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Robert H. Spigel & John C. Priscu
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Page 186
Right hand column, 9th printed line from the end
$a = 15.299 \quad b = 133.36$

Page 188
Left hand column, equation (A-1), line 3
$+ b_2 R_t + b_3 R_t^{3/2} + R_t^2 + b_3 R_t^{5/2}$

Page 189
Table A1. Coefficients in conductivity-salinity equations
line 2, column c_i $+ 2.005640$
line 4, column a_i $- 7.0261$

Left hand column, 14th printed line from end
secan should read **secant**

Equation (A12)
$K(S,t,p) = K(S,t,0) + Ap + Bp^2$

Evolution of temperature and salt structure of Lake Bonney, a chemically stratified Antarctic lake

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Abstract

A resurgence of interest in the ecology of perennially ice-covered lakes in the McMurdo dry valleys has necessitated a review of our knowledge of the physical and chemical properties of these unusual lakes. Salinities in the ice-covered lakes cover a range from freshwater to hypersaline brines. Recent measurements of salt composition and concentrations in Lake Bonney reveal little change below the chemocline since extensive measurements made in 1960–1961, although lake level has risen by approximately 5 m since that time. The rise in lake level has resulted in a thickening of the freshwater layer above the chemocline. Temperature structure has adjusted to the effects of increased lake level on heat transfer processes such as transmission and absorption of solar radiation in the water column.

Questions about how water-column stability affects biology in Lake Bonney have motivated the formulation of a method to compute density from *in situ* measurements of temperature, conductivity and pressure. Owing to high salt concentration and unique ion ratios, we modified the UNESCO Equation of State for seawater to predict density at salinities greater than 42. The modifications merge smoothly with the UNESCO equations at a salinity of 42. At salinities below 42 the UNESCO equations give excellent predictions of density.

Introduction

Recent studies on photo-acclimation of phytoplankton, nutrient cycling, circulation and mixing in Lake Bonney and other permanently ice-covered Antarctic lakes in the McMurdo dry valleys (Priscu *et al.*, 1978, 1988; Lizotte & Priscu, 1992 a,b, 1994; Spigel *et al.*, 1991) have highlighted the need for a re-evaluation of the findings of studies conducted in the 1960s on the physical and chemical properties of the lakes. These properties are also relevant to hypotheses concerning the effects of climate change on the evolution of the lakes (Chinn, 1993).

The dry valley lakes possess unusual thermodynamic properties and provide hydraulically stable environments for the micro-plankton that inhabit them. Salinity in some of the lakes ranges from freshwater just beneath the ice to nearly saturated brines, such as that in the bottom waters in the east lobe of Lake

Bonney (Craig *et al.*, 1974; Priscu, 1995). The chemistry of the salts varies from lake to lake and various hypotheses have been advanced to explain their origin (Burton, 1981; Wilson, 1981). Previous studies have noted the similarity of ionic ratios in seawater to those found in Lake Bonney as evidence for a seawater origin of Lake Bonney salts (Angino *et al.*, 1964; Hendy *et al.*, 1977).

Increasing temperatures with depth over part of the water column often accompany salinity gradients in the dry valleys lakes. In a climate with a mean annual air temperature of -17 °C (Clow *et al.*, 1988), the cause of elevated water temperatures [greater than 6 °C in Lake Bonney (Fig. 2), nearly 25 °C in Lake Vanda (Hoare, 1968)] has attracted considerable interest. The temperatures can be explained by the solar energy that penetrates the relatively transparent ice and water during the 24 h daylight of the austral summer (Shirtcliffe & Benseman, 1964; Shirtcliffe, 1964; Hoare *et al.*, 1964;

Hoare *et al.*, 1965; Hoare, 1968), although enhanced conductive heat fluxes through the bottom sediments have been measured in Lake Vanda by Ragotzkie & Likens (1964). Regardless of the details and variations, it is clear that density stratification caused by temperature and salinity gradients exerts a prominent influence on all aspects of the dynamics of Antarctic lakes. The effects of pressure are small in these lakes because of their relatively shallow depths, although complications arise from the effects of salinity on freezing point and on the temperature of maximum density. Moreover, the range of water temperatures overlaps regions of the temperature-density relation for which density increases and decreases with increasing temperature.

This paper presents recent data on the thermal and chemical structure of Lake Bonney, and compares these findings with measurements made approximately 30 years earlier. Rising lake levels have affected thermal structure, but the chemistry remains largely unaltered. These findings, although of interest in themselves, provide essential background information for biological studies now underway (e.g. Neale & Priscu, 1995).

