

**Concentrations of Heavy Metals
(Fe, Zn, Cd, Pb, Cu and Hg)
As Determined by Anodic Stripping Voltammetry in
Freshwater Ponds at Tarawa Atoll, Central Pacific**

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Abstract—Total element concentrations of Fe, Zn, Pb, Cd, Cu, and Hg have been determined in surface waters of 21 non-tidal freshwater ponds and in rainwater at Tarawa Atoll (Central Pacific) using DC and AC differential pulse anodic stripping voltammetry with rotating glassy carbon and gold disc electrodes. The metal concentrations in pond waters far away from the island's airstrip exceeded more recent reported seawater data, however, corresponded to rainwater concentrations; in pond waters close to the airstrip the concentrations were 5–10 fold greater. Considering organic metal sorption or complexing the present calcium ions will probably occupy the majority of the reactive sorption (binding) sites of the total dissolved organic matter.

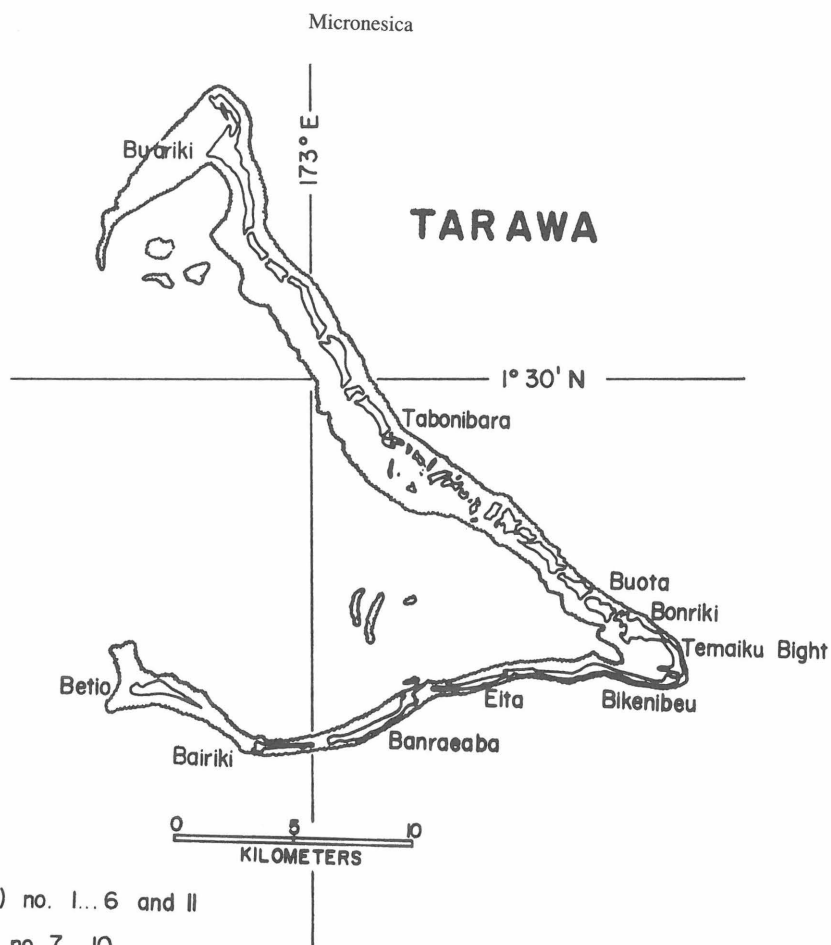
Introduction

Central Pacific atoll islands belong to the most remote freshwater habitats in the world. Their strict ombrogenic freshwater (Ghyben-Herzberg) lenses lie on the seawater, fill up part of the pore volume of the calcareous coral rock, and are poor in dissolved components except for dissolved $\text{Ca}(\text{Mg})\text{CO}_3$ (Catala 1957). This is due to the hydro-geochemical reaction between rainwater and the calcareous coral groundrock leading to increased pH's (≥ 8). As the coral rock is supposed to be extremely poor in heavy metals (Small 1972), the only source of trace metals for plant life may be the seawater spray (Cattell and Scott 1978) and the mixing action between fresh and marine waters in the marginal (and therefore tidal) parts of the lens. However, metal concentrations of rainwater which are increased by atmospheric pollution as well as accumulating effects in the poorly exchanged lenswater may finally create higher metal concentrations in the lenswater than in the surrounding ocean or lagoon waters. It was therefore interesting to study the concentrations of trace metals in non-tidal lenswater and in rainwater in order to find out what the metal input by rainwater, the impact of the alkaline conditions and the possible degree of accumulation of pollutants like mercury, cadmium or copper in the lenswater would be.

