A METHOD OF BULK SAMPLING WET AND DRY ATMOSPHERIC DEPOSITION FOR TRACE ELEMENT ANALYSIS

L.J. Hill[1] & P. de Caritat[2]

[1] CRC LEME, Geology Department, Australian National University, Canberra, ACT 0200
[2] CRC LEME, Geoscience Australia, GPO Box 378, Canberra, ACT 2601

Collecting rain for trace elemental analyses can be a difficult task. In Australia, most sampling of atmospheric deposition so far has been concerned with gauging the major element chemistry of atmospheric deposition to the Australian continent. Very little work has been conducted on the trace element chemistry of atmospheric deposition in the Australian landscape and, therefore, collector designs have not addressed trace element contamination. To counter this a collector has been designed to sample atmospheric deposition for trace element analysis. The design is presented here.

The collector is designed for the bulk sampling of wet and dry atmospheric deposition in semi-arid and arid conditions. Thus, it is important that the collector be able to collect and retain rainfall under exposure to wind, rain and heat conditions. Durable stands are also included to hold collectors, for up to several years, under exposure to the above climatic conditions as well as possible interference by stock and native animals.

COLLECTOR DESIGN

The rainfall collector design (Figure 1) is based on that used by Reimann *et al*. (1997) on the Kola Peninsula in Northern Europe. The design was modified to suit semi-arid climatic conditions and consists of a stand and the collector itself (bottle + funnel). We have experimented with two sizes of collectors: a smaller unit for monthly rain collection; and a larger unit for trimonthly collection. The stand consists of a section of white PVC stormwater tube (300 mm long x 90 mm diameter for the smaller units, 450 mm long x 150 mm diameter for the larger units) bolted to a 1,850 mm steel star-picket pole. When the picket is hammered solidly into the soil, it extends to a height of about 1,500 mm above ground. The PVC tube is bolted to the top of the star picket such that it extends about 25 mm above the top of the picket to reduce contamination from the steel. The height above ground is aimed at preventing contamination from soil and water splashing into the collection vessel from the ground (Bureau of Meteorology 1993). The stand provides a stable and sturdy base for the collection vessels. For a significant amount of time during the sampling period it is expected that the collectors will be heated by direct solar radiation or from radiant heat transferred to the collector from the ground, resulting in excessive loss of rainfall through evaporation. It is therefore important not to exacerbate this problem by ensuring that the tubing used in the construction of the collectors is of a light colour. The base of the PVC tubing has been left open to prevent insect infestation inside the tubing and facilitate retrieval of the full collectors. Collection bottles sit inside the tubing on wire that crosses the middle of the tubing.

The collection vessels for the smaller units consist of a 500 mL Nalgene® high density polyethene (HDPE) narrow-neck bottle (167 mm high x 73 mm outside diameter) with a 104 mm inner diameter Nalgene® polypropylene (PP) funnel. For the larger units, a half-gallon (approx. 2,100 mL) Nalgene® low density polyethene (LDPE) narrow-neck bottle (244 mm high x 121 mm outside diameter) with a 158 mm inner diameter Nalgene® PP funnel are used. These are taped together tightly using duct tape to prevent their separation and also to prevent insects from crawling into the collection vessel. Placement of the lip of the funnels above the top of the PVC tubing ensures that rain can not be deflected from the tubing into the funnel. The funnel also closes off the collection vessel to a large extent, limiting sample contamination from bird droppings and other solid matter. We found that inserting a small plastic plug (made for inserting screws into 'Gyprock' sheets) down the neck of the funnels significantly decreases the number of insects that get into the sampling bottles, thus decreasing the development of green algae that otherwise occurs in collectors, especially those that are left in the field for three months during the warmer parts of the year. This device also appears to decrease evaporation. The nature of the collection vessels mean that wet and dry bulk deposition is collected.

Several papers in the literature have focused on contamination levels derived from various plastic containers. The element concentration of plastics themselves have been reported in the Nalgene(R) catalogue after Moody and Lindstrom (1977); results of relevance here are that:

- LDPE contains '18 elements' to a total concentration of 23 ppm, major constituents being Ca, Cl and K;
- PP contains '21 elements' to a total concentration of 519 ppm, major constituents being Cl, Mg and Ca;

In: Roach I.C. ed. 2002. *Regolith and Landscapes in Eastern Australia*, pp. 54-57. CRC LEME.

- HDPE contains '22 elements' to a total concentration of 654 ppm, major constituents being Ca, Zn and Si.