In addition, in order to expedite calculations of water column stability we developed a temperature-conductivity-density relation for Lake Bonney that involved minor modifications of the UNESCO Equation of State for seawater (hereafter abbreviated UNES; Millero *et al.*, 1980). These changes permit application of UNES to the high salinities found below the halocline in Lake Bonney. Although in principle UNES is applicable only to standard seawater and practical salinities less than 42 (PSS78; Lewis, 1980), we chose it as the basis of our density relation for a number of reasons. In practice, UNES has been successfully applied over a wide range of oceanic, estuarine, lake and laboratory conditions (Chen & Millero, 1977, 1987; Millero *et al.*, 1976), and the use of the UNESCO formulas is so extensive that they are built into the data acquisition software of some commercially available conductivity-temperature-depth instrumentation (e.g., Sea-Bird Electronics, 1989 and subsequent releases). UNES represents the culmination of years of careful experimental work on the effects of temperature and (mainly chloride) salts on density. The formulas account for the effects of pressure on density and of salinity on freezing point and temperature of maximum density. Because of the sensitivity of conductivity-salinity and salinity-density relations to ionic composition (Wilson, 1975), the exact form of the modifications to UNES will vary from lake to lake; this was the case for the east and west basins of Lake Bonney. The basic approach, however, is straightforward and should be widely applicable.

Study sites

Lake Bonney occupies two steep-sided basins, east lobe and west lobe, respectively, in the Taylor Valley, Southern Victoria Land, Antarctica (Fig. 1). In 1989 the east lobe was approximately 4.5 km long, 820 m wide and 36.5 m deep, with a surface area of 3.47 km^2; the west lobe is smaller (1.8 km long, 750 m wide, surface area 1.08 km^2) but deeper (39 m in 1989). The basins lie in a steep valley and are separated by a narrow contraction and sill (approximately 45 m wide and 12 m deep). The lake is bordered to the north by the Asgard Range and to the south by the Kukri Hills; peaks of these ranges extend to over 1800 m. Mountain and cirque glaciers occupy hanging valleys between these peaks and supply meltwater intermittently to the lake during warmer periods in summer. The largest source of meltwater, however, is from the Taylor Glacier, which extends from the polar ice-cap and terminates in the western end of the west lobe of Lake Bonney. Approximately 20 m of the glacier terminus is submerged in the west lobe. During the melt season, streams can be seen and heard issuing directly from the Taylor Glacier into the lake as well as flowing alongside the glacier snout into the lake. Lake Bonney has no surface outlet; water loss occurs mainly as ablation from the ice surface (McKay *et al.*, 1985). The hydrology of Lake Bonney has been described in detail by Chinn (1993) and Weand *et al.* (1977) and the geology by Hendy *et al.* (1977).

Water sampling, and temperatures and conductivity measurements presented in this paper were carried out at central sites in the east lobe (E30, Fig. 1) and west lobe of Lake Bonney (W20, Fig. 1). The field station was located on the south shore of the east lobe, near the east lobe sampling station. For reasons of accessibility, sampling of the east lobe was more intense than the west lobe.