In this publication we report metal concentration data as determined by DPASV where the used acetate buffering procedure will correspond to analytical concentrations, i.e. $\text{Me}_{\text{DPASV}} \approx \text{Me}_{\text{T}}$ (Mart et al. 1980).

The Study Site

Tarawa Atoll (Fig. 1), the main island of the recent Republic of Kiribati (Gilbert Islands) is situated at $1^{\circ}30' \text{N}$, 173°E and belongs to the less humid tropical coral reefs of



- Bonriki (BR) no. 1...6 and II
- Buota (BT) no. 7...10
- Bikenibeu (BB) no. 12,13
- Tabonibara (TB) no. 14,15
- Temaiku Bight (TM) no. 16,17
- Eita (ET) no. 18
- Banraeaba (BA) no. 19
- Buariki (BU) no. 20,21

Fig. 1. Tarawa Atoll, Gilbert Islands (now Rep. of Kiribati), Central Pacific

the Central Pacific with a mean annual rainfall of 1780 mm. Nevertheless, the island suffered repeatedly from droughts killing even coconut palm trees (New Zealand Meteor. Serv. 1970). When taking samples for this study (August/September 1982) the rainfall corresponded to the longterm average. The same is due to the winds which have been predominantly easterly or north-easterly and have only once been interrupted by a westerly storm during two days.

Tarawa Atoll is mainly covered with coconut and Pandanus trees depending on the salinity of the groundwater which, in the middle part of the island, drops to calcareous freshwater conditions corresponding to spec. conductivities about $500 \mu\text{S}\cdot\text{cm}^{-1}$ (30°C). This is due to the development of a stable Ghyben-Herzberg freshwater lens developing by the continuous rainfall. Tarawa Atoll is uneven populated. The majority of the islanders live in natural huts or few concrete buildings in the southern part at Bikenibeu, Eita, Banraeaba, Bairiki and Betio (~ 0.6 ha per capita, Bailey, 1975).

In order to cultivate the Giant Taro plant (*Cyrtosperma chamissonis*) the islanders dig ponds into the coral rock which are mostly non-tidal or slightly tidal with 20–80 cm water depth, isolated from the marine groundwater and having a water surface between ten and several hundred square meters. With this study 21 corresponding ponds of about 80–120 m² surface which have continuously been cultivated for ≥ 10 years (pers. comm. from the villagers) and which have been spread over the whole island were considered (Fig. 1). The distances between these ponds and the ocean shoreline have been ≥ 50 m, thus outside the oceanic surf zone. All ponds were situated at the fringe part or outside of villages and are visited by the villagers only in order to harvest the Giant Taro root (once or twice a year) making a significant anthropogenic metal pollution by the islanders unlikely. No fertilizers or pesticides as potential metal pollutants are in use by the Giant Taro farmers.

The sampling sites in the southern part of the island were close to the island's airstrip (Bonriki, cf. Fig. 1) or within 10–50 m distance alongside the island's only road with a minibus passing 5–6 times a day.

Materials and Methods

The water samples from the freshwater ponds were drawn into sealed glass vessels and stored in the dark at less than 4°C . Within 3 weeks they were transported to Germany, acidified (1% vol. HNO_3 suprapure grade), and then TOC determined and metal analysed in the unfiltered samples. In order to diminish organic complexation the samples were UV irradiated for 2 hours after adding 1% vol. H_2O_2 (30% perhydrole suprapure grade). Rainwater was sampled while carefully preventing any contact with the ground, plants or buildings. Before sampling the glass vessels and stoppers had been carefully washed with concentrated HCl (p. a. grade) (24 hours), rinsed 5 times with aq. dest. and again rinsed 3 times with the sample waters. The aq. dest. was analysed as a blank. The corresponding concentrations have been 1/5 to 1/10 those of the samples or below the limit of detection (Hg, Cd, Cu).

