

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION

DIVISION of FISHERIES and OCEANOGRAPHY

Report No. 95

**ANALYSIS OF CADMIUM, COPPER, LEAD AND ZINC IN SEA-WATER
INTERLABORATORY COMPARISON AMONG AUSTRALIAN LABORATORIES**

By G. A. Major and R. W. Pettis

Reprint No. 963

Cronulla, N.S.W. 2230
1978

ISBN 0 643 02108 6

Printed by CSIRO, Melbourne

ANALYSIS OF CADMIUM, COPPER, LEAD AND ZINC IN SEA-WATER
INTERLABORATORY COMPARISON AMONG AUSTRALIAN LABORATORIES

G.A. Major and R.W. Pettis

This study was designed to determine the degree to which different Australian laboratories, working independently, could obtain the same values for specified trace metals in one sample of sea-water. The spread of results would indicate the reliability which could be placed at the present time on values being given in Australia for the concentrations of these metals in sea-water.

Twenty-four laboratories were arbitrarily selected through personal contact and for their reputed interest in the subject, and invited to participate. The number invited was limited by the size of the original bulk sample. Ten of these laboratories were unable to participate.

Using PVC Niskin samplers a bulk sample of about 30 litres of near-surface ocean water was collected at a position south of Tasmania during a Materials Research Laboratories cruise aboard H.M.A.S. *Diamantina* in 1975. The water was immediately acidified with nitric acid to pH 1.5 and stored in a large polythene container. The sample was stored unfiltered. Medium density polythene bottles from the same batch of manufacture and aged with nitric acid solution were used to send 1-litre aliquots to the 14 participating laboratories listed in Table 1.

Participating laboratories selected their own method of analysis, and carried out their analyses between November 1975 and May 1976.

Results

Some laboratories used more than one method of analysis and submitted more than one set of results. Each set of results was treated as a separate laboratory. Anodic stripped voltammetry (ASV) from a hanging mercury drop electrode was used for 9 sets of results, ASV from a mercury coated carbon electrode for 4 sets, and 3 sets of results were obtained from solvent extraction followed by atomic absorption spectrophotometry (AAS).

The results reported as "labile" concentrations of metals in the sample were those obtained when the original acidified sample was not subjected to further oxidative treatment (Table 2), although buffering and pH adjustment was common, especially for the zinc determination. "Total" concentrations refer to results obtained when some oxidation step was involved in the procedure (Table 3). Quite different oxidation procedures were used by the laboratories reporting "total" estimations, namely photo-chemical oxidation by ultra violet with hydrogen peroxide, ceric sulphate, warming on a hot plate, and boiling with nitric acid. Each value reported in Tables 2 and 3 is generally an average of three or more replicate determinations. Results are stated as they were received; all laboratories reported cadmium to 2 decimal places, other metal values were reported with a precision ranging from whole units only to 2 decimal places, i.e. to the nearest $0.01 \mu\text{g.l}^{-1}$.

Discussion

The results are summarized in Table 4 where the data have been rounded off to two significant figures and the nearest 5%.

Several analytical problems contributed to the wide scatter of results. Some participants reported interference problems in the ASV estimation, such as the Zn^{2+} wave overlapping the H^+ wave, and the Cu^{2+} wave overlapping the Cl^- wave. They attributed these troubles to the presence of unspecified organic or particulate material in the sample. The low absolute concentration of cadmium in the water was close to the detection limit of the ASV and AAS methods used. The volume of sample water supplied was adequate for ASV determinations, but was rather small for solvent extraction and AAS. There were insufficient results to warrant any statistical comparison to be drawn between ASV and AAS methods.

Because the blank value for the original stabilizing nitric acid added to the bulk sample was not given, the results do not represent absolute environmental values. The one purpose of the exercise was to test the level of reproducibility which could be expected from Australian laboratories.

The data were ranked for each metal over the 13 analysts who returned results for all 4 metals. These ranked results are shown in Table 5. A non parametric analysis of variance (Friedman's multi-sample test) showed significant differences between analysts ($P < 0.025$) based on rankings over the four metals. Two analysts (1 and 12) gave consistently low values, while analyst No. 13 recorded consistently high values.

It is debatable to what extent the non-routine nature of an interlaboratory calibration exercise such as this distorts the quality of the results sought. It was assumed that all participants were equally skilled and also equally enthusiastic in doing the calibration analyses. Some would have found the analyses routine and familiar. To others however, these analyses would have been a special exercise, perhaps even a nuisance. Probably more replicates were done by each laboratory in this exercise than in the course of routine daily work.

Conclusions

Because of such poor agreement, there is much to be done in improving and standardizing the basic techniques in this type of trace analysis before any environmental significance can be placed on subtle variations in particular values for these trace metals reported by any Australian laboratory.