Methods

Temperature (stable accuracy ± 0.1 °C) profiles were measured at approximately 1 m depth intervals with a Martek Mark 7 CTD. One-liter water samples were obtained with a 2-liter Niskin Bottle at approximately
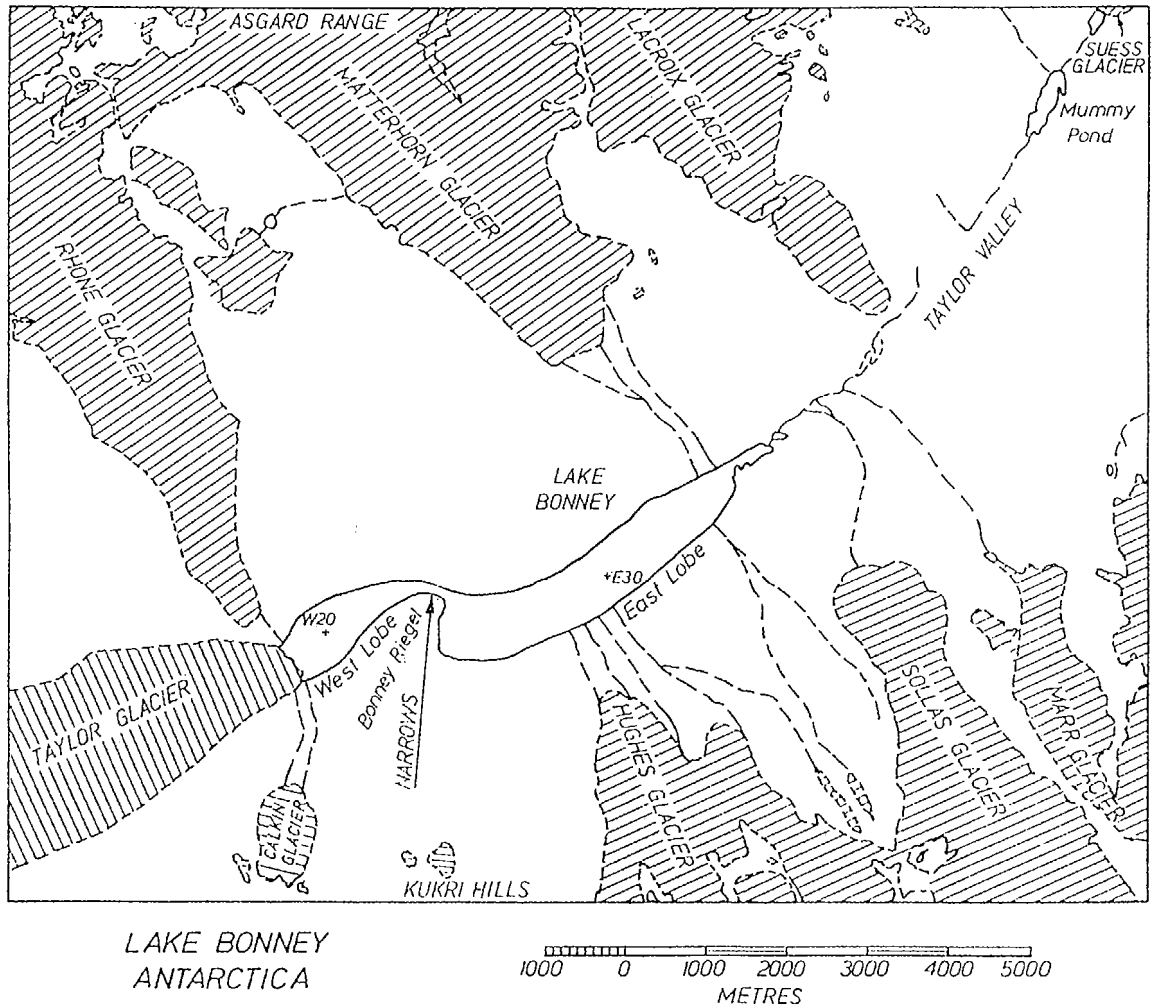
Fig. 1. Site map showing location of sampling stations, meltwater inflow channels, and various glaciers influencing the hydrology of Lake Bonney.

1 m intervals in the east lobe (29 November 1989) and 5 m intervals in the west lobe (14 January 1990). (Unless noted otherwise, all water depths are quoted relative to the free water surface, i.e., the level to which water would rise in a hole drilled through the ice; in Lake Bonney this is approximately 0.3 m to 0.4 m below the ice surface. The liquid water level is felt to be the most stable reference level in view of the considerable variation in ice thickness which occurs over the lake and throughout the season). The samples were stored in acid washed high-density polyethylene bottles and shipped to Christchurch, New Zealand for chemical and physical analysis.

