubber edges to the trap, need checking for trapping efficiency before the apparatus is used for sedimentation rate studies.

A square cross-section was convenient for building and testing this prototype; there is no reason why cylindrical (but not conical) alternatives could not be tried. Eventually production units should be made from a material more robust than perspex, such as polycarbonate (lexan) sheeting.

Each half of the apparatus is, in effect, the lid of the other. Hence the collecting surface is twice that of any design in which the lid does not have such a dual purpose. Despite this attempt to make the trap compact it is not as easy to handle in the field as was originally hoped. It is still too heavy and a little too awkward a shape for one person to carry; the trap weighs 3-4 kg empty but over 18 kg when full of water (15ℓ); the 18 kg stabilizing sinker which is used to keep the trap open and to keep the collecting surfaces horizontal is also rather cumbersome. However, the equipment has had little field use at this stage and without this experience there is no point in making changes.

The automatic opening and closing requirement is achieved through the use of electro-corrosive pins under tension and connected to a timer and battery power supply. When the timer releases a current through a pin it corrodes through by accelerated galvanic action in 10 to 15 minutes.

Moulded silicone rubber (Dow Chemical Co. compound RTV 51) seals are keyed into the perspex rims of each half and these prevent water and particles leaking from the trap. It remains to be seen whether marine growths, especially in the tropics or in the euphotic zone ultimately prevent the trap from closing satisfactorily.

The rubber springs used to close the trap are of the same material as used in spear-gun rubbers - a latex-polyurethane co-polymer - and are available in any length from UnderSee Products, 578 Harris Street, Ultimo, Sydney, complete with metal thimbles at each end.

The slack length of each of the pair of rubbers is 710 mm (the length exposed between the metal ends). In the closed trap position they are stretched to 805 mm (113% of slack length) to provide a closing force of 6.4 kg wt. In the open trap position the rubbers are stretched to 1165 mm (i.e. to 164% of their slack length) and are under a tension of 23.6 kg wt.

It can be seen that, in choosing the slack length, a compromise has to be made between achieving a tight closure and needing a massive counterweight. Another problem is rubber fatigue, which results in some permanent stretching with time; rubbers should be replaced regularly, perhaps every six months.

Operation. The two halves are clamped shut with a corrosive pin screwed into place below the handle. The clean trap is stood end-on and, with the uppermost cap removed, completely filled with particle-free (filtered) water leaving no air pockets. The trap is now clipped on to the two pins mounted on the deployment frame. Another corrosive pin is used to attach the nylon cords to the iron counterweight hanging on guide ropes below the trap. Batteries are changed and the pins are connected to the timer through the snap-on underwater connectors. The timer is reset to zero having been pre-selected to corrode the opening and closing pins after, say, 24 hours and 28 days respectively (see next section). The trap may be set at any depth between about 10m and 100m, i.e. below the turbulent wave zone but above the pressure level where water may penetrate the timer and battery cases. After the pre-set closing

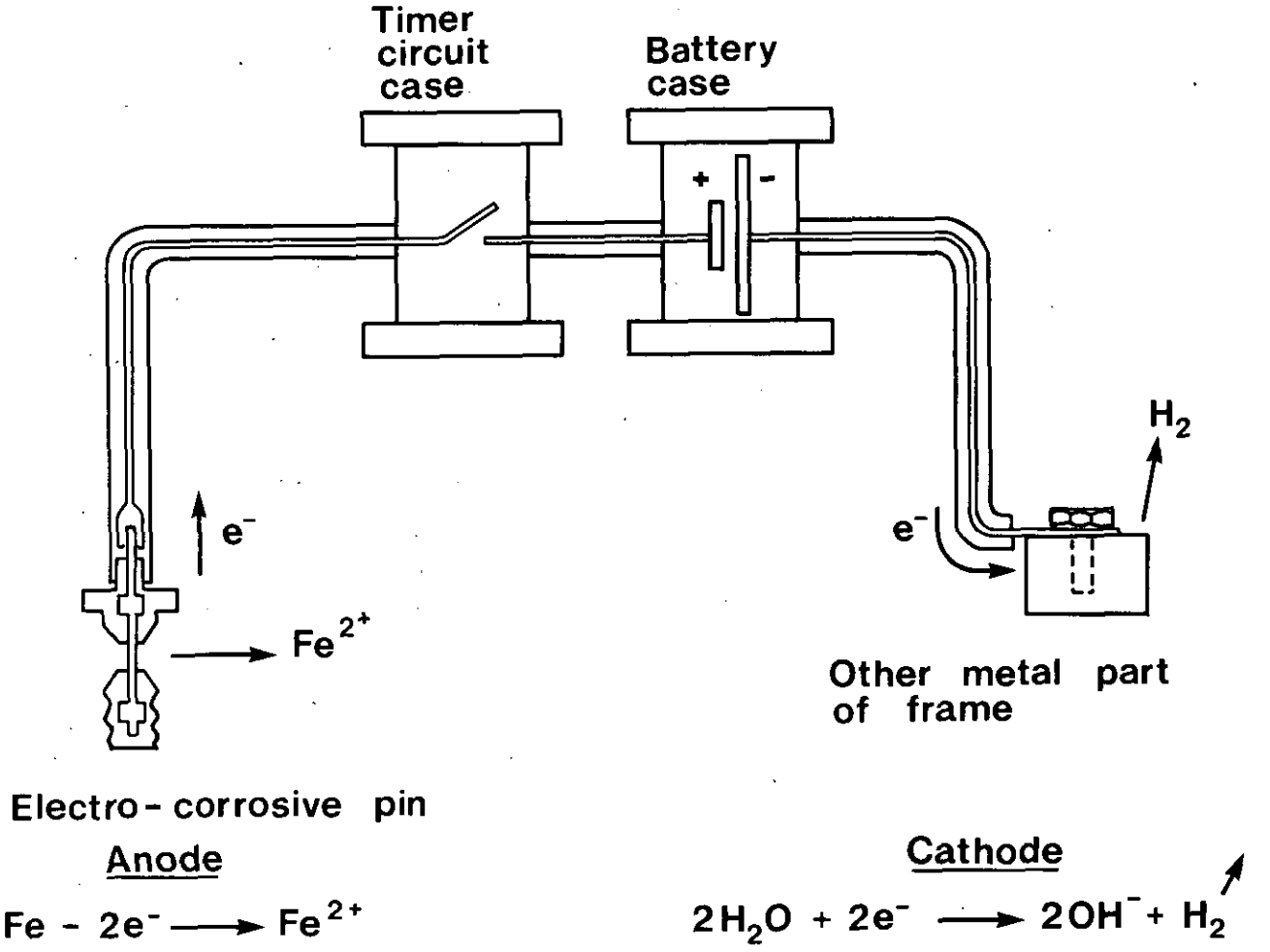


Fig. 5 Forced anodic corrosion.

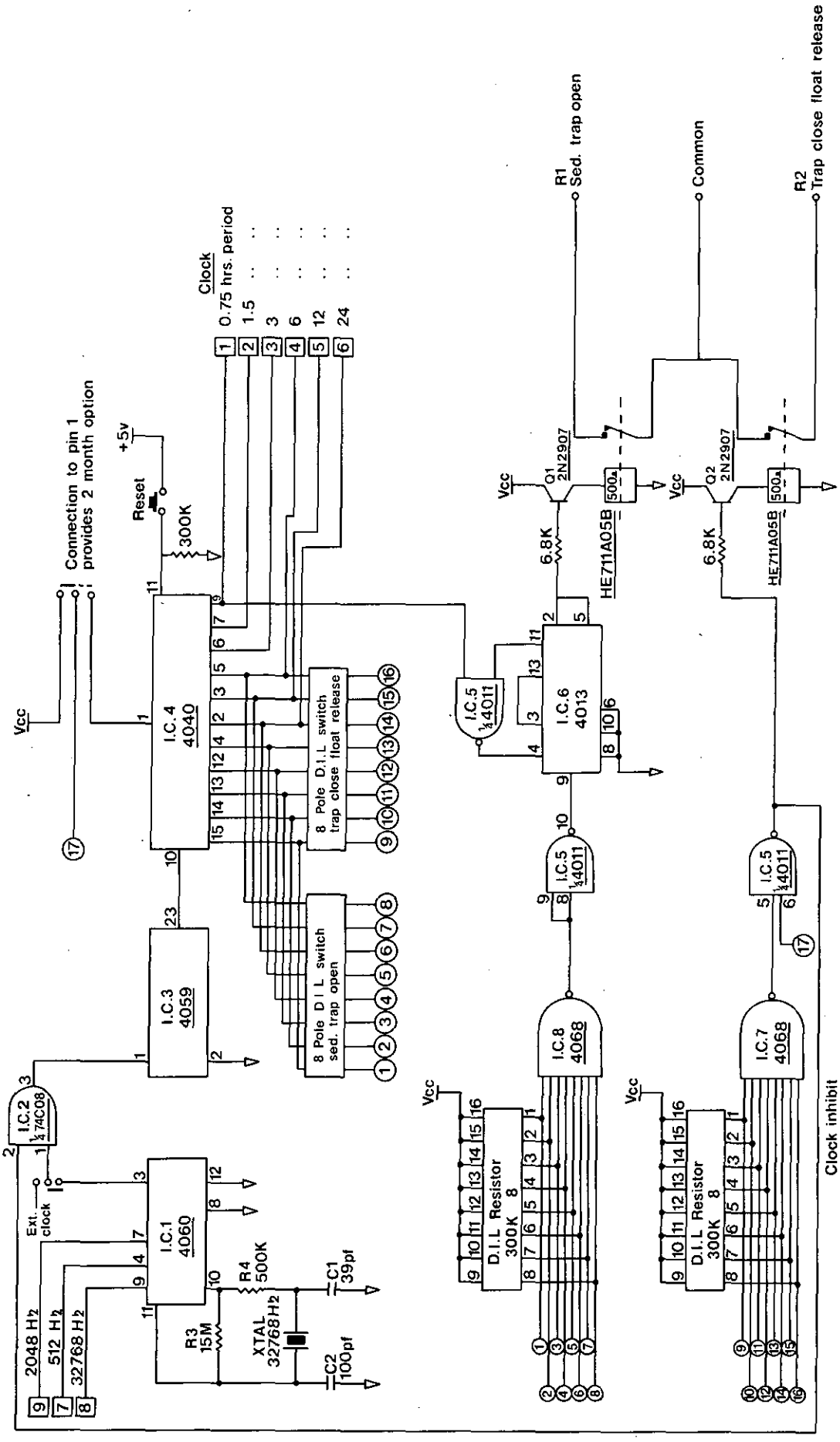


Fig.6 Circuit diagram of 3-point timer.

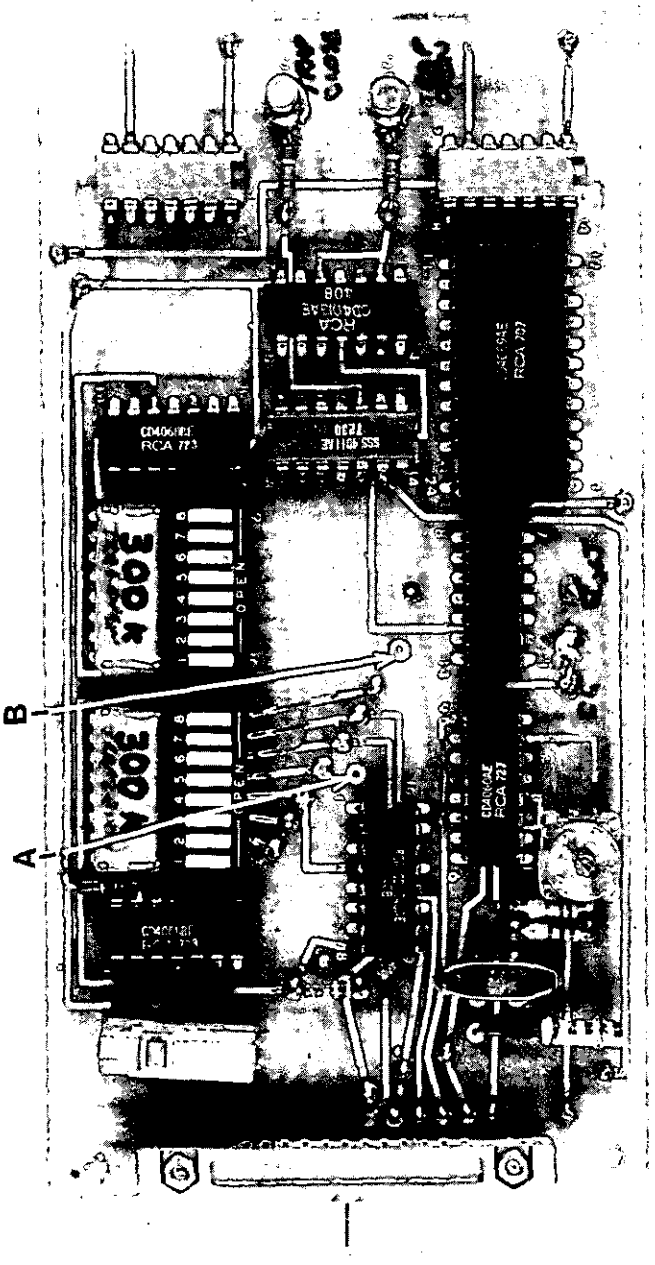


Fig.7 Circuit board of 3-point timer.
The maximum period of possible setting times can be doubled by joining points A and B.

time the trap should be found closed and floating at the sea surface. It is prudent to put a new pin into place immediately to give positive clamping, although when handled gently the trap should remain closed in air without a pin even when full of water. In the laboratory or on a bench, set the apparatus end-on, attach a plastic tube (13 mm, i.d.) to the uppermost part and leading into a 20ℓ plastic bucket, preferably one with a fitted lid. Invert the trap, remove the other cap, drain and rinse out the contents. Clean trap for next use. Let the sediment in the bucket settle (usually 1-2 hours), then decant or syphon off supernatant. Rinse remaining slurry through a 0.45 µm Millipore filter. Retain, dry and, if necessary, weigh the residues for subsequent chemical analysis.

3. Electro-corrosive Release Pin

Principle. A remote signalling system for triggering the automatically-operated detritus trap and for recalling the submerged buoy system to the surface had to be selected.

The three types of remote trigger devices are mechanical messengers, acoustic command releases and corrosive links.

A messenger was rejected for this prototype model but one may be utilized subsequently to trigger the resurfacing of the main equipment package after a surface marker-buoy has been released.

Acoustic releases also were considered unsatisfactory. They (and the associated deck command modules) are not only expensive but can be unreliable. The deck module would also take up valuable space and would possibly be unwelcome on a fishing vessel being used as a ship of opportunity, unless perhaps the same unit were also utilized to trigger submerged-floats to rock lobster pots (e.g. Poseidon International 1978).