Fe_T was determined by atomic absorption spectrophotometry (Varian-Techtron 1205) and Na by flame photometry; TOC was determined (total organic carbon) by Maihak IR detector (± 0.5 mg/l).

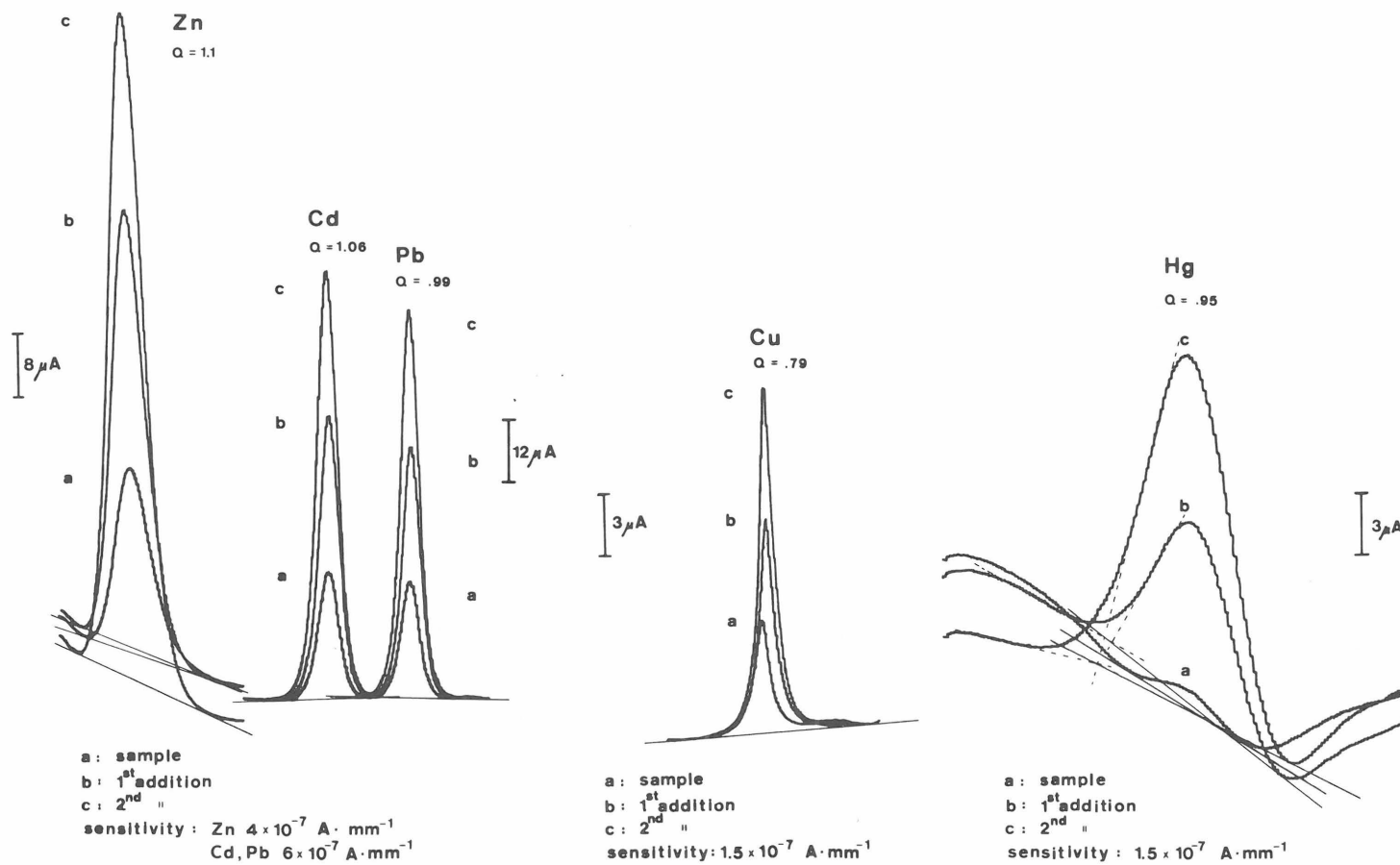


Fig. 2. Examples of voltammograms as obtained with pond water no. 14; a—sample current peak; b, c—after known standard additions (peak base lines weak); Q see text; sensitivity is chosen due to the optimum current yield ($Amp\grave{e}re \cdot mm^{-1}$). Sample concentrations are calculated from the diagrams due to $Me_{sample} = \Delta Me_{a \dots c} / (c-a) \cdot a$