Electrical conductivity was measured with a Radiometer CDM83 conductivity meter using a 11 mm diamter CDC 344 immersion cell. The cell was calibrated with 5 standard salt solutions (3 of NaCl, 2 of KCl) over a wide range of concentrations from 0.05% to 19% by weight; measured values were adjusted for temperature difference before comparison with the standard values in tables (Dauphinee, 1980 and Radiometer CDM83 operation manual). One of the KCl solutions was made up to the specification for the reference conductivity of standard seawater at salinity $S = 35$, temperature $t = 15$ °C and pressure $p = 0$ (concentration 3.24356%; Lewis, 1980). The differ-
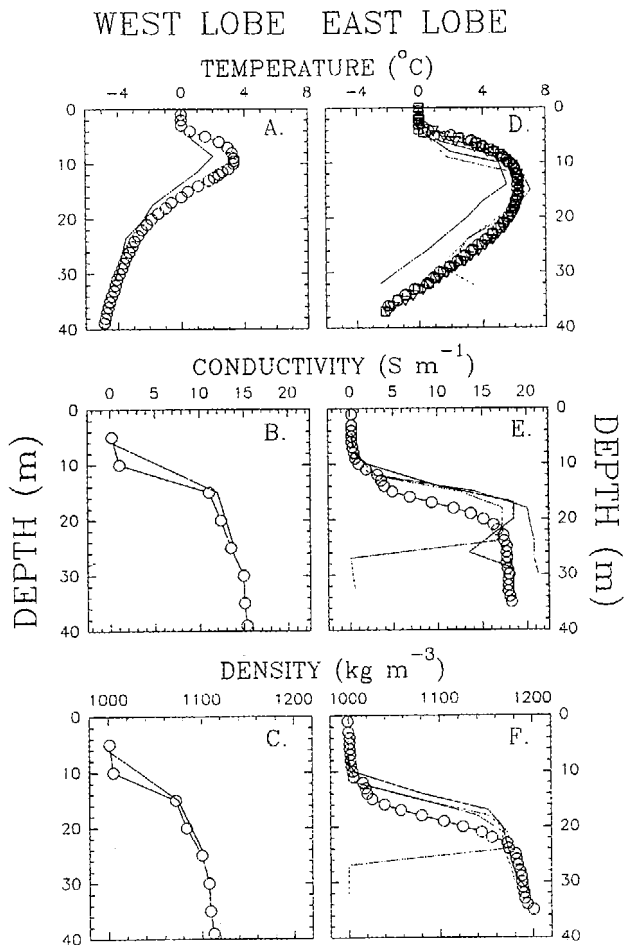
WEST LOBE EAST LOBE

Fig. 2. Temperature, conductivity (at 25 °C) and density profiles. West lobe (panels A, B, C): solid lines – data from Angino *et al.* (1964), 23 Oct. 1961, (their Fig. 3 and Table 3); circles – this study, temperatures measured 28 Nov. 1989, density (at 1.5 °C) and conductivity from samples collected 14 Jan. 1990. East lobe (panels D, E, F): solid lines – Angino *et al.* (1964), 3 Nov. 1961, hole 4; short dash – Angino *et al.* (1964), 16 Dec. 1961, hole 5; dash-dot-dot – Angino *et al.* (1964), 12 Jan. 1962, hole 3. Circles – this study, temperatures measured 29 Nov. 1989, density (at 1.5 °C) and conductivity from samples collected 29 Nov. 1989; squares, triangles – temperatures measured 15 Nov. 1989 and 10 Jan. 1990, respectively. Note that Angino *et al.*'s (1964) profiles are taken directly from their Table 3 with no adjustment for ice-thickness above the free water surface. Including this adjustment would result in an upward shift of all Angino *et al.*'s (1964) profiles by approximately 0.3 m.

ences between measured and predicted conductivities ranged from 2% to 6.7%, this latter value corresponding to the high concentratin (19%) solution; most of the differences were within 2% to 3%. For purposes of cal-

culation using UNES and the UNESCO conductivity-salinity relationship (Lewis, 1980; Fofonoff & Millard, 1983), the value of absolute conductivity for the reference seawater and KCl solutions was taken as 4.29140 S m^{-1} (Culkin & Smith, 1980).

Two sets of conductivity readings were made on each of the Lake Bonney samples, one in the temperature range 0.8–2.5 °C (referred to later as 1.5 °C samples), and the other in the range 24.8–25.9 °C (referred to later as 25 °C samples). This allowed salinities as calculated by the UNESCO salinity algorithm to be compared between each range, any bad measurements to be discarded, and an average salinity to be calculated with which to proceed. Because of the practical difficulties inherent in directly measuring salinity as the mass of salt per unit mass of a solution containing chloride salts (Lewis, 1980; Wilson, 1975), such direct measurements were not made in this study and where the term 'salinity' is used it is in the sense of 'practical salinity', i.e. as calculated from temperature and conductivity measurements by the UNESCO formulas (Lewis, 1980). Values of salinity as presented here are therefore only meaningful in a comparative sense, and are used only as a necessary intermediate step in calculating density from temperature and conductivity.