Corrosive links of magnesium may be satisfactory for triggering events after short periods of time, but commercially available links (e.g. Eggerton Connectors) have an upper limit of about 7 days before corroding through. Consequently an electro-corrosive trigger system was chosen because of its greater versatility, precision, and low cost of expendable items.

The requirement was for each of three terminals to send a current to a corrosive pin after pre-set intervals of time; the first to corrode the trap-opening pin, the second to corrode the trap-closing pin thereby releasing the counterweight, and the third to disengage the ratchet on the submersing-reel assembly and allow it to rise to the surface for sighting and recovery.

The basic process is one of Forced Anodic Corrosion. When the positive terminal of a battery is connected to the stainless steel pin (anode) immersed in seawater (electrolyte) and the negative terminals to, say, the metal ratchet arm of the submerging-submerging-reel assembly which is also in the seawater, accelerated corrosion of the exposed portion of the pin occurs due to dissolution of positive ions from it. See Figure 5.

Specification. The system consists of a timing circuit for two pre-set event timers and a temperature logging circuit. Electronics have been optimized for minimum cost, power consumption and size. All circuitry is based on CMOS (Complementary Metal Oxide Semiconductor) which has features such as very low power requirements and reliable operation over large variations in battery supply. The circuit diagram of the 3-point timer is shown in Figure 6 and circuit board in Figure 7. The second and third pins are on the same timing circuit but a resistor is inserted in series with the third pin to reduce its rate of corrosion. Consequently the trap will close prior to the whole system rising to the surface.

The temperature recording circuit diagram is shown in Figure 8 and circuit board pictured in Figure 9. (A more versatile data logger has since been designed which enables several parameters besides temperature to be recorded at field stations such as the type being described here).

The timer and temperature-recording circuit boards are fitted back-to-back and, together with one 9 V battery, housed in a case of PVC (Vitor) 3-inch water tubing, external dimensions 500 mm length x 85 mm diameter (see Figure 10). This container is opened by unscrewing a standard straight, threaded joint made watertight by a workshop-fitted groove and O-ring on one of the 2 flanges at the joint.

The battery case is of the same material, of 760 mm overall length, and holds six 9 V batteries (Eveready No. 276-P) wired in parallel.

The electro-corrosive pin is shown in Figure 11. The design is a refinement of one initiated by D.R. Lockwood of CSIRO Division of Fisheries and Oceanography. The metal core of type 316 stainless steel was turned down to 1.6 mm (1/16") diameter from 4 mm (5/32") rod leaving two lugs to key into the plastic moulding. The job was done by Di Santo Engineering Pty. Ltd., 11a Carrington Road, Marrickville, N.S.W. 2204, at a cost of 78 cents each for the run of 1000. An improved design would include a notch cut lengthwise on each lug to prevent the plastic mouldings from rotating around the shaft.

The plastic moulding is of tint-free (white) polypropylene which is both strong and easy to mould. The cost of each was 25 cents, from Braldon Plastics, 51a Captain Cook Drive, Caringbah, N.S.W. 2229 (excluding the $2200 cost of making the single cavity die), thus bringing the cost of each complete pin to about $1.

The threaded end to the pin permits it to be screwed firmly into place to minimize chatter and wear on parts and to prevent working loose in turbulent water. The screw slot may sometimes help to disengage the threaded portion of the pin after use.

The pin is compatible with standard underwater connectors, e.g. Geo-Marine part number GL21A1S-F-2 (Glenair Inc., 1211 Air Way, Glendale, CA 91201 U.S.A.).

In a strength test, a pin (with the plastic parts taking the load) supported a weight of 100 kg without breaking. The actual breaking point was not determined. The steel core itself supports a load of about 150 kg before breaking. When an impressed current (250 mA per pin) flows through from the batteries, accelerated corrosion occurs at the 1.5 mm length of steel exposed to the seawater and the pin breaks within 10 to 15 minutes. Corrosion of the broken pin will continue for as long as the impressed current continues to flow or until a bubble of hydrogen or other corrosion product blocks the access of seawater to the corroding face of metal receding into the plastic moulding.

Operation. Set and reset operations are made on a bank of eight miniature switches mounted on the timing board. Electro-corrosion release times are selected by opening or closing switches in the bank. Switch settings plus link-pin on the timing board correspond to binary sequences which are either open (off) or closed (on); the minimum setting is 6 hours with switch 1 closed, and maximum setting is 3066 hours with all switches closed. Table 2 illustrates the preset routine. To close the link-pin, solder a wire to connect points A and B in Plate Figure 7 (i.e. "Pin 1" and "17" indicated in Figure 6).

The desired settings need not be changed or touched again once an optimum routine has been established.

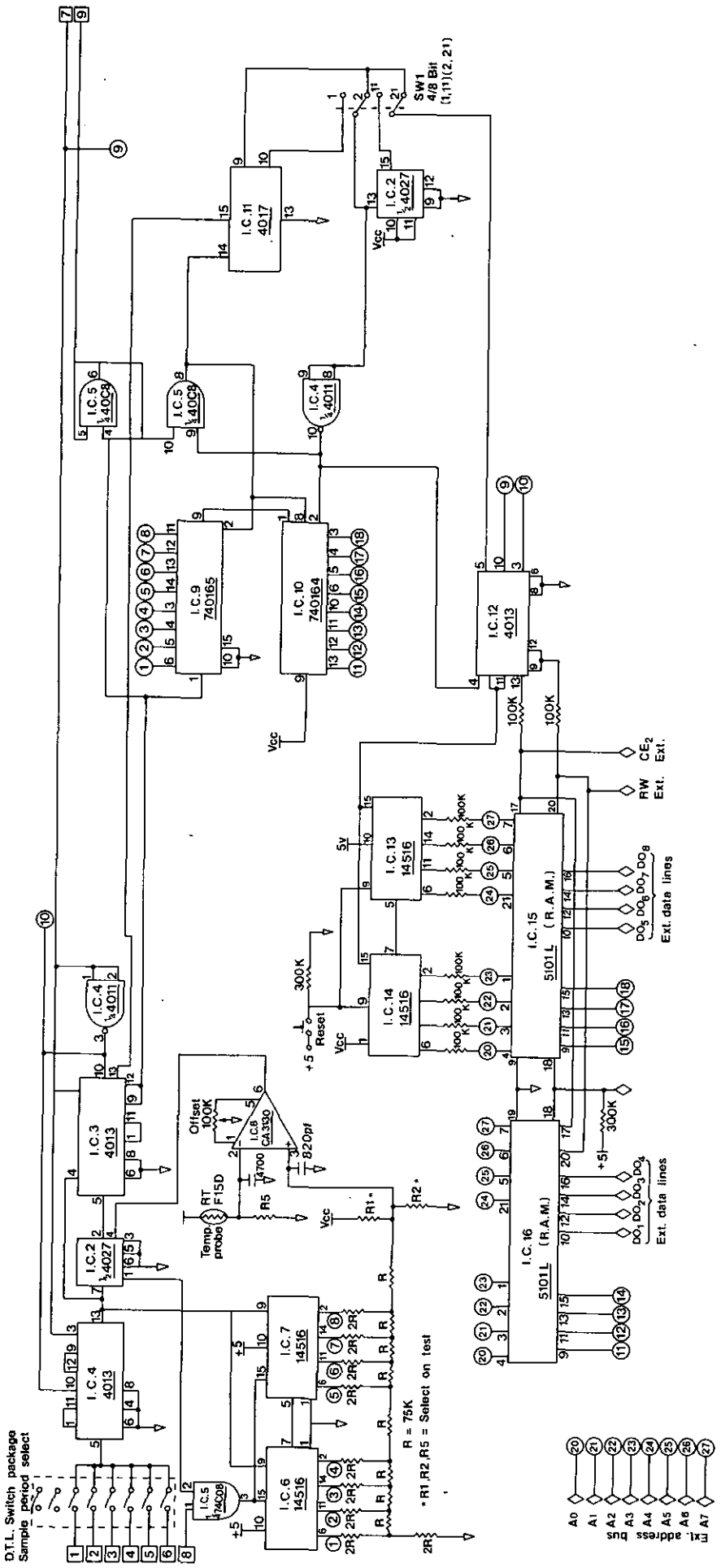


Fig.8 Circuit diagram of temperature data logger.

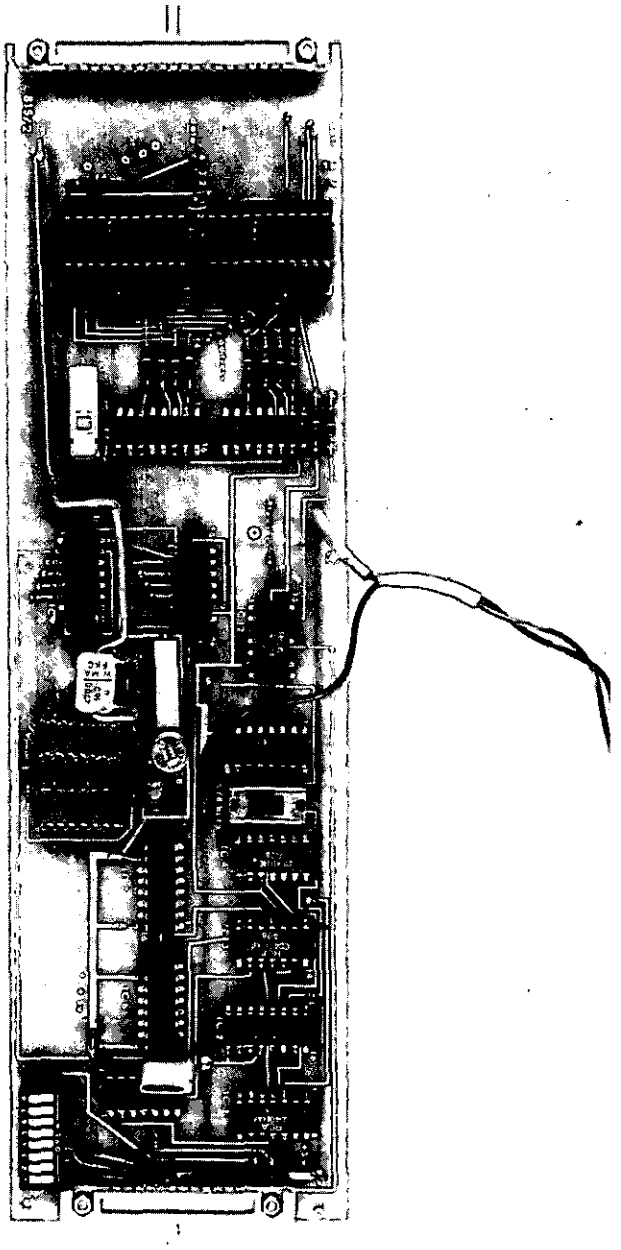


Fig.9 Circuit board of temperature data logger.

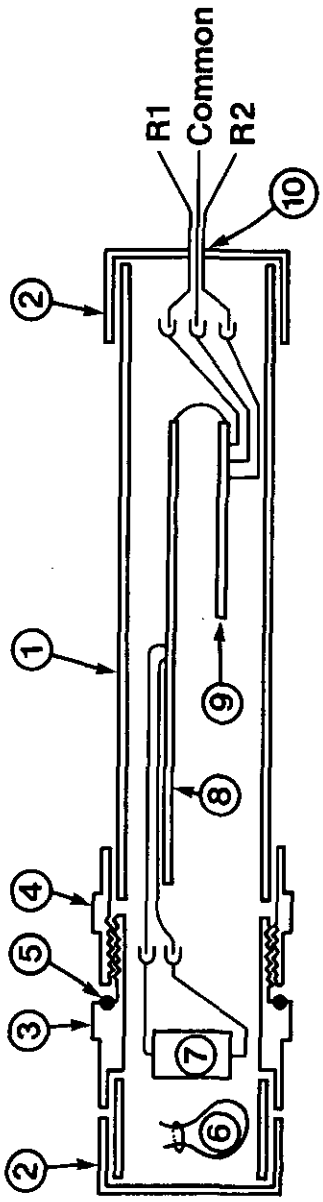


Fig.10 Circuit board housing.

1 to 4, 80 mm standard PVC water pipe fittings; 1, tube; 2, cap; 3, valve socket; 4, faucet socket; 5, O-ring 89 mm i.d., section 3.175 mm (BS 1806-238); 6, bag of silica gel; 7, 4 x 1.5 V dry cells in series; 8, temperature data logger board; 9, timer circuit board; 10, permanent water-tight seal through cap.

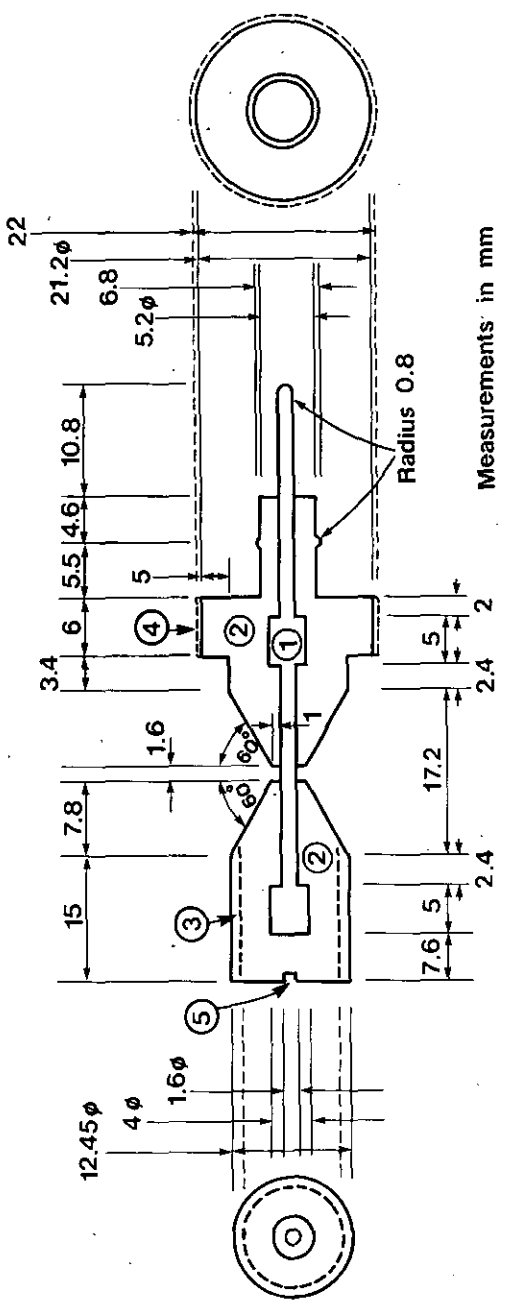


Fig. 11 Electro-corrosive release pin.