Of course, the rainwater spends very little time in the funnels and the most time between deposition and analysis inside the HDPE or LDPE bottle. Also, complete digestion of any of the plastic containers never occurs, and only partial leaching from the plastic walls of the bottles is likely to happen at most. Thus, it is probably more relevant to refer to studies that have looked at contaminants found in distilled water (blanks) contained in various plastic bottles. Hall (1998) and Reimann *et al.* (1999) have done exactly this and came to the following conclusions of relevance here:

- Of the bottles tested (Teflon, HDPE, PETG, PP and precleaned HDPE), Hall (1998) found that the cheapest (HDPE) show the 'best characteristics' and are 'highly recommended';
- Further, Hall (1998) found that using factory-new HDPE is acceptable, but a rinse with weak HNO_3 (5%) is 'probably advisable';
- PP bottles are acceptable after cleaning if Al is of concern (Hall 1998);
- Reimann *et al.* (1999) found that, in general, factory-new unwashed HDPE bottles are suitable for the collection of waters for ultra-trace ICP-MS analysis;
- The worst overall levels of contamination from plastic bottles were found for Al (medians of 2-5 µg/L across all types tested), Se (0.25-0.45 µg/L), Pb (0.19-0.36 µg/L) and Cr (0.08-0.22 µg/L) (Reimann *et al.* 1999).

Unfortunately, neither study has tested trace elements in blanks from LDPE bottles but the report by Moody and Lindstrom (1977) suggests that levels of contamination should be less than for HDPE bottles.

It is recommended that six collectors be set up at each collection station site within a 10 x 10 m area clear of tall vegetation to avoid interception of incoming rain by canopy and all collectors are at least two metres apart to avoid cross-contamination. Five of the six collectors are used to sample rainwater for analysis. The sixth collector is set aside from the analytical process and is used instead to estimate the amount of evaporation. This is achieved by adding a layer of about 5 mm of paraffin oil to the collection vessel. The lower density of the oil ensures that any rainwater sinks to the bottom of the collection vessel below the paraffin oil layer. The use of this method to estimate evaporation follows the success of Keywood (1995) in assuming that no evaporation occurs through the layer of paraffin oil. This is subsequently checked by comparing the concentration of conservative ions (like Cl) or stable isotope ratios (∂D, $\partial^{18}O$) in the paraffin-protected sample and in the bulked sample from the other collectors.

PRE-FIELD COLLECTION PROCEDURES

Because of the long-term nature of rainwater monitoring studies, the need for six collectors at each site and the desirability to have more than one site in any study, a large number of bottles and funnels are needed (6 sites x 6 collectors x 12 months monitoring = 432 sets of bottles and funnels). Since these analytical grade consumables are costly, we opted for reusing containers rather than use factory-new each time. All bottles funnels and plugs are cleaned thoroughly prior to collection in the field. The cleaning procedure we use involves detergent and acid washing and water rinsing and is conducted in a clean environment using non-powdered gloves. Collection vessels (after use) are scrubbed clean using Decon® and hot tap water to remove any substances from used collectors and then left to soak in a mixture of Decon® and distilled water for 24 hours. Vessels are then rinsed at least three times with distilled water and left to soak in 2% HNO_3 bath for 24 hours. In the final stage of cleaning, the vessels are rinsed in distilled water three times followed by rinsing with Milli-Q® water, and then left filled to the brim with Milli-Q® water for at least 24 hours. The vessels then need to be dried, preferably air-dried in a clean drying cupboard. For the three-monthly collectors development of algae can be a problem. Thus, the washing procedure described above is preceded by a wash and soak in a weak, warm bleach solution. For transportation to the field, bottles should be sealed with lids (washed as per the bottles) and funnels sealed in plastic. Both parts of the collection vessels should be packed and sealed to avoid contamination during travel.

The bottles used for the estimation of evaporation (i.e. those containing paraffin oil) are best kept separate from the sampling bottles for analysis to avoid cross-contamination from the paraffin oil. The paraffin bottles undergo a separate (but similar) washing process.

SAMPLE SELECTION

Samples with discolouration (due to algal growth or insect infestation), with water volumes significantly different from the vessel with the paraffin oil, or with bird droppings on collection funnels, are discarded and not used for chemical analysis on the basis of suspected contamination. The remaining samples may then be mixed in equal proportions into a single composite sample (or analysed separately). All sampling vessels in the field should be handled using disposable non-powdered plastic gloves and stored at 4°C prior to analysis.

REFERENCES

BUREAU OF METEOROLOGY 1993. *Inspections Handbook and amendments*.

HALL G.E.M. 1998. *Cost-effective protocols for the collection, filtration and preservation of surface waters for detection of metals and metalloids at ppb (µg l^{-1}) and ppt (ng l^{-1}) levels*. Report submitted to Aquatic Effects Technology Evaluation Program (Task Force on Water Quality Issues), 49 pp.

KEYWOOD M.D. 1995. *Origins and sources of atmospheric precipitation from Australia: Chlorine-36 and major-element chemistry*. Department of Geology, Australian National University, PhD Thesis, unpublished.

MOODY J.R. & LINDSTROM R. 1997. Selection and cleaning of plastic containers for storage of trace element samples. *Analytical Chemistry* **49**, 22-64.

REIMANN C., DE CARITAT P., HALLERAKER J.H., VOLDEN T., AYRAS M., NISKAVAARA H., CHEKUSHIN V.A. & PAVLOV V.A. 1997. Rainwater Composition in northern Europe (Finland, Norway and Russia). *Atmospheric Environment* **31(2)**, 159-170.