Densities were measured using an Anton-Paar vibrating tube digital density meter (DMA 60 processing unit, DMA 401 measuring cell). Temperature within the measuring cell was maintained at 1.5 °C (± 0.1 °C, as measured by a calibrated thermistor placed inside the cooling jacket) by pumping water from an ice-water bath through the jacket that surrounds the vibrating tube. The possible variation in temperature results in a possible error introduced into the density calculations of ± 0.0037 kg m^{-3}. Additional errors of the same order of magnitude can be ascribed to the density measurements used in calculating the two calibration coefficients used in the density calculations, so that the total error in measured densities is probably on the order of ± 0.007 kg m^{-3}.

Chemical analyses to determine the concentration of major ions in the samples were conducted for two reasons: firstly, to compare the ionic ratios of Lake Bonney water with those of seawater, and secondly, to compare concentrations with results obtained more than 26 years ago by Angino *et al.* (1964). The chemcal analyses were carried out by the Chemistry Division of the New Zealand Department of Scientific and Industrial Research at their Ilam Research Center based on standard ASTM methods; where necessary, samples were diluted with milli-Q (ASTM Type 1) water. Con-
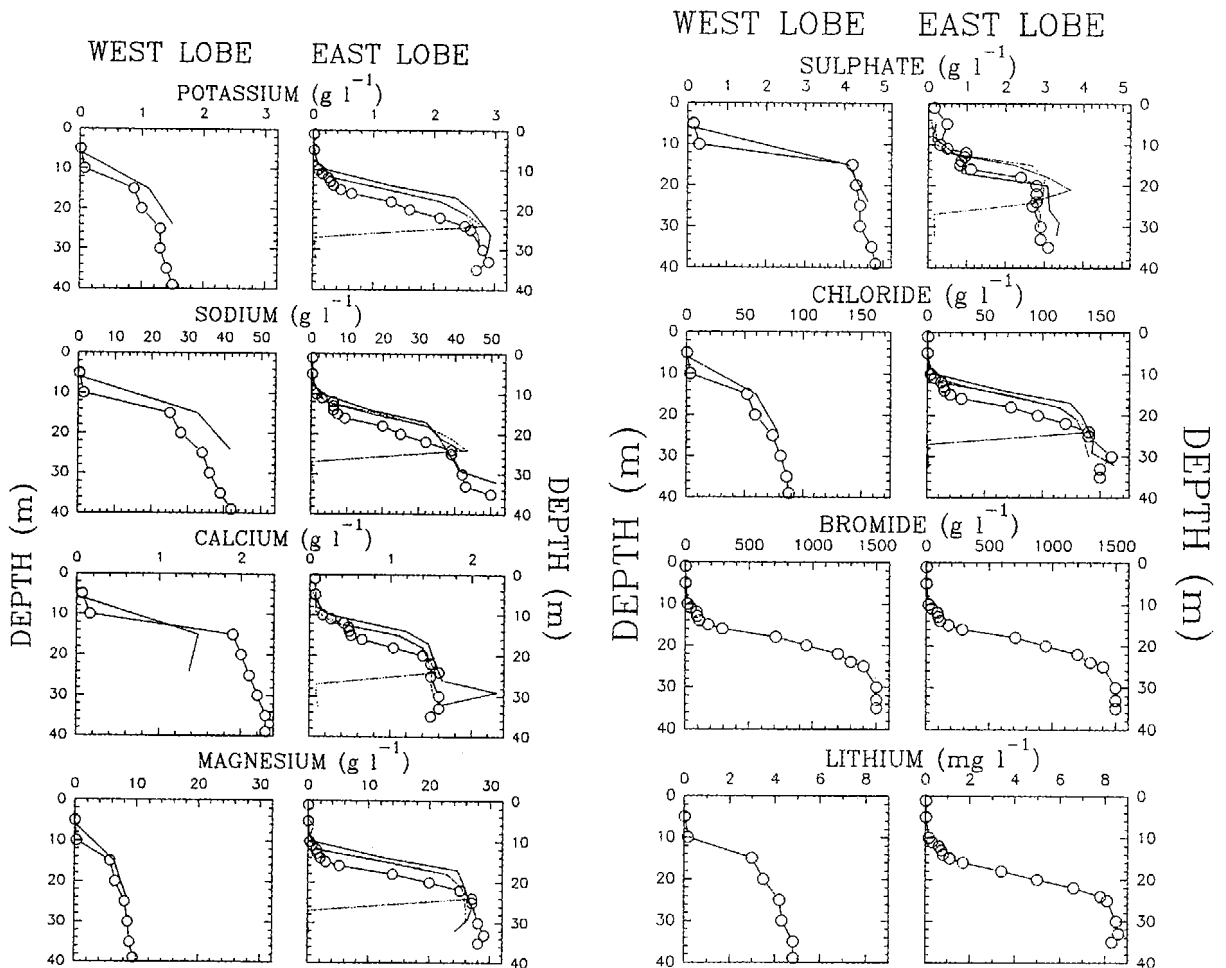
Fig. 3. Cation and anion profiles reported by various authors for Lake Bonney. Symbols and lines as for Fig. 2.