1. stainless (type 316) steel pin;
2. polypropylene moulding;
3. ½-inch moulded Whitworth thread;
4. finger grip ridges;
5. screw slot 1.5 mm deep x 1.5 mm wide

Table 2. Electro-corrosive Release Times - Miniature Switch Bank Settings

Switch Number								Link-pin	Release Time	
1	2	3	4	5	6	7	8		Days	Hours
1	0	0	0	0	0	0	0	0	0	6
0	1	0	0	0	0	0	0	0	0	12
1	1	0	0	0	0	0	0	0	0	18
0	0	1	0	0	0	0	0	0	1	0
1	0	1	0	0	0	0	0	0	1	6
0	1	1	0	0	0	0	0	0	1	12
1	1	1	0	0	0	0	0	0	1	18
0	0	0	1	0	0	0	0	0	2	0
1	0	0	1	0	0	0	0	0	2	6
etc.										
0	0	0	0	1	0	0	0	0	4	0
1	0	0	0	1	0	0	0	0	4	6
etc.										
0	0	0	0	0	1	0	0	0	8	0
etc.										
0	0	0	0	0	0	1	0	0	16	0
etc.										
0	0	0	0	0	0	0	1	0	32	0
etc.										
0	0	0	0	0	0	0	0	1	64	0
etc.										
1	1	1	1	1	1	1	1	1	127	18

0 = switch open (off)

1 = switch closed (on)

Table 3. Temperature Sampling Intervals - Miniature Switch Bank Settings.

Switch Number On (i.e. closed - all other switches open)	Sample Intervals (hours)
1	0.75
2	1.5
3	3.0
4	6.0
5	12.0
6	24.0
7) un-utilized	0
8) switches	0

Only the reset button has to be actuated at the beginning of each new sampling period. The circuit board has to be withdrawn from the case to gain access to this point and then returned and the case resealed. In future versions a reset switch external to the timer case could be provided.

Intervals ranging from 45 minutes to 1 day, between which water temperature is recorded can also be preselected from a separate bank of minature switches (see Table 3).

The temperature is sensed by a thermistor (temperature dependent resistor), digitized, and stored in a semiconductor memory which retains the data to very low levels of battery voltage. The memory holds up to 256 items. Hence the store capacity is exceeded only after about 8 days of sampling at 45 minute intervals, or after about 8 months of sampling at daily intervals. A saturated memory retains only the first 256 items of data received.

The raw temperature data is retrieved by connecting the memory board socket to the Intel microprocessor system located at the Electronics laboratory, CSIRO, Cronulla, where data is extracted and processed. (Investigation into the design and development of a suitable hand-held data retrieval unit with cassette storage is under consideration). After the data has been transferred, the unit is available for further storage and will start recording again when the reset switch is actuated.

When the memory has been filled 4 times, it is prudent to replace the battery for the temperature data logger; the batteries for the electro-corrosive release pin circuit should be replaced after every occasion to avoid the possibility of the submerged station not surfacing and thereby being lost through insufficient power being available from flat batteries to sever the reel pin.

Despite their description, "underwater connector" leads should not be connected to electro-corrosive pins under water. Once snapped together out of the water, however, the joins are then watertight below the surface.

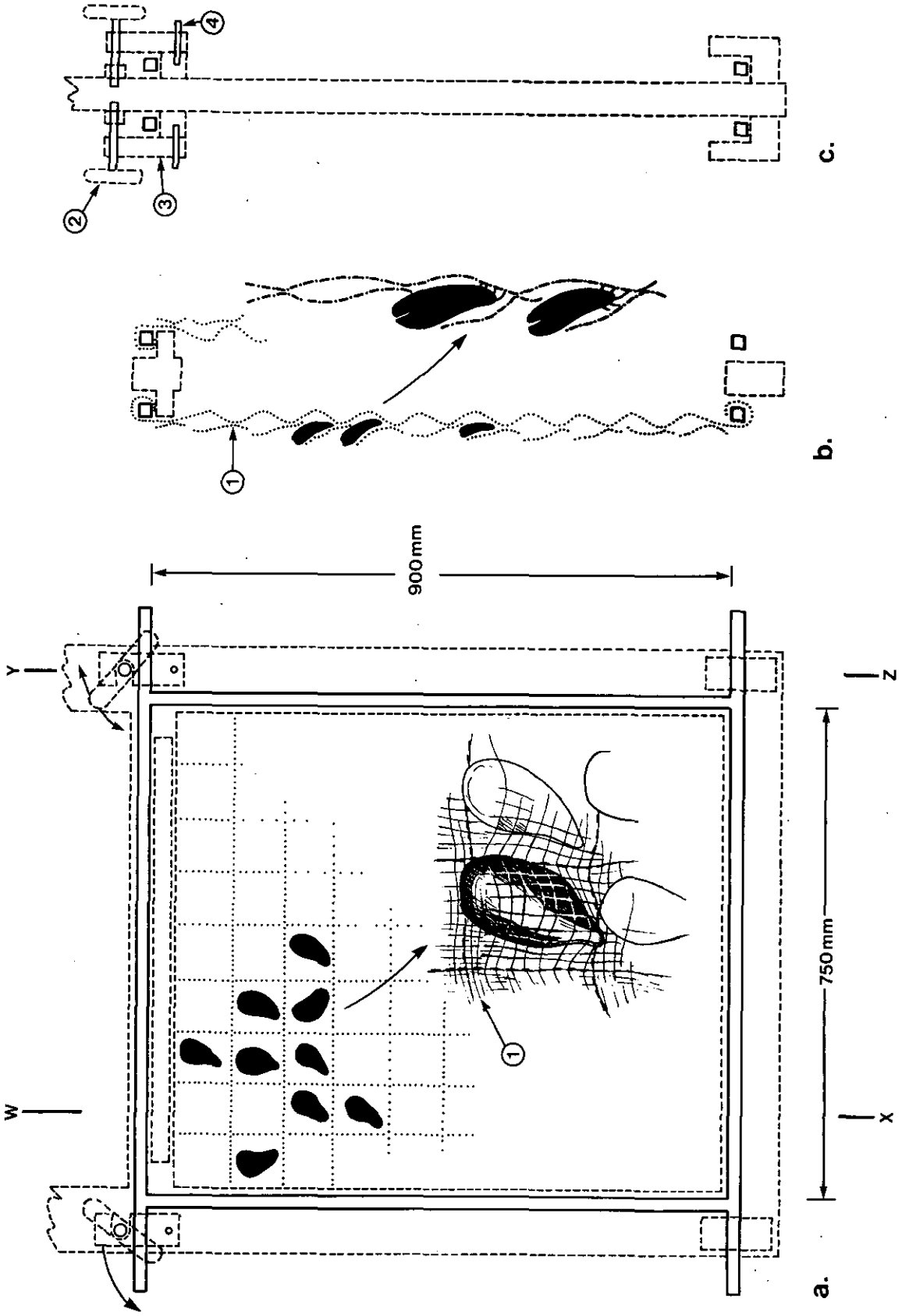


Fig. 12a Mussel exposure frame.
a, front view. b, cross-section WX. c, cross-section YZ.
1, polypropylene mesh; 2, clamp or wing nut; 3, gate; 4, hinge pin.

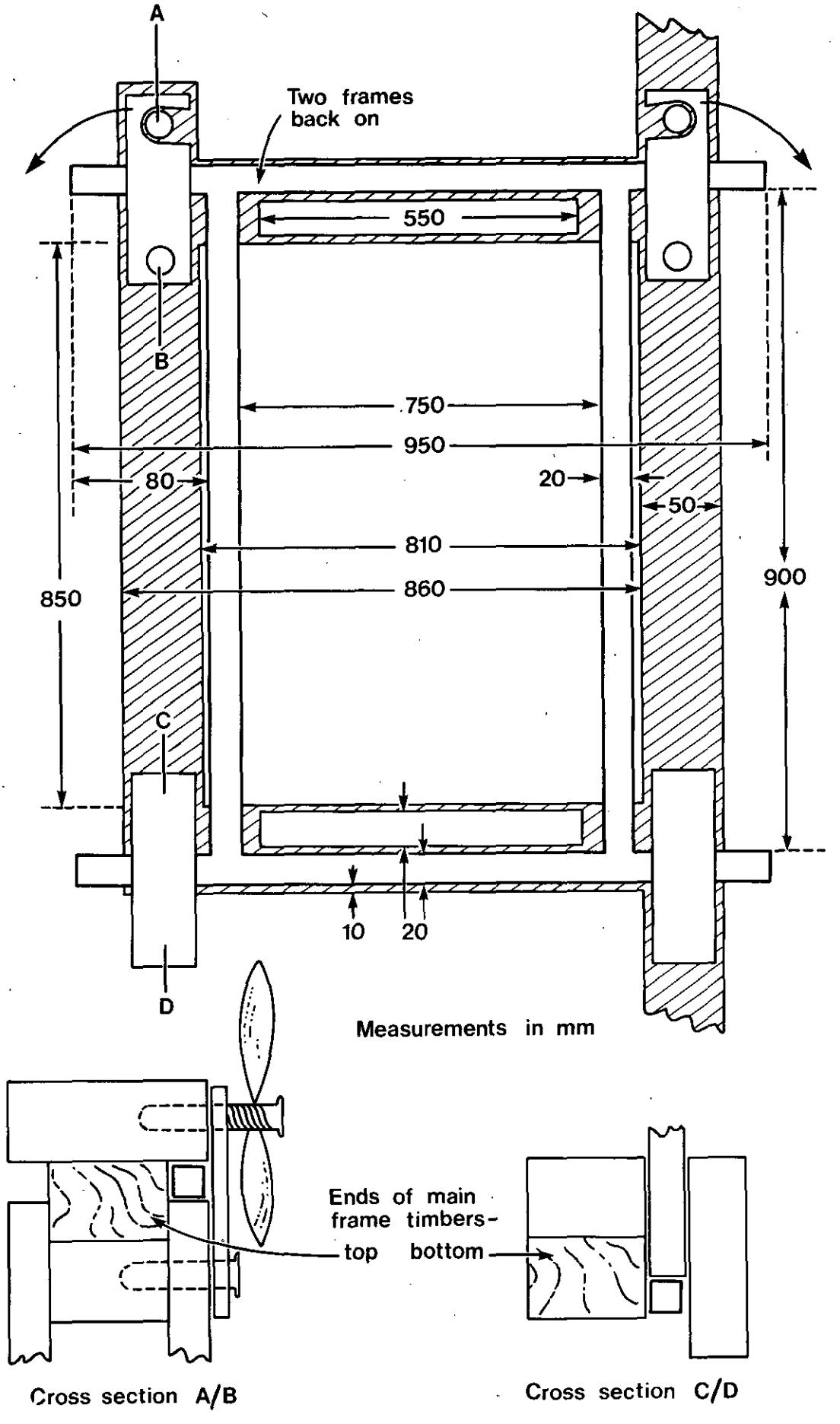


Fig.12b Mussel exposure frame.
Detail of deployment on field frame

(A little silicon grease over the male pin before joining ensures a dry connection).

One problem which should be recognized in utilizing these corrosive links in trace metal pollution studies is the possible contribution of corrosion product elements to material caught in a detritus trap or absorbed by biological accumulator animals. Type 316 stainless steel is composed of 18% chromium, 11% nickel, 2.5% molybdenum and the remainder mostly iron. Hence the exposed 1.5 mm rod of steel could yield 4.3 mg of chromium, 2.6 mg of nickel, 0.6 mg of molybdenum and 16.3 mg of iron if completely corroded away.

Of the three pins used on each "dip", only one, the trap-opening pin, would be expected to contaminate other material in a detritus trap; bio-accumulators may or may not be affected by any of the three depending on local water movements at the times of "firing".

If the elements in stainless steel are also under environmental study, the safest course of action would be to substitute the core metal with another such as titanium. If bio-accumulators are remotely located or absent on a particular program a standard 24 hour magnesium link could be used for opening a detritus trap, and stainless steel-cored pins used for the other two functions.

4. Mussel Exposure Frame

Principle. Mussels are one of the most suitable species of indicator organisms available for monitoring marine pollution.

Although devising a means of setting out transplanted mussels in open water is a seemingly simple mission, it has to be done in such a way as to maximize the chances of survival of the animals and at the same time to minimize the chances of their being contaminated, or of their metabolism being differentially modified by the presence of a supporting frame itself. Relevant considerations are: that the frame be of lightweight, cheap, and non-metallic or plastic-coated construction (for easy handling and replacement if damaged or rotted); that the mussels should be provided with adequate points for attachment, be uncrowded and have room enough for individual growth; that each individual should have equal access to surrounding circulating water for gathering food, and yet have some protection from predators; that the frame should have no 'blind' corners where rubbish and metabolic products could accumulate and smother or starve the animals; that resistance to water currents should be a minimum for the sake of maintaining stable positioning of the moored system; and that the system should permit easy identification, harvesting and replacement of individual mussels.

Specification. See Figure 12a and 12b. Two layers of loosely woven polypropylene meshing are stitched together in such a way as to provide an array of pockets known as a "mussel motel" - so called since each mussel is provided with its own separate unit.

The polypropylene mesh is cheap, non-metallic and readily available in long rolls of about 1m width; it is used commercially for onion-sacking.

It is convenient to prepare the pockets in long lengths of material - 20m or so. The netting is very loose so double stitching is necessary throughout. First, rows of double stitching, spaced 80 mm apart, are sewn across the width of one long length of polypropylene at right angles to the long side. This stitched material is laid over a second length of meshing, and the layers are stitched together both crosswise and lengthwise to produce a grid of 80 mm-sided squares. The crosswise stitching should be parallel to, but displaced 10 mm from the cross-stitching previously done on the upper layer. Finally, pockets are formed by cutting slits along the 80 mm long by 10 mm wide strips

bounded by the stitching in the upper layer only of the material. The sewing was done by Henry Simon (Aust.) Ltd., 40 Francis Street, Glebe, N.S.W. 2037.

After making the grid of pockets the material is cut with generous overlapping to fit the wooden frames and tied with venetian blind cord by blanket stitching or some other suitable means. The mesh should not be fitted too tightly. It must have enough slack to stretch into the third dimension when the mussels are placed in position. The polypropylene plus the sewing, but not including the slitting, costs about $5 per frame.

Operation. A source of mussels must be available to supply the programme with sufficient numbers (30 mussels. station^{-1}.month^{-1} - FAO 1976, p.33) and with background concentrations of contaminants homogeneously distributed throughout the area from which the shellfish stock is taken. It is important that such background levels be constant and low but not necessarily minimum possible values - translocated shellfish could lose as well as gain contaminants. R and R (resource and reference) stock need not come from distant and inaccessible areas. Besides, remoteness from human habitation is not a guarantee that mussels growing in the area have minimum trace metal levels (Thomson 1979).

The R and R stock should also be free from the parasitic pea crab. The N.S.W. South Coast around Eden may be a suitable area from which to obtain such stock. Port Phillip and environs are infested and therefore are unsuitable. So is the Sydney area, although the latter would be unsuitable anyway because the animal is near the northern limit of its range there and regular supplies would not be certain since spawning and growth are irregular. *Mytilis edulis* is restricted to latitudes higher than about 30^0 - approximately from Perth, W.A. round the southern coastlines to Port Stephens, N.S.W. Another bio-assay animal is required for warmer waters.