REIMANN C., SIEWERS U., SKARPHAGEN H. & BANKS D. 1999. Does bottle type and acid-washing influence trace element analyses by ICP-MS on water samples? – A test covering 62 elements and four bottle types: high density polyethene (HDPE), polypropene (PP), fluorinated ethene propene copolymer (FEP) and perfluoroalkoxy polymer (PFA). *The Science of the Total Environment* **239**, 111-130.

Acknowledgments: This research is supported with an Australian Postgraduate Award Scholarship and the Australian Government's Cooperative Research Centres Program.

Thanks to Frank Krikowa at the Ecochemistry Laboratory, University of Canberra for assistance in developing a cleaning procedure and Professor Tony Eggleton for inputs in tackling issues for rainfall collection.

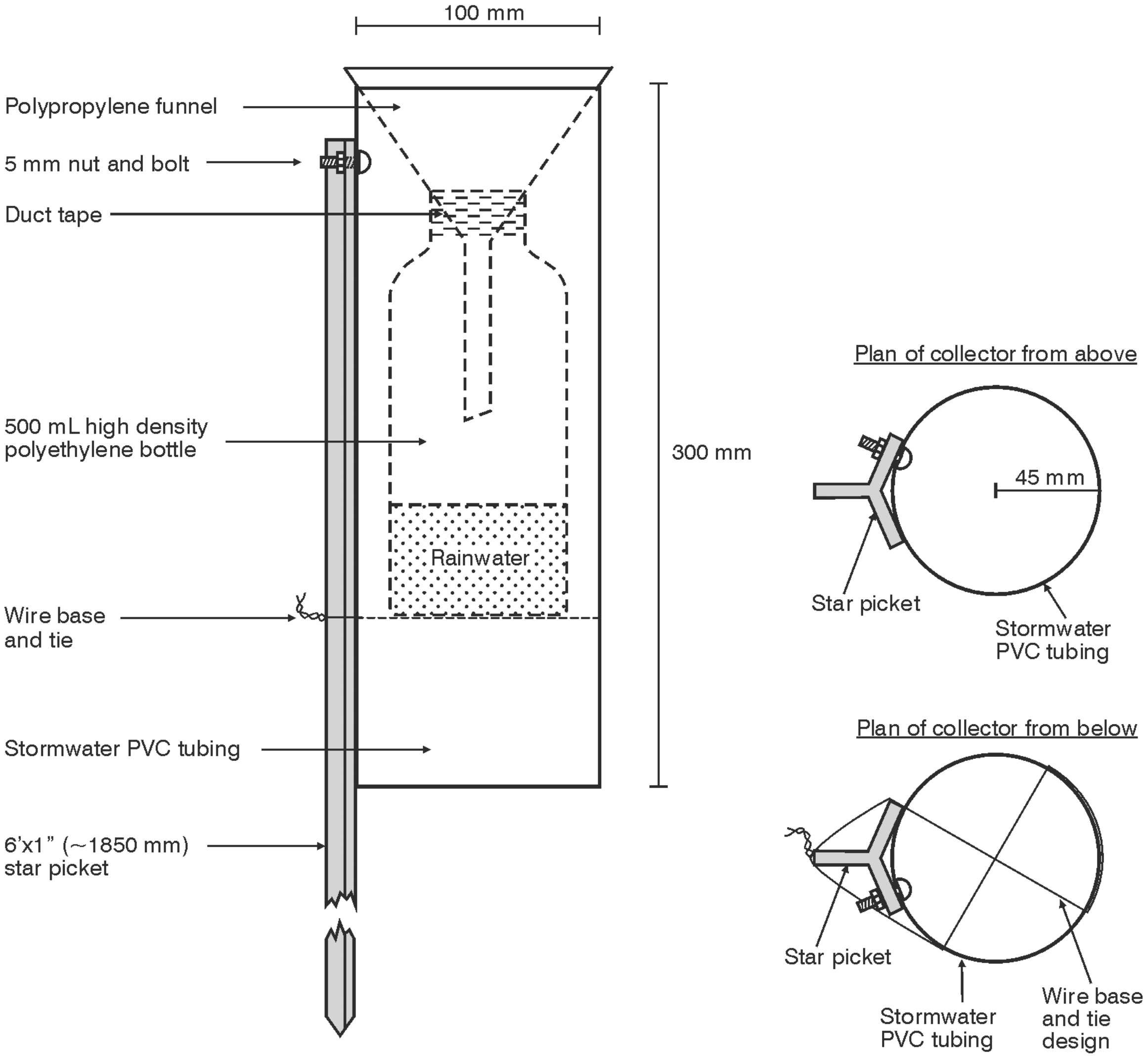

Figure 1: Design for a collector to bulk sample wet and dry atmospheric deposition for trace element analysis. Listed dimensions are for monthly collections. Three-monthly collector dimensions are described in the text.