centrations of chloride, bromide, sulphate, lithium, sodium and potassium were measured with ion chromatography; those of calcium and magnesium were measured with flame atomic absorption. Accuracies for Cl^-, Na^+, K^+, Ca^{2+} and Mg^{2+} were estimated to $\pm$ 4%; Br^- and Li^+ to 5%, and SO_4^{2-} to 8%. All of the west lobe samples were analyzed and 17 of the east lobe samples were analyzed (this was felt to be sufficient to resolve the main gradients in the water column).

Results

Comparison with previous studies: water depth, stratification, composition and ionic ratios

Comparison of present hydrographic features in Lake Bonney with previous studies is not completely straightforward because of differences in analytical methods, possible calibration errors for thermometers and the uncertainty in specification of the datum from which depth was measured (e.g., top of ice, free water surface, or bottom of ice). Nevertheless, two general trends emerge between the investigations of the early 1960's and the present: (i) lake level has increased and continues to increases; (ii) maximum temperature in the east lobe has decreased while that in the west lobe as increased. Information relating to temperatures and depths is summarized in Table 1.

Table 1. Comparison of ice-thickness and temperature-depth measurements in Lake Bonney.

Max depth[1] (m)	Ice thick[2] (m)	Min temp[3] (°C)	Max temp (°C)	Depth of max temp[1] (°C)	Year	Ref
East Lobe						
37.0[4]	3,3.75	−2.0	6.3	14.5	1989–1990	This study
32.5 (32.9–0.4)[1]	4.5	−2.5	7.0	14.6 (15–0.4)[1]	1961–1962	Angino *et al.* (1964)[5]
31.85 (32.15–0.3)[1]	3.5,4.3	−2.8	7.9	12.7 (13–0.3)[1]	1962–1963	Ragotzkie & Likens (1964)
31.7 (32.0–0.3)[1]	3.05	−2.65	7.0	13.4 (13.7–0.3)[1]	Dec 1963	Hoare *et al.* (1964)
31.5	3.5±0.2	−2.0	7.5	13	Jan 1963	Shirtcliffe & Benseman (1964)
West Lobe						
38.8	3,3.75	−5.0	3.1	9.5	1989–1990	This study
32.5 (32.9–0.4)[1]	4.5	−4.3	2.0	8.5 (8.9–0.4)[1]	1961–1962	Angino *et al.* (1964)[6]
33.2 (33.5–0.3)[1]	3.05	−5.35	1.35	7.3 (7.6–0.3)[1]	Dec 1963	Hoare *et al.* (1964)

[1] All depths are relative to free-water surface (see text); adjustments to authors' data for ice thickness (Eq. 1) shown in parentheses.

[2] Ice thicknesses for this study (and presumably for the others) relate only to smooth areas of ice. The variation in overall ice thickness, especially over rougher patches and in late summer, can be much greater than ranges shown here.

[3] All minimum temperatures were measured at the bottom.

[4] In this study, the deepest point of the east lobe was found to be at the western end of the basin, not at the main sampling station (depth = 36.5 m).

[5] Maximum temperature at Angino *et al.*'s hole 5, 16 Dec 1961; minimum temperature at Angino *et al.*'s hole 4, 3 Nov 1961.

[6] Values inferred from Angino *et al.*'s Fig. 3 for hole 23.

An estimate for ice thickness above the free water surface can be made from a buoyancy balance for the ice cover:

$$h_a/h = (\rho_w - \rho_i)/\rho_w \approx 0.0821, \qquad (1)$$

where h_a = ice thickness above the water surface, h = total ice thickness, ρ_w = density of water displaced by the ice ($\approx$ 999 kg m^{-3}), and ρ_i = density of the ice ($\approx$ 917 kg m^{-3}). Values for h_a calculated in this way are between 0.25 m and 0.37 m for the ice thicknesses noted in Table 1, and are in agreement with our observations. The greatest water depth we measured in the east lobe was 37.0 m, at the western end of the east lobe. Comparison with maximum depths measured by previous workers indicates an increase in water depth of between 4.5 m (Angino *et al.*, 1964) to 5.5 m (Shirtcliffe & Benseman, 1964). This is consistent with Chinn's data (Chinn, 1993), that show a 5.0 m increase in Lake Bonney water level from 1963–1990.