Mussels will live for 2 or 3 days out of water in cool, damp, hessian bagging, and can easily be transported live.

Each subsample of mussels consigned regularly to each monitoring site should, apart from being similar to each other in total weight, be chosen from a mixed population of R and R stock. Mussels taken from a sandy substrate are preferred since they have fewer external growths and therefore have cleaner shells than mussels grown on a muddy bottom. In long-term monitoring, which necessarily spans yearly cycles and variations of growth, dormancy and sexual change, size- and age-grading of the animals is probably not only unimportant but undesirable.

By comparison with our proposed technique, Davies and Pirie (1978) describe a similar scheme in which relocated mussels were used to minimize biological variations in natural stock variability: "Cultivated, sub-tidal mussels of a single year class, and similar in size were used. Batches of 70 were placed in plastic-coated wire mesh (2 mm gauge, 2.5 cm mesh) cages (60 x 45 x 10 cm) and animals periodically removed for analysis. Each cage was suspended 2m below a surface buoy anchored by a 20 kg weight, so that the cages would not touch the bottom at low tide." Because their experiment ran for only 153 days with no restocking after the initial placement, it was perhaps more important that their initial stock was similar in age and size.

Returning to this scheme, 30 mussels (3 vertical columns of pockets) are collected on each monthly visit to every monitoring site and their vacated places refilled with R and R stock. Dead mussels should not be

replaced, but the mortality should be noted every visit since this may be a significant environmental parameter. Since there are 2 exposure frames at each site holding 9 columns of 10 mussels each, individual mussels are exposed for 6 months on a rotating, overlapping basis. If the frame or polypropylene rots or the mussels are too hard to remove without damaging or cutting the pockets, 3 frames could be deployed at each site and each replaced every 8 months without disrupting the 6 months exposure time. See Table 4.

The mussels should put out byssal threads and attach themselves firmly to the mesh of the frame in 3-5 days. However there is a marked tendency for mussels to migrate 50 to 100 mm out of their original units while remaining attached elsewhere to the material.

Collected mussels should be kept cool and returned to base laboratory within 3 days. There is no need to depurate the animals; they are kept well off the bottom while on station and so residual gut contents originate from the water column only and are relevant to subsequent analysis. Any flushing with water would also cause re-equilibration of the animals' body burdens of trace metals, thus negating the purpose of the program.

For trace metal analyses the live shellfish are opened preferably with a plastic (polycarbonate) knife. If the elements in stainless steel are not to be analysed or their contribution to the determination were shown to be negligible, then a stainless steel blade could be used. The flesh is scooped out and lifted with teflon-coated forceps into 200 mℓ (6 oz) Whirl-Pak polythene bags. For organic analyses a stainless steel blade may be used and the excised flesh put into aluminium foil. The open Whirl-Paks are then dipped into liquid nitrogen for 20 seconds to freeze the contents then immediately placed on to the trays of a freeze dryer and left to freeze-dry overnight. The Paks are closed. The samples are now biologically and chemically stable at room temperatures for as long as necessary while awaiting chemical analysis.

5. Submersing-Reel Assembly

Principle. Submerged buoy and instrument systems are relatively common. However, they all suffer from one or more of 3 disadvantages:

1. A new mooring block has to be laid after every retrieval.
2. The submerged buoy has to be found and released by acoustic sounding.
3. Once released the surface float and associated equipment packages drift away from the station site.

These deficiences are overcome by incorporating a submersing-reel assembly into the mooring system; heavy mooring blocks are handled only once and thereafter used repeatedly, the submerged buoy is released automatically and found visually, and the complete assembly stays moored on site at all times.

Extra lengths of lines are necessarily involved in raising and lowering the buoy and instrument frame and would be slack at all other times and inevitably tangle if not neatly accommodated in some fashion. The solution to this problem is to include a reel and ratchet mechanism into the mooring system. The upper part of the mooring line is wound around the reel; the rest, leading down to the block on the sea-bed, is taut at all times and hence not likely to foul the equipment. A surface line is unwound from the same reel - which action pulls the buoy and frame down below the surface - and eventually disengages when the assembly reaches the desired depth. This line can then be removed completely, thus eliminating the possibility of it fouling the equipment now set in position.

Table 4. Mussel Sampling Sequence

Elapsed time (months)	Frame 1			Frame 2			Frame 3		
	1-3	4-6	7-9	1-3	4-6	7-9	1-3	4-6	7-9
	(columns)			(columns)			(columns)		
0	R	-	-						
1	1	R	-						
2	2	1	R						
3	3	2	1	R	-	-			
4	4	3	2	1	R	-			
5	5	4	3	2	1	R			
6	S(S/R)	5	4	3	2	1	(R)	-	-
7		S(S/R)	5	4	3	2	1	(R)	-
8	-	-	S(S/R)	5	4	3	2	1	(R)
9	)			S(S/R)	5	4	3	2	1
10	)-M				etc.				
11	)								
12	R	-	-						
13	1	R	-						
14	2	1	R						

R = Restock

\- = Empty pockets

S = Sample. When 3 frames are cycled, mussels which have been in frame 1 for 6 months are taken, their vacated pockets left empty, and the third frame restocked.

S/R = Sample and Restock. When 2 frames only are used, vacated pockets are immediately restocked.

M = Maintenance. After 8 months (with 3 frames in use) frame 1 is empty of mussels and may be repaired for service again after 12 months when frame 2 would become empty.

a. General arrangement (schematic)

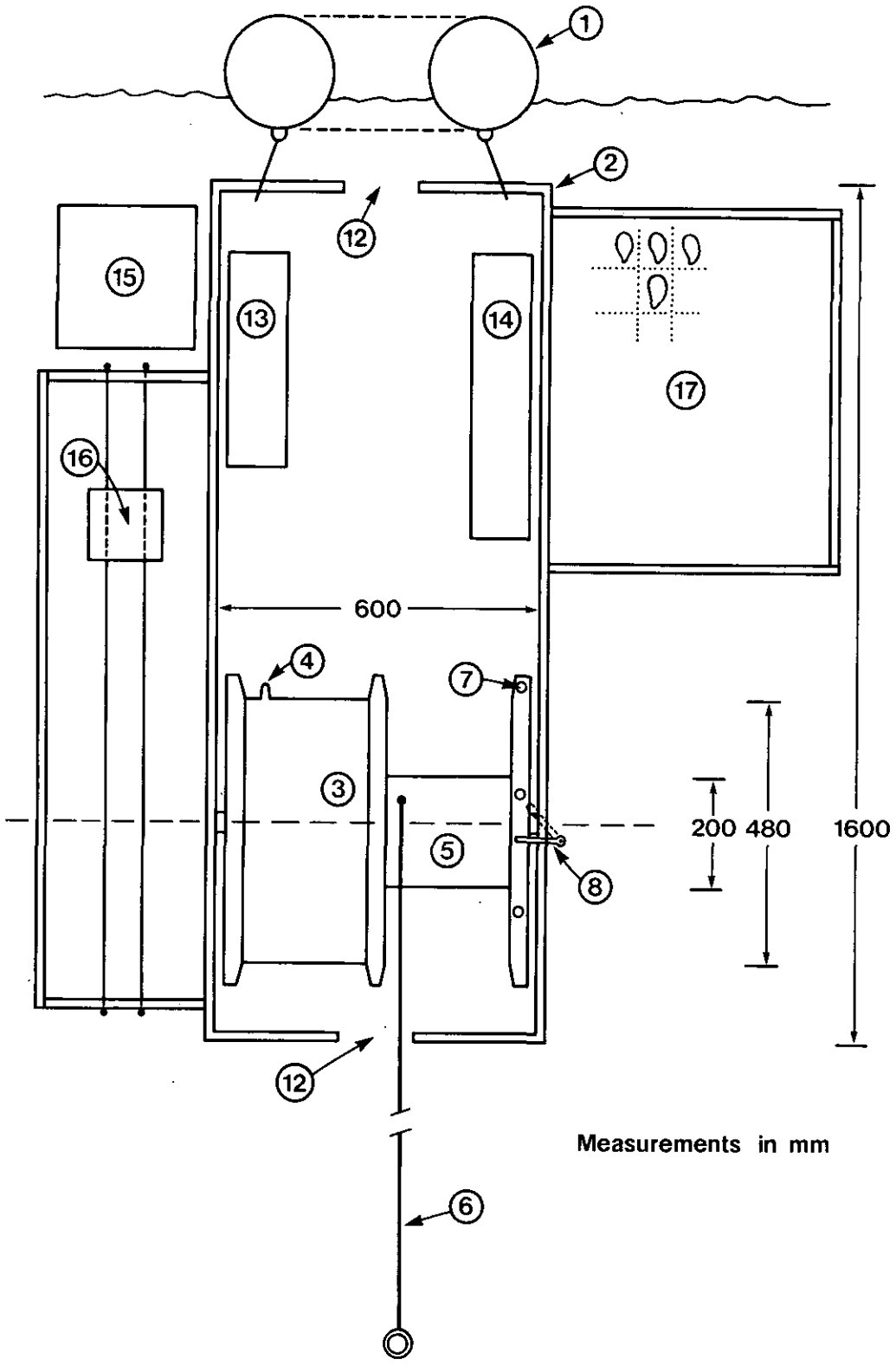


Fig. 13a Submersing-reel assembly.

1, toroidal float; 2, wooden frame; 3, surface line spool with pin; 4, from which line slips off easily; 5, mooring line spool with fixed connecting line, 6;7, one of six ratchet lugs on flange of spool; 8, pawl; 9, pawl support arm; 10, wooden framework; 11, electro-corrosive pin; 12, guide rings for surface and mooring lines; 13, temperature logger and timing circuit case; 14, battery case; 15, mid-water detritus trap; 16, counter weight; 17, mussel exposure frame.

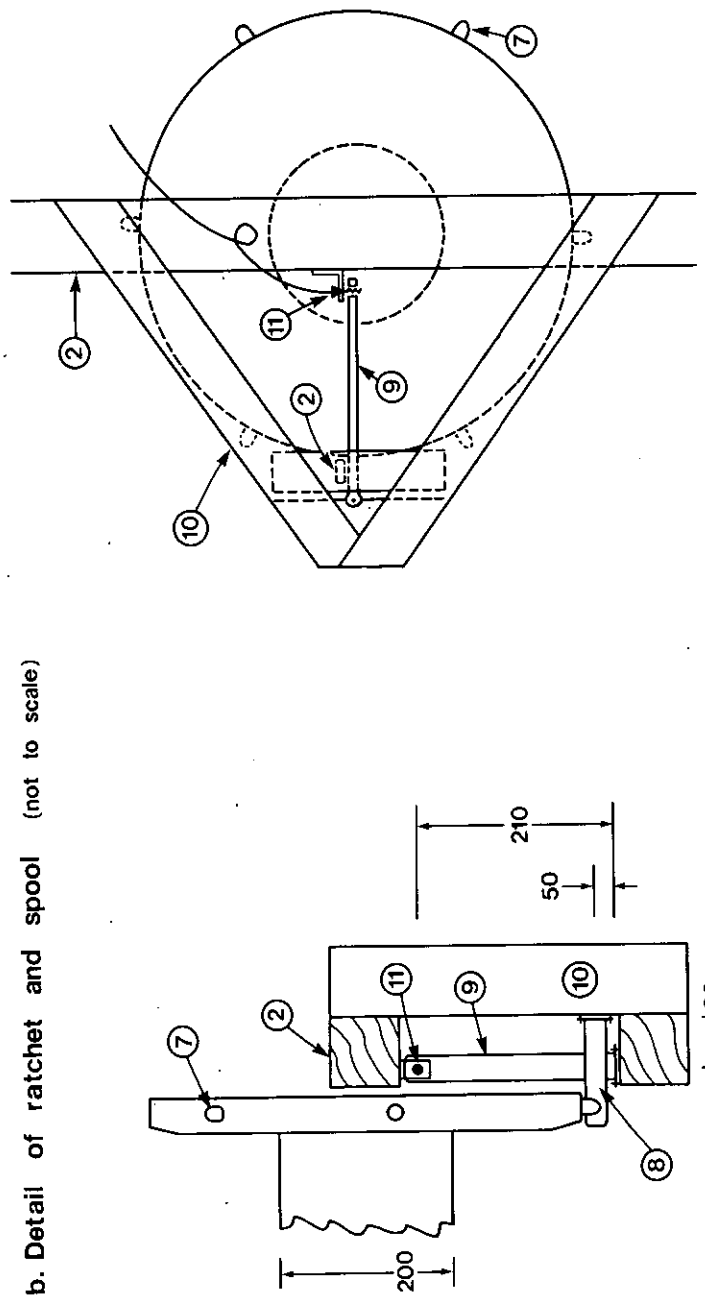


Fig.13b Submersing-reel assembly.
See legend for Figure 13a.

When the ratchet on the reel engages the pawl on the assembly frame, the reel can turn in one direction only. So, as the mooring line is wound on (and the surface line off) the submerging assembly cannot rise to the surface. An intact corrosive release pin holds the pawl in place. When it corrodes through, the reel is free to turn in either direction and positive buoyancy forces the assembly to the surface.

Specification. See Figure 13a and b. The prototype has both the mussel frame and the detritus trap attached to the reel assembly. This is not an essential arrangement. A more versatile system would have the reel assembly developed as a separate unit to submerge and recover any type of instrument package.

The frame is made of wood with lead weights attached to make it neutrally buoyant in water. The only purpose in using these materials was to have a cheap and simple structure for testing the operating principle of the reel; reinforced fibreglass will probably be used in subsequent units.

The surface line comes off a larger spool than does the mooring line. Since both lines are wound around the reel in opposite directions, equal and opposite tension is exerted on the same side of the axle. The difference in spool diameters provides a resultant turning moment of forces about the axle which forces the reel to rotate when sufficient tension is applied to the surface line to overcome the nett buoyancy of the floats. The diameters of the surface and mooring line spools are 480 mm and 200 mm respectively giving a mechanical advantage of 2.4 to the surface line. The tension in the surface line (8 mm diameter polypropylene rope, breaking strain 850 kg) needed to submerge the complete assembly was measured as 120 kg. The toroidal submersible float has a nett buoyancy of 74 kg, and the "Nokalon" marker float a nett buoyancy of 8 kg approximately.

The submersible float is made from a truck tyre inner tube filled with polyurethane foam and coated with fibreglass. Four steel rings are set into the fibreglass to provide attachment points for the equipment below. The toroidal shape enables the surface line to be withdrawn through the centre hole without fouling other parts of the apparatus.

The spools have tapered flanges. These were intended to minimize chafing of the polypropylene rope. However this feature has now become redundant due to the adoption of guide rings on both sides of the reel; any chafing of the rope is now caused by its rubbing on the rings only. The guide loops keep the two lines on their respective sides of the spool and keep the reel correctly orientated, while the lower one prevents the marker-buoy from fouling the reel - it allows the lower connecting shackles but not the marker buoy, which is a 280 mm (12") diameter "Nokolon" float, to pass through.