For Zn, Cd, Pb, and Cu we used DC differential pulse anodic stripping voltammetry with rotating disc glassy carbon electrode (DPASV/glassy carbon RDE) in a known addition mode (cf. Valenta et al. 1977): 20 ml of the acidified sample water (1% vol. HNO₃ suprapure grade) was bubbled with purified N₂ for 10 min; 5 ml of Hg(NO₃)₂ (40 ppm) p.a. grade was added and buffered by adding CH₃CO₂Na (suprapure grade) to pH 4.7 . . . 5.0. For Zn, Cd and Pb the cathodic deposition time was 15.5 min (rotating electrode) and 0.5 min (stationary electrode) at -1.2 V; for Cu the deposition time was 2.5 min (rotating) and 0.5 min (stationary) at the same voltage. Two standard additions were made where the ratios Q of the current peak heights above the base lines were 0.8 . . . 1.2 (averages of all detections, 99% confidence: \bar{Q}_{Zn} 1.0 ± 0.5; \bar{Q}_{Cd} 0.9 ± 0.1; \bar{Q}_{Pb} 1.0 ± 0.1; \bar{Q}_{Cu} 1.0 ± 0.2) indicating a sufficiently precise linearity between the added standard solutions and the voltammetric response. Each sample was analysed twice where we found a maximum deviation of ± 19%. After each run the glassy carbon surface was cleaned with paper tissues.

For Hg we used the AC mode of DPASV with rotating Au electrode; the Au electrode had to be pre-conditioned in the manner described by Frahne (1982). Then to 15 ml of acidified sample water (1% vol. HNO₃ suprapure grade) 0.5 ml H₂O₂ (30% suprapure grade), 0.5 ml 1 M NaCl (suprapure grade), and 0.2 ml HClO₄ (70% suprapure grade) were added. The deposition time was 14 min (rotating) and 1 min (stationary) at +0.4 V and 25 Hz. At the end of the stripping phase the electrode remained 20 sec at +0.9 V. After each analysis the Au surface had to be polished with corundum powder and thoroughly washed with double distilled H₂O. The standard additions and evaluation were made as described with Zn and Cd where the standard solutions had been redox stabilized by additions of H₂O₂ as described above. \bar{Q}_{Hg} was 0.9 ± 0.2 (99% confidence), the maximum deviation was ± 30%. Figure 2 shows typical recorder voltammograms. We used a Metrohm E 506 as detector system.

Results

The results of the analyses are shown in Table 1. We used Na as a tracer for seawater. In all ponds the Na concentrations were of the same order of magnitude as in rainwater except for ponds no. 4, 5, 6, and 16. These ponds either had hydraulic connections to the saline and tidal lagoon water or were in areas where the freshwater lens was made unstable by seawater intrusions (no. 16 at Temaiku Bight). However, the increased Na concentrations in the ponds would require the addition of only 2.1 . . . 2.7 ml sea- to one liter of rainwater. Thus, the seawater intrusion to the freshwater must have been very low.

When compared to the mean cation concentrations of average seawater (Brewer 1975), or of more recent surface water determinations of the Central Pacific (Mart et al. 1982), our rainwater sample concentrations are higher than seawater concentrations mainly for Pb and Cd. Most metal concentrations in the pond waters, however, were even higher than in the rainwater, especially in the case of Fe, Zn, Pb, Cu, and Hg. There is further significance that in ponds no. 1 to 13 (Bonriki, Buota, Bikenibeu) all concentrations (except of Fe) are much higher. As can be seen in Figure 1 these ponds are in the southeastern part of the island close by the Bonriki airstrip where two aircraft (Boeing 727) arrive and depart weekly, where the minibus passes several times a day and where the