The most comprehensive published set of physical and chemical measurements relevant to our study are those of Angino *et al.* (1964), made on Lake Bonney during the summer October 1961–January 1962. Figure 2 shows temperature, conductivity (referenced to 25 °C as in Angino *et al.*, 1964) and density profiles from the present study compared with those of Angino *et al.* (1964). Profiles for chemical species are illustrated in Fig. 3, with the values for this study summarized in Table 2.

A peculiar feature of Angino *et al.*'s (1964) results was the temperature rise and salinity and conductivity drop measured at their hole 3 on 12 January 1962 (Figs 2, 3). This site was located midway between the center and eastern end of the lake; Angino *et al.* (1964) postulated possible influx of geothermal water

Table 2. Ion concentration (mg l^{-1}) in the east and west lobes of Lake Bonney. Samples were collected on 29 November 1989 and 14 January 1990, respectively. Depth is in meters.

Depth	Cl$^-$	Br$^-$	SO$_4^{2-}$	Li$^+$	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}
East Lobe								
1	490	2.3	150	0.03	250	15	67	48
5	480	2.3	160	0.03	250	15	73	41
10	3200	20	300	0.16	1500	86	160	310
11	6400	43	490	0.31	3000	150	260	670
12	12000	89	980	0.61	6200	250	420	1400
13	14000	95	950	0.72	6200	290	480	1600
14	15000	110	860	0.79	6200	340	490	2000
15	20000	180	820	1.10	7300	460	510	2900
16	30000	290	1100	1.70	9400	640	650	5200
18	73000	710	2400	3.40	20000	1300	1040	14000
20	96000	950	2800	5.00	25000	1600	1400	20000
22	120000	1200	2800	6.60	32000	2100	1500	25000
24	140000	1300	2800	7.80	39000	2500	1600	27000
25	140000	1400	2700	8.10	39000	2600	1500	27000
30	160000	1500	2900	8.50	42000	2800	1600	28000
33	150000	1500	2900	8.60	43000	2900	1600	29000
35	150000	1500	3100	8.30	50000	2700	1500	28000
West Lobe								
5	500	2	150	0.03	250	14	65	38
10	3200	17	300	0.17	1500	76	160	270
15	52000	250	4200	3.00	25000	870	1900	5700
20	59000	290	4300	3.50	28000	1000	2000	6500
25	74000	360	4400	4.20	34000	1300	2100	8100
30	81000	380	4400	4.30	36000	1300	2200	8600
35	86000	400	4700	4.80	39000	1400	2300	8900
39	88000	400	4800	4.80	42000	1500	2300	9500
Seawater concentration @ $S = 35$:[1]								
	19833	68.97	2779	0.18	11037	409	422	1322

[1] From Wilson (1975) and Brewer (1975). Conversions from g kg^{-1} to mg l^{-1} were made assuming a density of seawater = 1024.763 kg m^{-1} at salinity $S = 35$ and temperature $t = 20$ °C.

to explain the heat and relative freshness of their bottom water samples there. We have observed no such trend, either in measurements presented here (made only in the center of the lake) or in CTD measurements made along an east-west transect through the lake (Spigel *et al.*, 1991). The temperatures measured at E30 changed very little over the course of the summer, as shown by the superposition of three profiles (Fig. 2). We observed no variation in water column or bottom water temperatures either throughout the season or with position (transects measured 1990–1991) in the east lobe as observed by Angino *et al.* (1964; their

Fig. 3) or as discussed by Craig *et al.* (1974). Minimum and maximum temperatures remained at −2.0 °C at the bottom (36.5 m), and 6.3 °C at 14.5 m. These values are consistent with those measured in 1990–1991 with a Sea Bird SBE-25 CTD (Spigel *et al.*, 1991) but differ in some respects from those of previous investigators (Table 1).