The strain on the corrosive pin which supports the ratchet pawl is reduced by providing it with some mechanical advantage over the load acting on the pawl itself. The mechanical advantage equals the multiple of load : effort ratios on pawl (1), pawl support arm (2), and spool (3). These are proportional to the respective distances between fulcrums and points of applied forces. Therefore, mechanical advantage = $\frac{30 \text{ mm}}{75 \text{ mm}}$ (1) x $\frac{210 \text{ mm}}{50 \text{ mm}}$ (2) x $\frac{480 \text{ mm}}{200 \text{ mm}}$ (3) = 4. The breaking strain of a corrosive pin itself lies between 90 and 150 kg wt. Therefore it will withstand forces of between 360 and 600 kg wt. exerted on the mooring line.

Based on previous experience and practice (Boland *et al.* 1975), the mooring line itself is made of 12 mm diameter polypropylene rope which has a breaking strain of 1900 kg wt. Unlike nylon, polypropylene line does not stretch in water and is less dense than water. Its positive buoyancy can be useful during recovery operations. The mooring block is a concrete block, approximately 200 kg, cast with a ringbolt of 12 mm steel. A swivel, Ronstan R.F. 75, joins the polypropylene line to the ringbolt.

Several improvements on this prototype submersing-reel assembly could be suggested. As mentioned earlier, the spools and frame could be constructed from dimensionally-stable reinforced fibreglass, light to handle out of water, with slight negative buoyancy when submerged, and designed to present minimum resistance to water currents. Ten standard 280 mm (12") trawl floats may be substituted for the specially-built toroidal float. A wormed axle would assist even layering of the mooring line as it winds on to its spool, minimizing jams and also preventing rapid increase in the diameter of spooled rope being wound on at one spot and thereby decreasing the mechanical advantage of the surface line. The strain on the electro-corrosive pin should be decreased further by an increase in its mechanical advantage. A brake pin is needed to prevent the surface line from unwinding before deployment. A marker buoy alone could be released automatically, leaving the reel and instruments below the surface for recall only when the service ship reaches the site. Finally, an emergency release system could be considered if the assembly's overall cost is considered to be worth the extra expense.

Operation. The sequence of steps needed to set and recover the submersing-reel assembly and associated equipment is shown in Figure 14a-d.

The length of surface line wound around the longer spool before deployment,

$$S = [D + (M - W)] \times R,$$

where D = desired depth of reel below surface,
M = length of mooring line,
W = water depth,
and R = ratio of large: small spool diameters.

The optimum length of mooring line has not been determined but 1.5 times the water depth may be necessary in open water situations, in which case quite a long length of surface line is required. For example;

When D = 20m, W = 50m, and
R = 2.4,
M = 1.5 x 50 m
= 75m
Then S = 108m

Results and Discussion of Field Trials

Because the RIMCO-CSIRO sampler was available at the beginning of the trials period there was ample time to collect a reasonable quantity of data on trace metals in the particulate matter of sea-water. However, for the bio-accumulator and detritus fractions, most of the available time was spent building, experimenting with and modifying novel field gear and methods. Only one short set of data for each parameter is available, sufficient only to indicate the metal concentration levels in these fractions and the validity of techniques being discussed in this report.

1. Trace Metals in Particulate Matter

Analytical techniques. Millipore filter discs, type HAWP04700, were used to collect particulate matter from 5ℓ of sea-water in the RIMCO-CSIRO samplers. Filters plus adhering particulates were then sent to Amdel, Adelaide, for chemical analysis. The use of acid-cleaned

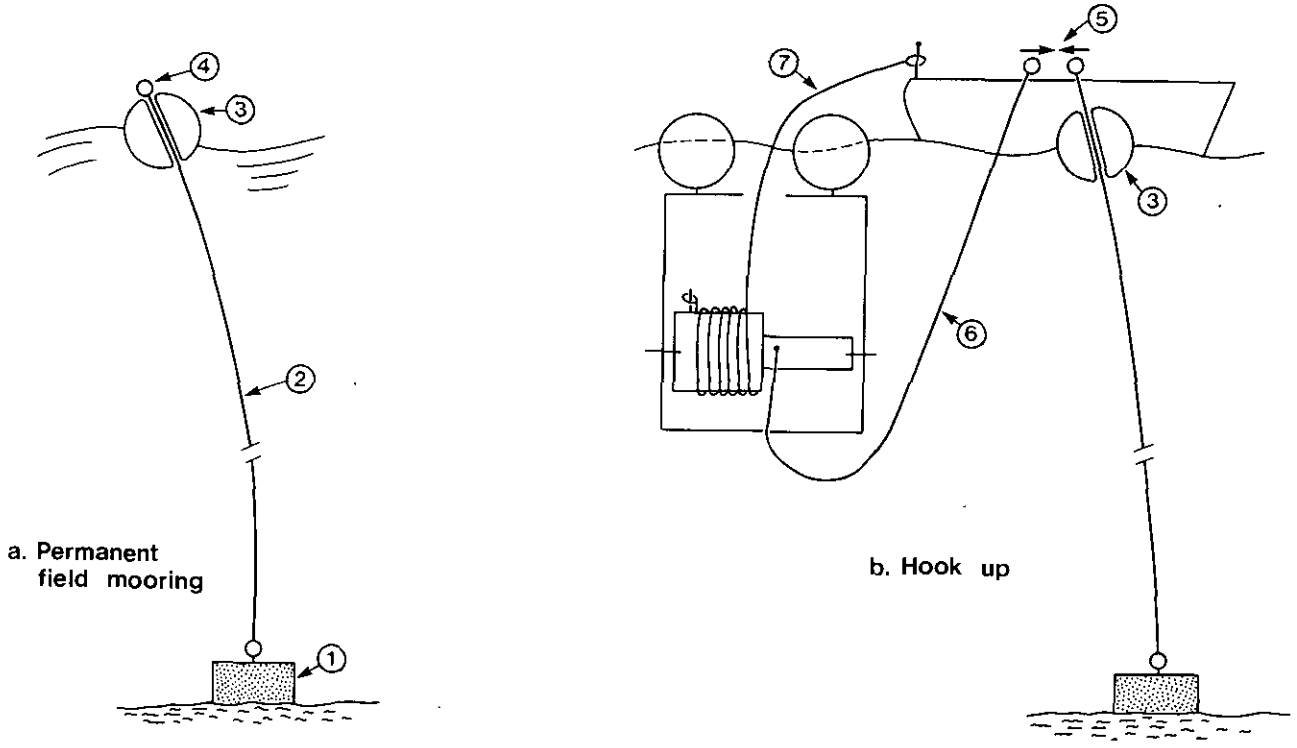


Fig.14 Deployment and recovery of submersing-reel assembly.

(a) Permanent field mooring. 1, 200 kg mooring block; 2, 12 mm polypropylene mooring line; 3, 280 mm Nokolon float; 4, stainless steel ring.
(b) Hook up. An 8 mm polypropylene surface line, 7, is wound around larger diameter spool, one end secured to vessel, and reel assembly placed in water. Mooring line, 2, and connecting line, 6, are shackled together, 5.

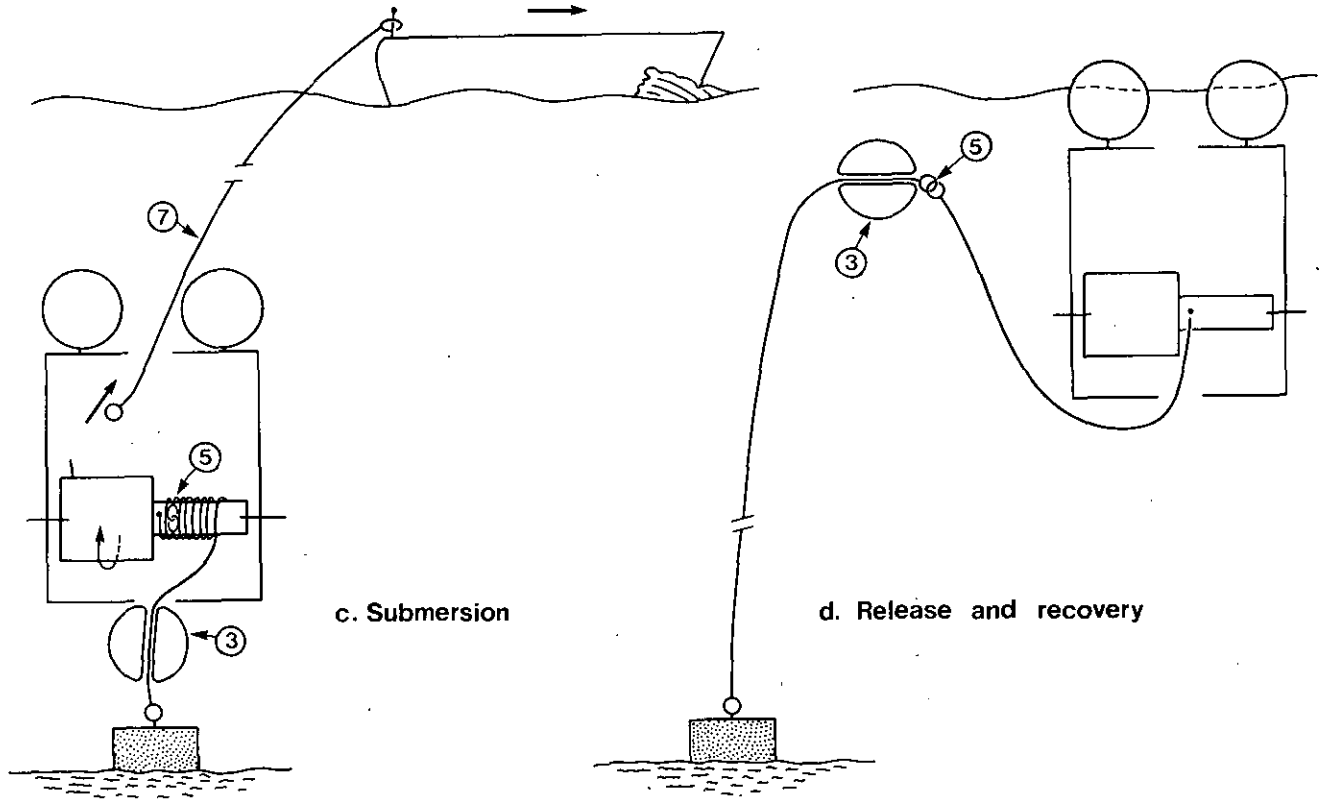


Fig.14 Deployment and recovery of submersing-reel assembly.

(c) Submersion. Vessel moves away until surface line unreels completely and detaches from spool. Mooring line remains spooled and assembly submerged until pin corrodes through.

(d) Release and recovery. In most current and wind conditions float, 3, is not on surface. Tow assembly upwind until mooring line slack to let float and shackled connection point to rise to surface.

Table 5

Analytical methods used for trace elements on Millipore filter discs

Element	Detection Method	Detection Limit ($\mu g.\ filter\ disc^{-1}$)
P	spectrophotometry	0.1
Hg	cold vapour AAS	0.005
Fe	direct flame AAS	1.0
Zn	direct flame AAS	0.1
Cd	filament in flame AAS	0.001
Cu	filament in flame AAS	0.02
Pb	filament in flame AAS	0.02

polypropylene containers with caps for storage and shipping enabled digestion of samples to take place directly in the tubes and minimized manipulation and contamination.

Samples were solubilized by oxidative hydrolysis with nitric acid (Garnys and Matousek 1975; Garnys and Smythe 1975). Four millilitres of ultrapure nitric acid (Merck Suprapure) was added to each vial using a 2.0 mℓ Oxford Pipette with an acid cleaned polyethylene tip. The container was tightly capped and placed in a drilled aluminium block held at 90°C.

Hydrolysis was allowed to proceed until the first brown fumes of nitrogen peroxide were visible. This usually occurred within 5 minutes. Millipore filters were totally dissolved, but if under-digested the hydrolysate would precipitate upon dilution. After cooling, 20 mℓ of doubly distilled water and 0.1 mℓ of ultrapure perchloric acid (Merck Suprapure) were added and mixed.

This solution was then suitable for direct AAS analysis. It was clear and quite stable during storage. All the trace elements had been converted to their nitrate salts which facilitated AAS calibration with trace element nitrate solutions. Also conversion of sodium chloride to sodium nitrate almost eliminated spectral interferences during furnace AAS analysis.

For phosphorus determinations an aliquot of the nitric acid digest was evaporated to perchloric acid fumes to remove nitric acid. After diluting with a few millilitres of water the acid was neutralized with sodium hydroxide, the solution then being made just acid, and diluted to 10.0 mℓ. The molybdenum blue colour was developed by adding 2.0 mℓ of reagent outlined in the method of Murphy and Riley (1962).

The trace elements of interest were determined by the methods summarized in Table 5.

Filter washing test. Blank filter discs contain traces of some heavy metals which can be of the same order of concentration as in the sample particulates. In relatively unpolluted sea-water containing a minimum of heavy metals, the blank contribution is significant. Therefore filters should be acid washed to lower the concentrations of interfering metals to acceptable levels.

Table 6

Blank filter discs from same batch of manufacture washed with 0 ml, 30 ml and 90 ml 5% HCl

Acid wash volume	Statistic	Residual metal concentration ($\mu g.disc^{-1}$) Cd	Cu	Fe	Pb	Zn
0 mℓ	$n = 20$					
	$\bar{x}$	<0.002	0.90	<1	<0.1	<0.1
	std. dev.		0.11			
30 mℓ	$n = 10$					
	$\bar{x}$	<0.002	0.19	<1	1.67	<0.1
	std. dev.		0.01		0.19	
90 mℓ	$n = 10$					
	$\bar{x}$	<0.002	0.10	<1	1.65	<0.1
	std. dev.		0.00		0.15	

Hydrochloric acid (5% in de-ionized water) was the acid of choice because it did not attack the perspex filter-washing apparatus and would not carry over and damage the samplers themselves. It was used to wash all filters in this work - 100 mℓ of 5% HCl followed by 100 mℓ deionized water. Five percent nitric acid attacks perspex and embrittles delrin, but on the other hand it is more easily commercially obtainable free from trace metals.

Table 6 shows that a 5% hydrochloric acid wash lowered the level of copper but increased the level of lead in filter discs. While no test was made to find out whether the lead came from the acid or the make-up water, commerical high purity hydrochloric acid is known to sometimes contain relatively high lead levels. However much, if not all, of the lead is removed again by a subsequent water wash, and values of lead in actual samples of particulate matter collected on hydrochloric acid-washed discs are in the range 0.2 to 0.5 µg per filter paper.

If a nitric acid wash is contemplated, filter washing apparatus should be made of plastic resistant to the oxidizing acid such as polythene, polypropylene, polycarbonate or polymethylpentene. Lusil O-rings should be placed where they would not come into contact with the acid.