Even if one of these laboratories was generating valid data, e.g. accurate to within, say, $\pm 30\%$ of the true environmental concentrations, no other local laboratory could substantiate its data at present.

More careful consideration and definition need to be given to the chemical species being measured by the different analytical techniques.

It has been claimed that trace metal concentrations of about 10 times the natural environmental level are biologically deleterious. This study shows that it is difficult to establish the background concentrations of Cd, Cu, Pb and Zn, at least, within this one order of magnitude. Without improvements in the reliability of the analytical estimation of metals, investigations into the effects of sub-lethal pollution by these metals will be severely hampered.

Acknowledgement

We thank the fourteen participating laboratories for performing the analyses, and Mr D. Dunbar-Reid for statistical assistance.

TABLE 1

Participating Laboratories

Analyst or Administrative Contact	Organization
G.E. Batley	A.A.E.C. Research Establishment, Lucas Heights, N.S.W.
H. Blutstein	E.P.A., Melbourne, Vic.
P.L. Boar	Scientific Division, S.E.C., Vic.
A. Bond	Department of Chemistry, The University of Melbourne, Vic.
G. Dal Pont	CSIRO Division of Fisheries and Oceanography, Cronulla, N.S.W.
G. Fabris	Marine Chemistry, Department of Agriculture, Vic.
B. Hart	Caulfield Institute of Technology, Vic.
A. Morley	Research School of Chemistry, The Australian National University, Canberra, ACT.
R.W. Pettis	Materials Research Laboratories, Maribyrnong, Vic.
J.F. Pottinger	Department of the Environment, Hobart, Tas.
D.K. Rowley	A.M.D.E.L., Frewville, S.A.
J.H. Sharp	N.S.W. Institute of Technology, Broadway, N.S.W.
R.F. Shaw	Department of Physical Chemistry, Latrobe University, Vic.
G. Stuart	M.W.S. & D.B., Paddington, N.S.W.

TABLE 2

"Labile" metal ion concentrations in the sea-water sample, as determined by the participating laboratories. Both AAS and ASV methods have been incorporated. Mean values submitted by each laboratory ($\mu\text{g}\cdot\text{l}^{-1}$).

Cadmium	Copper	Lead	Zinc
0.05	0.52	0.27	1
0.05	0.6	0.28	1.4
0.05	0.61	0.46	2.5
0.07	0.62	0.49	2.7
0.07	0.81	0.52	2.97
0.10	<1	0.57	3.1
0.10	1.0	0.72	3.27
0.11	1.1	1.0	3.5
0.12	1.25	1.12	5
0.21	1.6	1.27	5.29
0.23	2.09	1.30	6.76
0.24	2.15	1.4	8.86
0.28	2.16	<3	9.6
<0.5	4.1	3	
0.80	6.2	4	

TABLE 3

"Total" metal ion concentrations in the sea-water sample, as determined by the participating laboratories. Both AAS and ASV methods have been incorporated. Mean values submitted by each laboratory ($\mu\text{g.l}^{-1}$).

Cadmium	Copper	Lead	Zinc
0.05	0.67	0.52	1.3
0.06	0.67	0.62	3.1
0.14	0.7	0.78	3.6
0.16	0.87	0.88	4.9
<0.5	2.0	1.0	8.6
	8.3	1.2	

TABLE 4

Summary of Results*

	Cadmium	Copper	Lead	Zinc
Number of observations	14	14	14	13
Mean ($\mu\text{g.l}^{-1}$)	0.18	1.7	1.2	4.3
Range ($\mu\text{g.l}^{-1}$)	0.05-0.80	0.52-6.2	0.27-4	1 -9.6
Coefficient of variation (%)	110	90	90	60
95% Confidence limits	0.18 \pm 0.1	1.7 \pm 0.9	1.2 \pm 0.6	4.3 \pm 1.6

(a) "Labile" metal concentrations

	Cadmium	Copper	Lead	Zinc
Number of observations	4	6	6	5
Mean ($\mu\text{g.l}^{-1}$)	0.11	2.2	0.8	4.3
Range ($\mu\text{g.l}^{-1}$)	0.05-<0.5	0.67-8.3	0.52-1.2	1.3-8.6
Coefficient of variation (%)	45	140	30	65
95% confidence limits	0.11 \pm 0.1	2.2 \pm 3.2	0.8 \pm 0.3	4.3 \pm 3.4

(b) "Total" metal concentrations

* The data given only as upper limits were omitted from the calculations

TABLE 5

Ranking of analysts for each metal in order of increasing magnitude of results

Analyst number (random)	1	2	3	4	5	6	7	8	9	10	11	12	13
Rankings: Cd	1	10	8	9	11	6	3	5	7	12	2	4	13
Cu	1	9	11	10	7	5	8	6	4	3	13	2	12
Pb	2	10	4	7	9	13	12	6	3	8	1	5	11
Zn	6	12	4	11	10	1	8	9	7	5	2	3	13