Table 1. Heavy metal, Ca, Na concentrations as found in freshwater ponds (Giant Taro pits); SO_4^{2-} and $\text{S}_{\text{tot}}^{2-}$ always $\leq 10^{-6}$ M.

sampling site pond no.	rain water* 28.08.82	BR						BT			
		1	2	3	4	5	6	7	8	9	10
Fe _T (ppb)	<8 (2.0)	25	25	17	42	<8	<8	17	33	17	8
Zn _T (ppb)	<1.0 (<1.0)	44.1	43.0	15.1	32.2	n.d.	3.6	6.7	24.6	n.d.	1.4
Cd _T (ppb)	.05 (.004)	1.12	.22	.12	.40	.20	.14	.12	.15	.11	.25
Pb _T (ppb)	.9 (.014)	19.7	9.1	5.6	24.1	3.0	2.9	3.1	2.5	2.4	2.7
Cu _T (ppb)	n.d. (.088)	4.3	5.5	1.6	4.9	<.5	2.5	9.4	15.5	10.6	6.0
Hg _T (ppb)	.1 (.03)	3.3	2.1	.9	3.7	27.7	17.3	.9	6.5	1.3	2.1
Na (ppm)	7.8 (10.75 g/l)	6.2	5.4	6.5	35.0	36.5	30.0	6.7	9.4	7.4	5.9
Ca _T (ppm)	<1.0 (.4 g/l)	46.2	56.0	55.0	24.2	17.2	42.3	39.6	46.6	54.8	46.4
Temperature (°C)	23.5	29.5	31.0	28.0	27.4	30.0	28.0	30.0	31.0	31.0	31.0
pH	6.51	7.73	8.31	7.85	7.54	8.88	7.67	8.36	8.65	7.92	7.83
Conductivity ($\mu\text{mhos}\cdot\text{cm}^{-1}$)	17	385	316	477	588	568	592	481	416	577	446
Alkalinity (mM)	.06	3.01	3.48	4.95	4.35	3.21	5.02	4.55	3.75	5.35	4.11
TOC (ppm)	8.5	24.2	23.5	38.9	23.0	22.1	47.1	24.4	44.6	88.7	41.8

sampling site pond no.	BR	BB	BB	TB	TB	TM	TM	ET	BA	BU	BU
	11	12	13	14	15	16	17	18	19	20	21
Fe _T (ppb)	17	8	67	291	25	25	42	<8	25	n.d.	25
Zn _T (ppb)	14.7	3.0	7.3	<1.0	n.d.	3.7	3.3	<1	n.d.	n.d.	9.3
Cd _T (ppb)	.35	.07	.17	<.06	.10	.06	.08	.09	.05	n.d.	.10
Pb _T (ppb)	12.3	2.2	4.8	1.6	1.3	1.4	1.4	.8	1.5	n.d.	1.4
Cu _T (ppb)	16.8	1.0	5.3	<.5	.8	.3	<.5	2.8	.4	n.d.	<.5
Hg _T (ppb)	.1	1.7	.1	.1	1.7	.5	.9	1.7	.5	n.d.	n.d.
Na (ppm)	9.0	11.9	7.0	4.8	12.0	37.5	4.7	8.2	6.9	n.d.	11.5
Ca _T (ppm)	46.4	52.6	56.7	24.6	55.8	37.2	39.3	43.9	44.4	n.d.	69.3
Temperature (°C)	30.0	27.0	31.5	32.5	28.0	30.5	33.0	31.5	29.0	28.5	28.0
pH	8.23	7.46	8.46	9.39	7.74	8.12	8.84	8.29	7.44	7.67	7.69
Conductivity ($\mu\text{mhos}\cdot\text{cm}^{-1}$)	426	459	366	207	500	596	303	365	326	507	503
Alkalinity (mM)	4.15	4.58	3.58	2.17	4.58	3.41	3.01	3.44	3.34	n.d.	5.32
TOC (ppm)	22.1	47.0	58.5	22.1	47.5	44.0	26.0	42.3	44.5	n.d.	57.2

abbreviations: BR–Bonriki; BT–Buota; BB–Bikenibeu; TB–Tabonibara; TM–Temaiku Bight; ET–Eita; BA–Banraeaba; BU–Buariki. n.d.–not determined (cf. Fig. 1) *–values in parentheses due to mean surface seawater concentrations (Brewer 1975 and Mart et al. 1982)

population density is highest. Thus, considering the predominant wind directions (NE, E or W) it is likely that the increased concentrations are due to the local pollution and that the ponds in northern Tarawa (Tabonibara, Buariki) reflect more the pristine conditions, i.e. concentrations which are unchanged by anthropogenic inputs. Obviously the increased metal concentrations will not be diluted by the frequent rainfall.