All three copper levels are significantly different from each other. A significant increase in residual lead concentration was recorded after the 30 mℓ wash; concentrations were statistically similar after 30 mℓ and 90 mℓ washes.

Method sensitivity. Particulate trace metal concentrations in seawater vary between stations and between different times at the same station. Several short tests were run to determine the sensitivity - precision - of the sampling and analytical method in detecting such variations, and at what distances apart in position and time metal concentration differences were statistically significant.

Table 7

Mean trace element concentrations in particulate matter

Station	Statistic	Element concentration (μg.filter disc^{-1}) P	Cd	Cu	Fe	Pb	Hg	Zn
N.S.W.	$\bar{x}$ (n = 12)	0.8	0.009	1.99	18.0	0.327[(a)]	0.012	1.3
	std. dev.	0.8	0.004	0.77	8.5	0.142	0.005	0.6
	rank (b)	3	3	3	3	3	1	3
W.A.	$\bar{x}$ (n = 7)	<0.1	0.008	1.67	3.3	0.093	0.021	0.3
	std. dev.		0.007	1.09	1.8	0.050	0.017	0.1
	rank	1	2	2	2	2	2	1
S.A.	$\bar{x}$ (n = 6)	<0.1	0.005	1.00	1.2	0.061	0.145	0.5
	std. dev.		0.004	0.30	0.6	0.041	0.135	0.4
	rank	1	1	1	1	1	3	2

(a) outlying sample 3b (2.4) excluded

(b) rank : lowest (1), intermediate (2) and highest (3) mean values for each element from each station

Table 8

Statistically significant differences between elements from each station

Station pair	Statistic	Element P	Cd	Cu	Fe	Pb	Hg	Zn
S.A.~W.A.	t	-	1.0	1.6	2.9	1.3	2.2	1.2
d.f. = 12	sig. diff.				Yes		Yes	
t_{90} = 1.78	(90% level)							
W.A.~N.S.W.	t	3.1	0.3	1.5	5.8	5.2	1.4	5.6
d.f. = 18	sig. diff.	Yes			Yes	Yes		Yes
t_{90} = 1.73	(90% level)							
S.A.~N.S.W.	t	3.1	2.0	3.9	2.7	6.0	2.4	3.3
d.f. = 17	sig. diff.	Yes	Yes	Yes	Yes	Yes	Yes	Yes
t_{90} = 1.74	(90% level)							

(a) Comparison between widely spaced stations - N.S.W., S.A. and W.A.

The N.S.W. site was on the 20m depth contour due east of Port Hacking. A short series of 6 particulate samples was taken daily between 4 and 10 June 1979. The S.A. samples were taken from the southern end of Spencers Gulf, two stations near South Neptune Is. and one near Althorpe Is. in mid-September 1979 on a cruise of the F.R.V. Joseph Verco. The samples from W.A. were taken at the CSIRO 50m station off Rottnest Is. at approximately weekly intervals in September and October 1979.

All samples were taken in duplicate using two RIMCO samples (one for each of the duplicates) and were sent to the same laboratory (Amdel) for chemical analysis. Raw data is tabulated in Appendix 2. Means and standard deviations are compared in Table 7 and the statistical significance of differences between means shown in Table 8. For these comparisons the duplicates are treated as independent samples.

Table 7 shows that there is high variability in the concentration levels of trace elements in particulate matter. This could arise from experimental error, environmental fluctuations, or both. The sample size here is too small to permit an estimate of the contribution of each factor, but it could be deduced from a longer term program, since analytical precision and environmental variability are independent parameters, unless environmental distribution really does become increasingly erratic when elements occur in very low concentrations, and this would correlate with decreasing analytical precision where such concentrations were approaching the method detection limit.

Table 8 shows that despite the wide scatter of values, most mean differences between elemental concentrations at the three stations were statistically significant at the 90% level of probability. The ranking of stations on relative concentration levels is as would be intuitively expected. The Port Hacking station is closest to obvious sources of pollution, Rottnest Is. is intermediate, and Spencer Gulf is relatively remote from obvious industrial or domestic waste sources.

The mercury anomaly is an interesting exception. The southern Australian and Bass Strait waters have been controversial sources of mercury-contaminated fish. While mercury levels in fish are undoubtedly species and age related, there also may be natural environmental elevations of mercury in the waters of those regions compared with elsewhere around the Australian coast.

(b) Comparison between closely spaced stations - Hacking Point and Boat Harbour

These two stations were 6.7 km apart in open water on the 20m depth contour in Bate Bay east of Port Hacking, N.S.W. The Hacking Point station was about 700m from the undeveloped headland, and the Boat Harbour site about 200m from the rocky shore and adjacent to a minor sewerage outfall.

Samples were collected in duplicate or triplicate at each site between 13 and 27 November 1978 and analysed by Amdel. Result details, in sampling sequence, are given in Appendix 3.

Statistical analysis of the data (Table 9) shows no highly significant differences in particulate metal concentrations between the two stations over the relatively short sampling period. Any contribution of effluent from Boat Harbour was not significant when superimposed upon the large ambient variability associated with the parameters being measured. Perhaps studies over a longer period would show significant zonal variations under different seasonal conditions.

Table 9

Comparative trace element levels in particulate matter

Station	Statistic	Element (µg. filter disc^{-1}) P	Cd	Cu	Fe	Pb	Hg	Zn
Boat Harbour (BH)	$\bar{x}$ (n = 15)	3.8	(a)	0.6	24	0.4	0.076	1.1
	std. dev.	2.5		0.45	7	0.2	0.061	0.7
	rank	2		1	1	1	2	2
Hacking Point (HP)	$\bar{x}$ (n = 15)	4.3		0.5	20	0.3	0.106	1.2
	std. dev.	2.0		0.2	7	0.1	0.064	0.9
	rank	1		2	2	1	1	1
BH~HP								
(t_{90} = 1.7)	t	0.6		1.1	1.5	0.5	1.3	0.6
(t_{80} = 1.3)	sig. diff.				80%		80%	

(a) Five Cd readings were above the detection level at the Boat Harbour station, and eight readings at the Hacking Point station.

Table 10

Analyses of particulates from sampling grid shown in Figure 15. Concentration unit = µg. filter disc^{-1}

Sample No.	P	Cd	Cu	Fe	Pb	Hg	Zn
1	1.5	0.016	1.7	10.6	0.3	0.011	2.4
2	2.1	0.008	1.7	7.7	0.2	0.013	0.5
3	0.8	0.006	1.0	5.1	0.1	0.011	0.4
4	4.6	0.037	1.1	11.5	0.3	0.011	1.0
5	4.6	0.007	0.8	14.3	0.2	0.011	4.0
6	0.7	0.010	1.2	20.0	0.3	0.011	0.9
$\bar{x}$	2.4	0.014	1.2	11.5	0.8	0.011	2.0
Std. Dev.	1.8	0.012	0.4	5.2	0.9	0.001	1.4

Table 11

Correlation coefficients between concentrations of elements in samples taken on the same day from Bate Bay (as shown in Table 10).

	P	Cd	Cu	Fe	Pb	Hg	Zn
P	1	.5	-.3	.2	.2	.3	.5
Cd		1	.1	.1	.6	.1	-.1
Cu			1	0	.5	.7	-.2
Fe				1	.7	.2	.4
Pb					1	.4	.2
Hg						1	0
Zn							1

(c) Variation within closely spaced sampling grid - Hacking Point

To obtain some indication of particulate trace metal variability around one site a grid of stations was sampled as shown in Figure 15. The work was done on 5 June 1979 using several RIMCO samplers and took from 1 to 1½ hours to complete. Analytical results are shown in Table 10.

Several hypotheses were tested to see if significant environmental differences in trace element concentrations were apparent within the area sampled:

Samples 1 and 2 should be more similar than other paired samples. This was true only for Cu and Pb (standard deviations lower);

The four inshore samples had higher mean concentrations than the outer two, samples 3 and 4, except for Cd and P, and the inshore pair, 5 and 6, were higher than 3 and 4 for all except Cd. While this trend could be logically expected - a concentration gradient from inshore to offshore - none of the differences was significant;

Samples 4 and 5 on the northern side of the grid compared with 3 and 6 on the southern side had higher mean concentrations for P, Fe, Hg and Zn but lower for Cd, Cu and Pb. Only P was significantly different (at the 90% level);

A comparison of diagonal positions 4, 6 and 3, 5 showed significantly higher values of both Cu and Pb at 4 and 6, and higher but non-significant levels for P, Cd and Fe.

From such comparisons as those above, with trends indicated but most at non-significant levels, the grid area was not large enough to enable clear recognition of boundaries or intrusive tongues of polluted water as they may exist in open coastal water. A tentative suggestion for station separation would be a minimum of 10 km apart for non-specific monitoring purposes. Water within a 5 km radius may be considered homogeneous.

Correlations between elements in the same sample, with few exceptions, were quite low, indicating that trace metal levels associated with particulate matter were independent of each other. See Table 11.

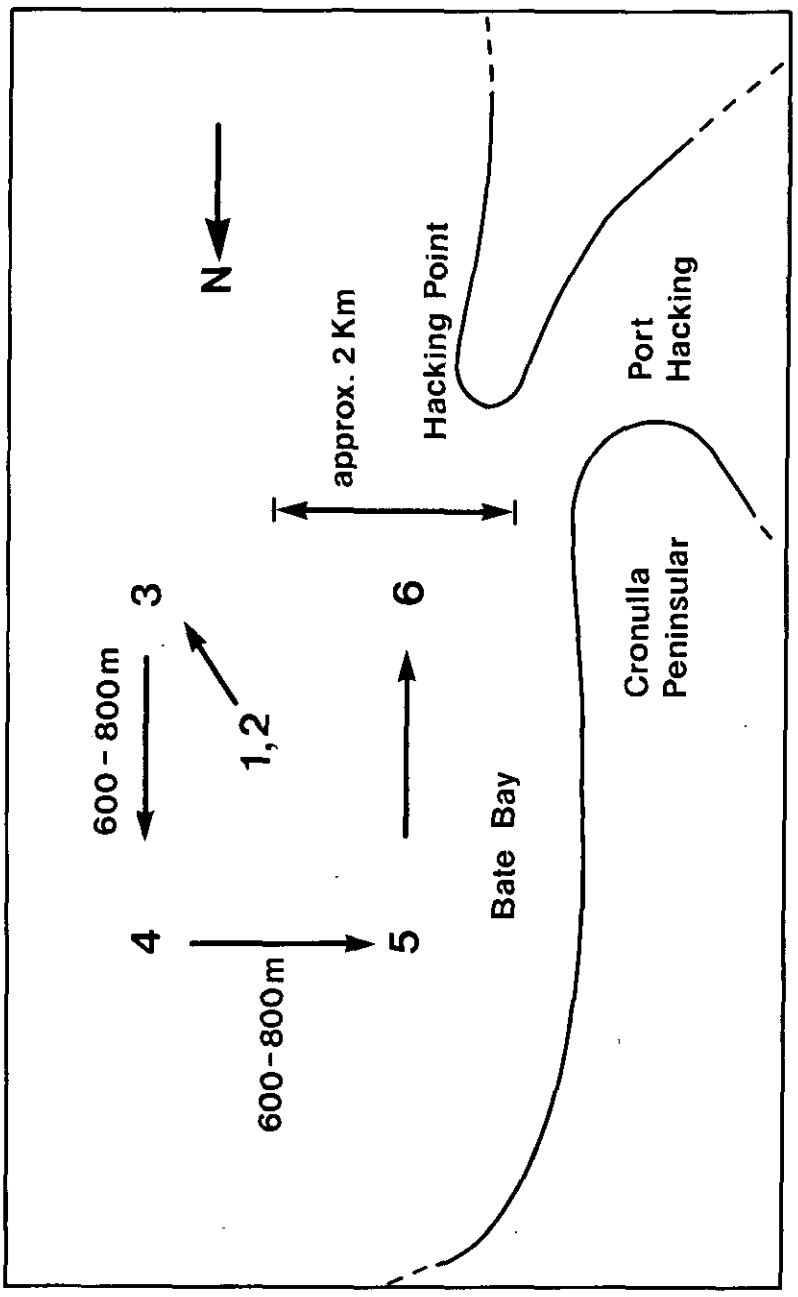


Fig. 15 Position and sequence of sampling grid stations (not to scale).

Correlation coefficients were also calculated for the other stations discussed in this report and the values of the correlation coefficients, r, between any two elements at different sites were apparently quite erratic. See Appendix 4. One might expect less erratic associations of elements in the more stable, unpolluted areas, and consequently perhaps higher r values. Although this appears to be so when comparing the S.A. and W.A. stations with the others, the trend is not strong. Features of the S.A. data are the strong negative correlations between mercury and other metals, and also the relatively strong positive r values of iron with the other elements (except mercury). Without further study and data, the validity of and reasons for these interesting associations must remain speculative only. The W.A. correlations are intermediate in magnitude and consistency between the S.A. and N.S.W. figures. Since phosphorus concentrations in the S.A. and W.A. samples were low, those particulates would have been comprised mostly of inorganic materials. This may have accounted for the more consistent correlations from there.

(d) Variation at Hacking Point 20m station over one week

A short time series was obtained by taking duplicate samples on each of six days from 4 to 12 June 1979. See Appendix 5 for resultant analytical data. Correlation coefficients between elements are shown in Appendix 4. The correlations, means and deviations are statistically similar to the distribution patterns of trace elements in samples from the grid sampling exercise.

A plot of the time series, Figure 16, shows a short period of higher concentrations within the sampling period. The peaks occur in all elements at about the same time and the transitions on either side are relatively smooth. Hence the perturbation is probably truly environmental and not an analytical error. It was most likely due to a temporary increase in the total density of particulates in the water - probably a denser patch of plankton. These plankton probably had been contaminated with components of sewage but at some time past, having since aged and equilibrated to the typical composition of suspended particulates in the area. This is suggested by the maintenance of a fairly constant metal to organic ratio, with phosphorus values - representing organic matter - elevated at the same times as metal concentrations.

That subtle conclusions as the foregoing may be inferred from the brief and unpromisingly variable data gathered in these trials, promises that longer term monitoring programs should yield ample information to justify their implementation.

2. Trace Metals in Mid-water Detritus

The prototype trap was suspended in the CSIRO's sea-water pool at Cronulla for four days in February 1979. The water in the pool was quiescent during this period. The detritus which collected was rinsed into a 20ℓ plastic bucket and left to settle out overnight. The clear supernatant water was siphoned off and the residual slurry filtered. About 6g of air-dried detritus was obtained which reduced to 1.3g when dried in an oven at 70°C.