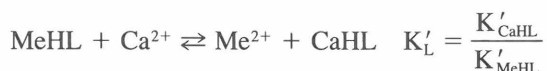
Discussion

Our results indicate that some of the freshwater ponds studied on Tarawa island are significantly enriched by heavy metals (particularly by the potentially toxic metals Hg, Cu, Cd, Pb and Zn). There can be no doubt that the total concentrations we found (some even more than ten times higher than in rain- or seawater) are the consequence of a local pollution independent of the input rates of rainwater. We could not determine the water exchange rates of the studied ponds; however, in any case their exchange rates must have been low with regard to their non-tidal character and their mean water tables less than 1 m above sea level.

Reliable informations about heavy metal concentrations in fresh lenswater of atoll islands are lacking. The majority of available data are either restricted to alkali or earth alkali metals and some nutrient elements (phosphate, inorganic nitrogen compounds, Donaldson and Whitton 1977) or to the geochemistry of the coral rock (Trudgill 1981). More data have been reported from running waters on crystalline (granitic) islands which, however, cannot be compared with lenswater conditions of coral reefs (Weninger 1977). Thus, we are unable to compare our results with the concentration conditions on other coral islands.

Comparing our data with more recent reported ones from the Central Pacific (Mart et al. 1982), we recognise, however, increased metal concentrations in all pond waters (incl. the northern remote pond 21 (at Buariki, cf. Fig. 1) and in the rainwater. Thus, Tarawa Atoll (and possibly other coral reef islands) has to be considered as accumulating heavy metals which may come in by rainwater and/or by anthropogenic pollution.

Unlike Hg, Cd, and Pb the metals Fe, Cu, and Zn are at lower concentrations, essential trace elements for atoll plant life (Small 1972). Even if they are more concentrated in lenswater than in the rain or seawater it cannot be concluded that these elements will be sufficiently bioavailable, or (at higher concentrations) sufficiently deactivated. As is well known, organic complexing of heavy metals will either increase their bioavailability or decrease their toxicity (Provasoli 1966). Thus, it is interesting to consider the potential complex binding impact of organic ligands (incl. sorption to particles which we cannot distinguish here) in the presence of much more highly concentrated Ca^{2+} ions (as is the case in our results):



where HL = partially protonized organic ligands roughly detected as TOC.

Assuming $K'_L \approx 1$ (i.e. the complexing and sorption intensities of Ca^{2+} will be similar to Me^{2+}), which is realistic considering the labile complexing and sorption sites of the dissolved organic matter (O'Shea and Mancy 1978) we obtain

$$\frac{[\text{CaHL}]}{[\text{MeHL}]} \approx \frac{\text{CA}_T}{\text{Me}_T} = \beta_{\text{CaMe}}$$

Corresponding β_{CaMe} values show that Ca^{2+} complexation probably prevails in all pond waters about $10^3 \dots 10^5$ fold. Thus, complexation of the considered heavy metals by organic ligands should be possible if TOC is roughly $10^3 \dots 10^5$ times more concentrated than Ca^{2+} , which is clearly not the case due to our data (cf. Table 1).

Conclusions

- 1) The total concentrations of the considered heavy metals in freshwater ponds on atoll islands are increased (compared to the surrounding seawater) which may naturally be determined by the corresponding concentrations in rainwater (incl. precipitated aerosols). Local emission sources in the vicinity of open pond waters can additionally lead to drastic concentration increases (including the ones of strictly toxic metals like Hg and Cd), which will probably be enhanced by the low exchange rates of the lenswater;
- 2) Sorption and complexation of the metal ions with organic ligands (roughly given by TOC) will probably not compete at least to the labile Ca^{2+} complexing capacity.

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