The oven-dried material was analysed by Amdel, Adelaide. Results are included in Table 12. It can be seen that all elements are present in concentrations high enough to be easily determined. Other sets of data in the table are not strictly comparable. But they do indicate the dilution effect of barren sand and silt on trace metal concentrations in sediment samples, even when the samples come from polluted estuarine environments (Ellis and Kanamori 1977, Lake

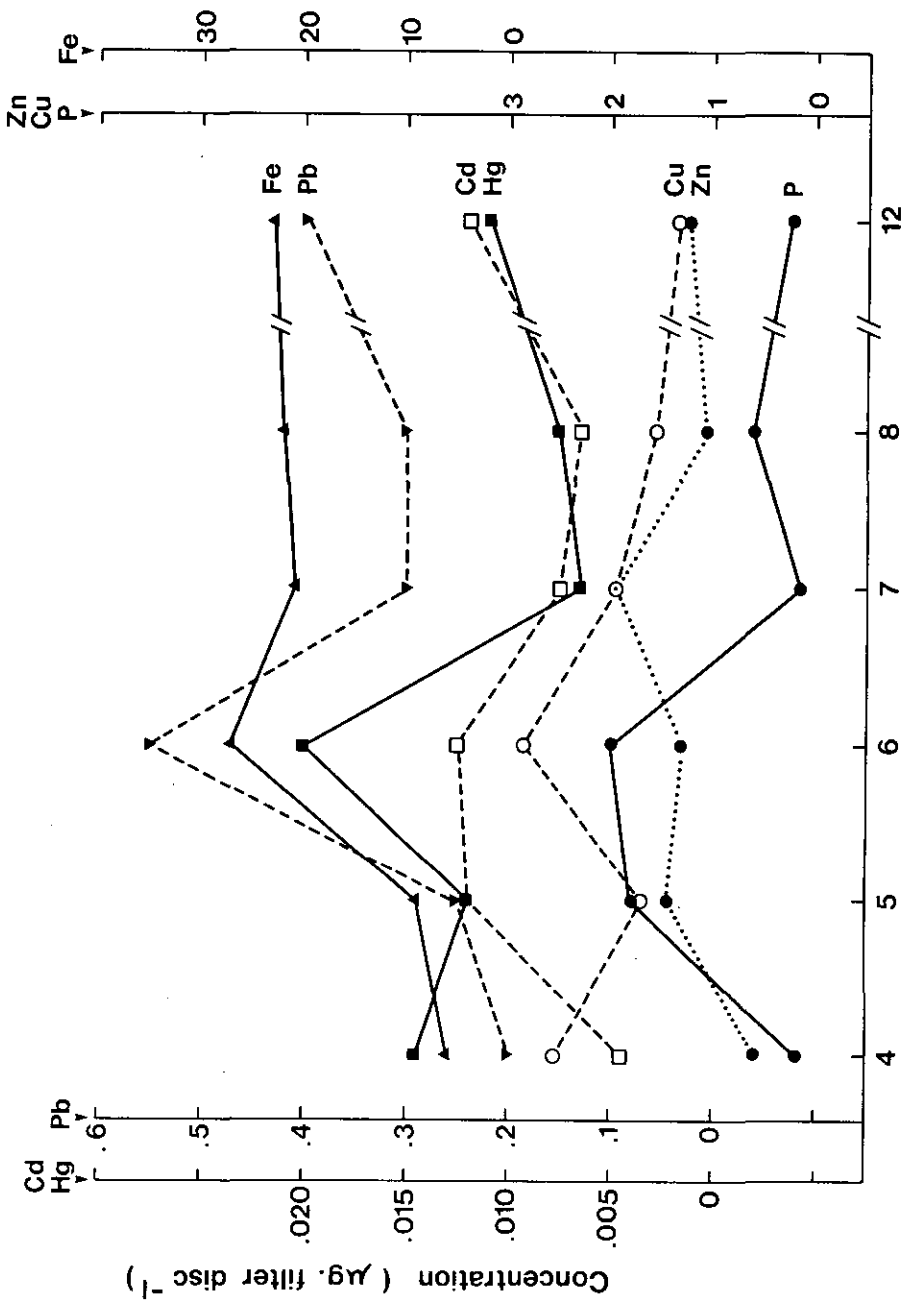


Fig. 16 Time series of trace element levels in particulates at Hacking Point 20m station between 4 and 12 June 1979. Means of the daily duplicate values have been plotted.

Table 12

Trace metal levels in marine sediments and suspended particulates

Sample and number (n)		Reference	Element (Fe-%, P-%; others-ppm) Fe	P	Cd	Cu	Hg	Pb	Zn
Suspended particulates (17) Antarctic Ocean 0-100m		Harris and Fabris (1979)	-	-	21	530	-	160	1500
Settling detritus Cronulla Sea-water pool 0-1m	(1)	this work	1.8	0.21	1.6	500	31	340	680
Sediment L. Illawarra 0-0.2m	(12)	Ellis and Kanamori (1977)	-	-	-	75	-	60	320
Sediment L. Illawarra 0.1-0.2m	(10)	Ellis and Kanamori (1977)	-	-	-	38	-	15	44
Sediment NSW central coast 0-20mm	(20)	de Forest *et al.* (1978)	-	-	-	6	-	21	40

Illawarra 0-200 mm surface layer-polluted, compared with unpolluted material from 100-200 mm deeper), or from Continental Shelf sediments (de Forest *et al.* 1978, N.S.W. coast between Sydney and Wollongong) where only the top 20 mm of material was shaved from the sediment surface and could reasonably be expected to contain a minimum of country rock.

Harris and Fabris' (1979) data from Antarctica waters exemplify the relatively high trace metal levels in oceanic particulates. Their data have the typically high variability expected from grab samples.

One can surmise that the particles which would settle into a detritus trap, comprising a large proportion of particle-aggregates of intermediate age and density between neutrally buoyant particulates (as reported by filtration from grab water samples) and denser sea-floor sediments, might also have intermediate trace metal concentrations. While this is indicated to some extent in Table 12, one single sample of detritus is no basis for confirmation.

Table 13

Comparison between trace element levels in mussel tissues from common stock, divided and transferred to two different estuarine sites for 26 days

Site	Average wet weight (per 3 mussels) g	Concentration of elements in freeze-dried samples (ppm, $\mu g.g^{-1}$) % P	Cd	Cu	Fe	Pb	Hg	Zn
CSIRO pool	7.12	0.81	6.6	4.9	74	7.0	0.20	190
(std. dev.)	(1.21)	(0.10)	(1.2)	(1.1)	(13)	(1.1)	(0.07)	(75)
S-W Arm bay	7.98	0.80	5.4	4.8	62	4.7	0.15	140
(std. dev.)	(1.54)	(0.15)	(1.3)	(1.0)	(8)	(1.3)	(0.06)	(60)
pool : bay	0.89:1	1.01:1	1.2:1	1.0:1	1.2:1	1.5:1	1.3:1	1.3:1
$t_{(calc.)}$	1.39	0.20	2.22	0.36	2.46	4.24	1.70	1.64
level of sig. difference (deg. free = 18)	80%	-	95%	-	95%	95%	80%	80%

3. Trace Metals in Mussels

A random batch of adult mussels from a muddy substrate was supplied by Mr. Geoff Adamson of Sans Souci, a commercial supplier of Port Phillip Bay mussels to the Sydney market, and kept in the sea-water pool at the CSIRO, Cronulla site for six months.

Two motels of mussels were filled from this environmentally-equilibrated stock. One motel was set at a depth of 15m on the submersing-reel assembly in South West Arm, a bay of Port Hacking estuary surrounded by the Royal National Park. The other motel was kept in the pool. After 26 days - 11 December 1978 to 4 January 1979 - 30 mussels from each site were analysed for total phosphorus and trace metals by Amdel.

The shells were opened with a stainless steel scalpel, bysall threads discarded, the flesh scooped out and placed directly into pre-weighed Whirl-Pak polythene bags. The soft parts from three mussels were put into each bag to make up one sample thus making 10 samples from each site. After re-weighing, the samples were freeze-dried with bag mouths open, then closed and sent for analysis. The tissues were not ground, homogenized or depurated before despatch.

Analytical results are shown in Table 13.

From the ratios of trace metal concentrations from the two sites all six show a higher concentration in the pool environment. The probability of this occurring by chance

alone is only $(0.5)^6 = 0.016$. This suggests that the mussels showed that the pool was generally more contaminated with trace metals than the open bay for the test period, although only three of the differences - Cd, Pb and Hg - were at the 95% significance level. Copper concentrations showed no significant difference at all. However mussels accumulate copper at a relatively slow rate (d'Silva and Kureishy 1978) and are therefore poor indicators of copper pollution, at least in the short term (less than 6 weeks environmental exposure).

The concentration of total phosphorus in mussels from each site is a rough indication of the metabolic activity by which they process and incorporate trace metals into their tissues. Other measures of essential organic matter present could be used, such as total nitrogen or carbon, but total phosphorus is chemically convenient to determine. The concentrations of phosphorus at each site were statistically similar, hence the significant differences in accumulated trace metals were not due to different levels of biological activity.

Temperature is an important factor affecting rate of metabolic activity, and there would have been differences between the two sites here. But no data were collected for such a comparison to be made on this occasion. Since growth rate of mussels decreases above about 18°C and the temperature in the pool would have been near this level and higher than that in S-W Arm, metabolic activity and hence metabolic metal accumulation would have been less, other factors being equal. Since trace metal levels in the pool mussels were in fact higher and not lower than in the bay mussels despite a probably lower rate of pumping, the results again suggest higher environmental concentrations of metals in the pool.

The lower average wet weights of the pool mussel samples tend to support the view that their growth rate was being suppressed by the high summer water temperature. However the parameter of total sample weight, wet or dry, is unreliable. Variable amounts of water associated with sample tissues are an obvious source of unreliability in wet weights. The same source of unreliability occurs in dry weights with the salt content of the original variable water content contributing to the sample weight.

Removing the salt by depuration in fresh water for 24 hours is not feasible since the process removes many of the elements of interest too. If the flushing-water contains higher levels of metal ions than the sea water where the mussels were located - which is quite likely - the net tissue metal load may increase.

It is impossible to determine wet tissue weights of sample batches directly before relocating live stock animals from reference site to test environment. So there is no proof that differences in the weights measured after the trial period are less, equal or greater than before. One possible approach would be to weigh the dry empty shells of mussels retrieved for analysis. Shell weight may be assumed to be proportional to original wet tissue weight, since the reference stock comes from a common site where individuals would have been similarly healthy. Of course this assumption ignores differential shell growth during the test period.

Sample batches containing the same number of animals in each batch, with individuals not necessarily of the same size, could be closely matched in biomass by making the total shell length of each batch the same, and conveniently measured by putting individuals end to end along a metered groove before placing them into their polypropylene pockets.

Such special care was not taken in selecting the two batches whose

results are given in this section. However final wet weights showed significant difference only at the 80% level. Therefore the more highly significant differences between Cd, Fe and Pb concentrations were almost certainly environmentally induced, if not the Hg and Zn also. Plausible explanations could be given why trace metal levels were expected to be higher in the pool than in S-W Arm, but the purpose of this report is rather to demonstrate that trace metal differences can be unambiguously detected by using indicator species.

Uncertainties in the validity of weight data make it a risky parameter on which to base detailed inferences about relative pollution levels, but it cannot be ignored completely. If batches of significantly different total tissue mass were put into the same sea-water, both would physically accumulate trace metals passively at the same rate. Such physical adsorption and absorption of trace metals is a function of surface area, and therefore proportional to $volume^{2}/^{3}$. However trace metal concentration is reported as a function of weight, which is directly proportional to volume. Hence as volume (and weight) increases, relative surface area decreases and concentrations of physically accumulated trace metals in the larger samples would be lower than in smaller samples. However, gross differences in initial biomass would be required for physical accumulation effects to mask the uptake of pollutants through biological activity.

If significant changes in weight after monitoring site exposure occur between batches which were similarly matched for biomass before relocation and which cannot be accounted for by differences in water temperature or food availability, then environmental stimulation or poisoning by trace metals or organics could be suspected. Seasonal fluctuations in growth rates are automatically compensated for by batches being exposed at the test sites concurrently.

An advantage of open ocean siting of monitoring stations is the limited availability of food most of the time. At low seston concentrations ($0.25\ \mu g.\ell^{-1}$) mussels will process all suspended particulate matter greater than 2 µm in diameter (Widdows *et al.* 1979). Under such conditions, all trace metals associated with the particulates will therefore be metabolised, ingested and absorbed at constant pumping rate. As particulate concentrations increase, mussels start to incompletely digest potential food material and eventually, at a seston level of about $5\ \mu g.\ell^{-1}$, totally reject excess material as pseudofaeces. The pumping or filtering rate of mussels in turbid water also slows down. These are problems which complicate the use of filter feeders as pollution indicators in estuarine situations but which may be ignored in open sea work. Thus mussels which are placed in an environment where they barely maintain condition or actually start to waste away are probably better - more standard - pollution monitors than mussels in inshore waters high in suspended particulates.

No trial or technique development was undertaken to test the potential of translocated mussels as indicators of organic pollution. However the literature suggests that it should be quite feasible to use mussels or other bivalves for hydrocarbon pollution detection, at least as a screening system if not for quantitative estimations (Hansen *et al.* 1978; Lee *et al.* 1972).

Hydrocarbons in sea-water, especially aromatic compounds, are rapidly absorbed by mussels, with accumulating avidity increasing with increasing molecular weight. Mussels have a natural hydrocarbon content of about 1 mg per animal. In the presence of mineral oils they can absorb a further 10-15 mg from the

environment before becoming saturated. After a return to clean seawater conditions 80-90% of absorbed hydrocarbons is discharged within 24 hours, but a residual 1-3% remains in the tissues and can be detected up to 3 weeks or more after initial exposure (depending on the specific hydrocarbons involved).

Mussels do not metabolize absorbed hydrocarbons; they retain and discharge them without degradation. Accumulation is believed to be a passive process of partitioning between water and tissue lipids on a relative solubility basis. The absence of any biological attack on retained hydrocarbons is a characteristic of the species which would be an advantage in pollution detection work.

Hydrocarbons are first rapidly taken up by gill tissues which absorb them and then pass them on to other tissues. After a period of time hydrocarbons appear in the gut. The mantle, adductor muscle and other tissues receive lower proportions. Thus there are differential concentrations of hydrocarbons in different organs at different periods of time after exposure.

A monitoring scheme could be envisaged whereby the time when polluting oil encountered test mussels may be deduced from the relative concentrations of hydrocarbons in excised tissues. However, for reasons similar to why whole tissue rather than organ analysis is being recommended for trace metal monitoring, and in view of the lack of a standardized means of interpreting such data at the present time, the benefits of carrying out such a procedure routinely are not yet worth the trouble and skill needed to separate out individual organs.

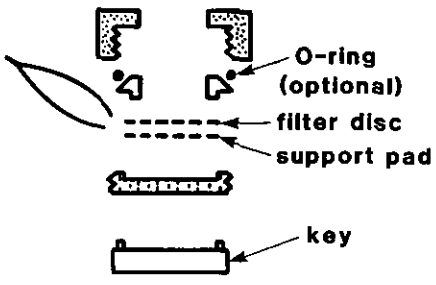
Appendix 1

RIMCO - CSIRO SAMPLER
Operating Instructions

1. Preparation of Filter Assembly

1. Use a clean area - preferably a clean air cabinet - to mount filter discs into assembly.
2. Place support pad, then the collecting filter disc on filter assembly. Use non-metallic forceps. Re-assemble parts.

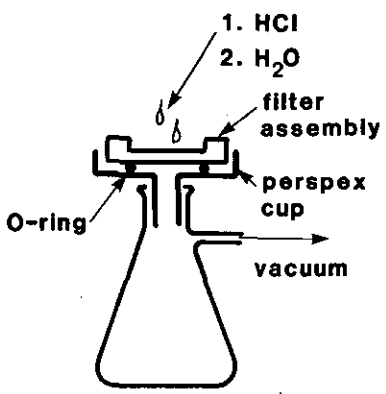
FILTER ASSEMBLY



2. Washing

1. Assemble filter washing apparatus in clean area:- perspex cup with lusil O-ring 2 7/8" x 2 5/8" x 1/8"; vacuum flask; hand, tap or motor vacuum pump.
2. Place filter assembly mounted with unused filter disc in perspex cup.
3. Suck through 100 mℓ of 5% HCl in *deionized water. Beware of Pb* impurity in HCl.
4. Follow with 100 mℓ of deionized water.
5. Store the assembly in plastic bag and keep in box until transferred into base of sampler.

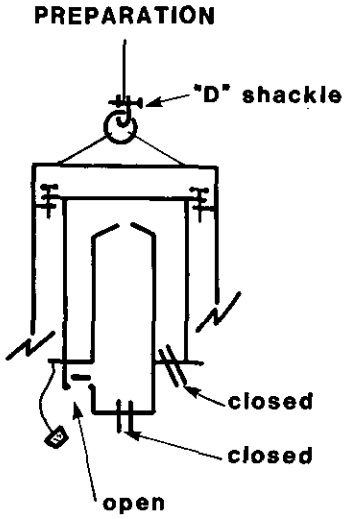
WASHING



3. Preparation for Sampling

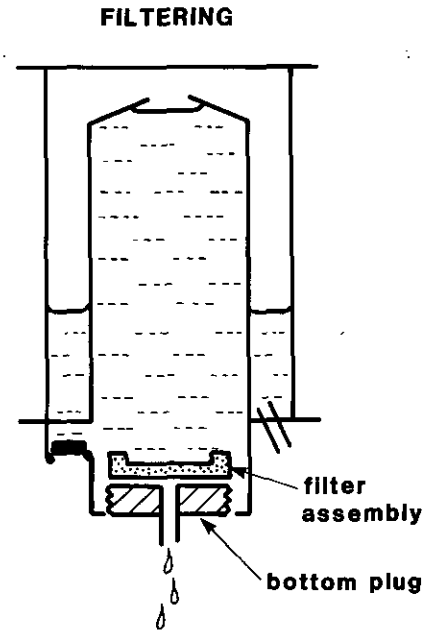
1. Attach bridle-ring to 20 m of line with "D"-shackle.
2. Close both taps to finger tightness.
3. Check that the plug for the water inlet valve is out.

PREPARATION



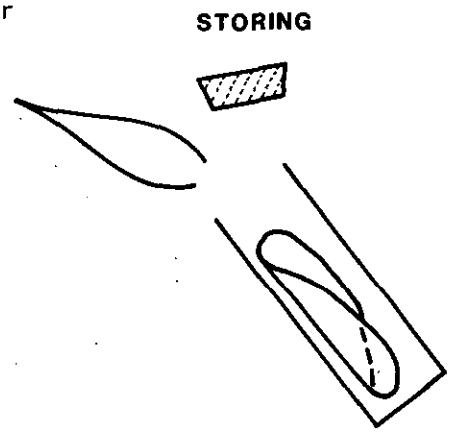
4. Sampling Procedure

1. Use sampler on first arriving at site.
2. Lower through 20 m depth.
3. Haul in almost immediately.
4. Open bottom tap and drain central chamber.
5. If collecting filtrate, let first 2 ℓ run to waste; collect next 1 ℓ or so).
6. Open side tap and drain outer chamber.
7. In cleanest environment available, unscrew bottom plug.
8. Remove filter assembly; immediately place it in plastic bag.
9. Insert replacement filter assembly containing new washed filter pad and membrane disc.
10. Screw bottom plug back in.



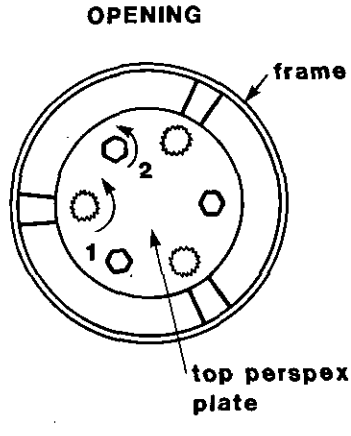
5. Storage and Despatch of Filter Discs

1. With non-metallic forceps, put top filter disc (with adhering particulate matter) into clean plastic specimen tube.
2. Replace cap; label tube.
3. Store in cool place until enough samples accumulated to despatch to analytical laboratory.



6. Cleaning of Sampler

1. After each use, hose down outside to limit rusting.
2. Clean inside every 6 months or as necessary.
3. To remove sampler from frame, unscrew 3 knurled nuts, twist slightly and lift.
4. Undo 3 hexagonal nuts (9/16" AF spanner) to take the plastic components apart.
5. Wash or soak perspex parts (colourless) in 5% HCl and deionized water.
   NB: Do not use HNO_3 - this acid attacks and crazes perspex.
6. The delrin parts (white) are slowly attacked by all dilute acids. Rinse these parts more briefly.
7. Do not subject O-rings to acids.
8. Check yearly for signs of rust in pressure relief valve (green cap). Replace if necessary: Nupro Cat No. SS-4CPA-3



7. General Information

1. A complete description of this apparatus is given by Major (1977).

2. Parts supplied by manufacturer:

   One plastic sampler complete, in stainless steel frame.
   Two stainless steel bridles.
   Four filter assemblies - one in sampler, three for exchange.
   One large key for opening filter assembly.
   One small key for gaining access to inlet valve.
   One pressure test adapter; fits into inlet hole for mains water (filtered) pressure test if necessary.

3. Other items needed by user:

   Filter membranes, 47 mm diameter, e.g. Millipore HAWP04700.
   Filter support pads, e.g. Millipore AP1004700.
   Filter washing assembly, all plastic-ware; e.g. in-line filter holder, vacuum flask, hand vacuum pump, 2 bottles marked in 100 mℓ intervals around side, one containing 5% HCl, the other dionized water, wash bottle, funnel, teflon-coated forceps.
   Plastic bags for storing filter assemblies.
   "D" shackles. Snap shackles have proved to weaken and become unreliable with resultant loss of equipment.
   10-20 kg sinker - optional. Attach to bottom of sampler by second bridle - advisable in strong currents or bad weather.
   Storage vials with caps. Check each batch for con tamination; preferably wash with dilute HCl or HNO_3, stand, rinse, and drain, in accordance with Aust. Std 2031 Part 1, paras 3.2.2 or 3.2.3.

3.2.2 Polyethylene and glass.

(a) Wash container with a phosphate-free detergent and tap water.
(b) Rinse thoroughly with tap water.
(c) Rinse with dilute (approx. 2M) hydrochloric acid.
(d) Rinse thoroughly with tap water.
(e) Rinse twice with distilled or deionized water.
(f) Drain thoroughly and replace cap.

3.2.3 Acid-washed polyethylene and glass.

(a) Wash container with detergent and tap water.
(b) Rinse thoroughly with tap water.
(c) Rinse with nitric acid (approx. 7M).
(d) Drain and fill with approximately 1M nitric acid.
(e) Cap and store until required, but for at least 1 week.
(f) Empty immediately before use but do not rinse.

NB: The containers prepared in this manner should not be used for samples on which nutrient determinations are to be made.

Appendix 2

Concentration of elements in particulate matter sampled from stations in N.S.W, S.A. and W.A.

Station	Sample Number	Concentration (µg. filter disc^{-1}) P	Cd	Cu	Fe	Pb	Hg	Zn
Port Hacking (Hacking Point) (NSW)	1	0.2	0.005	1.8	7.7	0.2	0.015	0.6
		0.2	0.004	3.3	4.2	0.2	0.014	0.6
	2	1.5	0.016	1.7	10.6	0.3	0.011	2.4
		2.1	0.008	1.7	7.7	0.2	0.013	0.5
	3	2.6	0.012	3.8	32.5	0.7	0.023	1.6
		1.4	0.013	1.9	22.0	2.4	0.017	1.0
	4	0.1	0.009	1.9	18.5	0.3	0.004	2.0
		0.2	0.006	2.0	23.0	0.3	0.009	1.9
	5	0.5	0.008	1.4	22.6	0.3	0.009	0.8
		0.7	0.005	1.7	21.3	0.3	0.006	1.3
	6	0.1	0.017	1.1	23.2	0.4	0.011	0.9
		0.4	0.007	1.6	23.0	0.4	0.011	1.6
Rottnest Is. (W.A.)	7	<0.1	0.018	1.1	1.9	0.06	0.010	0.2
		<0.1	0.001	1.4	3.8	0.10	0.030	0.2
	8	<0.1	0.017	0.8	2.4	0.06	0.010	0.3
		(duplicate lost)						
	9	<0.1	0.003	2.0	5.4	0.19	0.010	0.6
		<0.1	0.005	1.8	5.9	0.11	0.010	0.2
	10	<0.1	0.007	3.9	1.9	0.09	0.060	0.2
		<0.1	0.005	0.7	1.8	0.04	0.020	0.2
Spencer Gulf (S.A.)	11 (New Neptune)	<0.1	0.001	0.9	0.4	<0.01	0.315	0.2
		<0.1	0.001	1.1	1.0	0.02	0.315	0.3
	12 (Old Neptune)	<0.1	0.006	1.3	1.4	0.06	0.060	0.5
		<0.1	0.012	1.3	31.0	0.11	0.025	1.2
	13 (Althorpe)	<0.1	0.008	0.5	1.6	0.08	0.120	0.5
		<0.1	0.002	0.9	1.8	0.09	0.040	0.3

Appendix 3

Concentration of elements in particulate matter sampled from Hacking Point (HP) and Boat Harbour (BH)

Station	Date Nov. 1978	Concentration (µg. filter disc^{-1}) P	Cd[(a)]	Cu	Fe	Pb	Hg	Zn
BH	13	1.6	0.003	0.4	15	0.2	0.031	0.6
		1.2		0.3	15	0.1	0.030	0.7
		0.7	0.003	1.8	18	0.3	0.003	1.0
HP	13	1.9	0.003	0.4	31	0.3	0.077	1.0
BH	14	1.6	0.020	0.4	18	0.2	0.027	0.4
		1.6	0.004	1.2	21	0.8	0.039	3.2
		1.9		1.1	41	0.6	0.059	0.7
HP	14	1.9		0.4	30	0.2	0.048	0.9
		2.3	0.005	0.3	27	0.1	0.067	0.2
HP	22	3.7		0.4	19	0.2	0.048	0.2
		2.1		0.5	20	0.4	0.041	1.2
		8.3		0.9	33	0.5	0.081	1.3
BH	22	3.7		0.2	20	0.2	0.046	0.5
		5.3		0.2	25	0.3	0.031	0.5
		2.8		0.8	27	0.8	0.018	0.9
HP	23	4.9	0.002	0.5	15	0.4	0.183	0.7
		5.1		0.4	15	0.3	0.220	0.6
		7.2	0.003	0.5	17	0.4	0.243	1.2
BH	23	6.0		0.6	26	0.3	0.166	1.1
		6.5		0.4	26	0.3	0.190	1.2
		9.5		0.7	32	0.4	0.147	1.4
HP	24	4.6		0.3	20	0.2	0.046	1.1
		6.0	0.002	0.8	12	0.5	0.132	3.5
		6.2	0.007	0.4	19	0.4	0.089	1.9
BH	24	4.9		0.2	18	0.2	0.088	0.7
		4.9		0.4	21	0.2	0.166	1.0
		4.9	0.005	0.5	31	0.4	0.143	2.1
HP	27	4.9		0.4	14	0.4	0.120	2.8
		4.4	0.005	0.5	12	0.4	0.083	1.4
		4.9		0.4	12	0.2	0.116	0.6

(a) Cd values not entered are all <0.002

Appendix 4

Correlation coefficients between elements from the five sample sets discussed in this report

Element-pair	Sample Set					
	Bate Bay (Table 11)	Time Series	Boat Harbour	Hacking Point	W.A.	S.A.
P - Cd	.5	.3				
P - Cu	-.3	.4	-.4	.6		
P - Fe	.2	.2	.4	-.3		
P - Pb	.2	.3	-.1	.6		
P - Hg	.3	.6	.8	.5		
P - Zn	.5	.1	.1	.4		
Cd - Cu	.1	-.2			-.3	.1
Cd - Fe	.1	.3			-.5	.8
Cd - Pb	.6	.4			-.5	.7
Cd - Hg	.1	.2			-.3	-.7
Cd - Zn	-.1	.3			-.2	.9
Cu - Fe	.0	.1	.2	.1	.1	.5
Cu - Pb	.5	.1	.5	.8	.4	-.1
Cu - Hg	.7	.6	-.3	.1	.8	-.2
Cu - Zn	-.2	.0	.4	.5	.0	.4
Fe - Pb	.7	.3	.5	-.2	.8	.6
Fe - Hg	.2	.1	.3	-.5	-.4	-.9
Fe - Zn	.4	-.3	.2	-.3	.5	.9
Pb - Hg	.2	.4	-.1	.3	-.1	-.5
Pb - Zn	.2	.0	.6	.7	.8	.7
Hg - Zn	.0	-.3	.1	.1	-.3	-.6

Appendix 5

Concentration of elements in particulate matter sampled from Hacking Point 20m station

Sample	Date (June 1979)	Concentration (µg, filter disc^{-1}) P	Cd	Cu	Fe	Pb	Hg	Zn
1	4	0.2	0.005	1.8	7.7	0.2	0.015	0.6
		0.2	0.004	3.3	4.2	0.2	0.014	0.6
2	5	1.5	0.016	1.7	10.6	0.3	0.011	2.4
		2.1	0.008	1.7	7.7	0.2	0.013	0.5
3	6	2.6	0.012	3.8	32.5	0.7	0.023	1.6
		1.4	0.013	1.9	22.0	2.4	0.017	1.0
4	7	0.1	0.009	1.9	18.5	0.3	0.004	2.0
		0.2	0.006	2.0	23.0	0.3	0.009	1.9
5	8	0.5	0.008	1.4	22.6	0.3	0.009	0.8
		0.7	0.005	1.7	21.3	0.3	0.006	1.3
6	12	0.1	0.017	1.1	23.2	0.4	0.011	0.9
		0.4	0.007	1.6	23.0	0.4	0.011	1.6

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