Differences are also apparent in the ion-concentration profiles (Fig. 3), although these appear to be due mainly to an apparent downward shift in the salt profiles over time owing to rising lake level from input of relatively fresh melt-water. The total shift is on

the order of 4 to 5 m, when adjustment is made for the thickness of ice above the free water surface (see note at end of caption for Fig. 2; adjustments made to other workers' measured depths are given in Table 1). Ionic concentrations both above and below the chemocline measured in our study do not appear to differ significantly from those of Angino *et al.* (1964) with the exception of data from their hole 3 (Fig. 3). Water temperatures are not nearly as conservative as salt concentrations, however, being controlled by solar heating, conduction in the water column, heat transfer through the ice and heat loss to the atmosphere. Hence the apparent downward shift characteristic of the conductivity, density and all of the ion-concentration profiles does not appear in the temperature profiles. Although the main features of the temperature profiles have been preserved since 1961–1962, changes have occurred in response to increased water depth, meteorological conditions, inflows and possible geothermal inputs. Mathematical models to quantify the heat balance of the water column and the ice-cover have been discussed by Hoare *et al.* (1964), Shirtcliffe & Benseman (1964), Shirtcliffe (1964) and McKay *et al.* (1985); the details are beyond the scope of this paper.

Ion concentration and ion ratios (Tables 2, 3 and Fig. 3) show that the deeper waters of the east and west lobes, i.e., below the 12.5 m depth of the sill separating the two basins, are chemically distinct, while above the level of the sill, similarity in composition indicates that horizontal exchanges do occur between the two basins. The west lobe is colder than the east lobe. The reasons for this temperature difference are not clear; differences between lobes in amounts and temperatures of meltwater inflows and in shading by surrounding peaks are possible causes.

Previous authors (Angino *et al.*, 1964; Hendy *et al.*, 1977) have remarked on the possibility of a seawater origin for Lake Bonney. Evidence for this is usually cited in terms of the ionic ratios for the dissolved salts, some of which are listed for Lake Bonney in Table 3, together with the ratios for standard seawater at a salinity $S = 35$. The seawater ratios were computed from the concentrations given by Wilson (1975) and Brewer (1975), listed at the bottom of Table 2; salinities corresponding to $S = 35$ occur in the east lobe between 15 and 16 m, and in the west lobe between 10 and 15 m (Fig. 4). The deeper-water west lobe ratios resemble those of seawater much more closely than those of the east lobe. Variation from seawater values have been attributed by Hendy *et al.* (1977) to the addition of salts from leaching of the Taylor Vallye soils by melt-
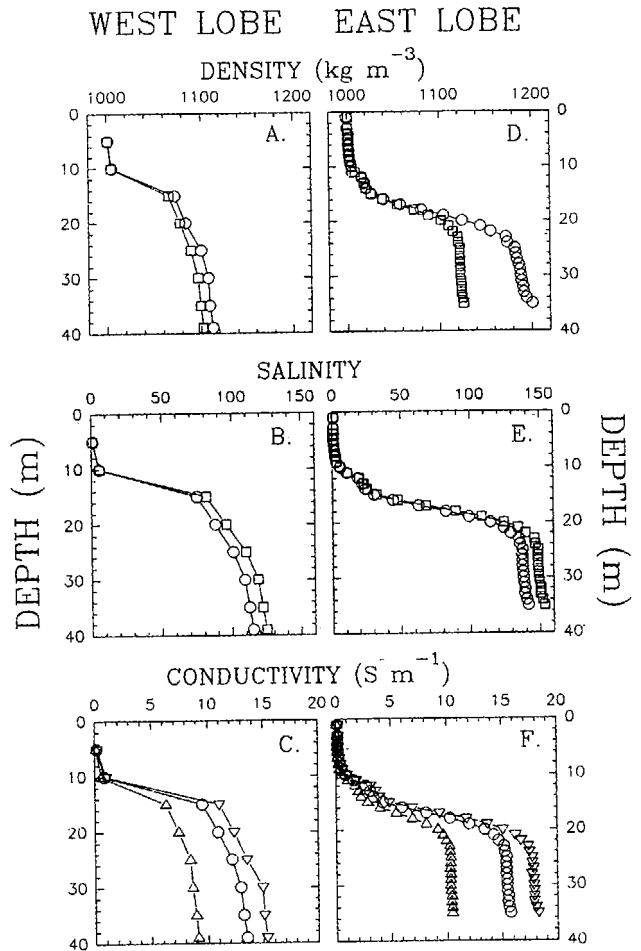

Fig. 4. Density profiles: squares – densities predicted from UNESCO equation of state assuming a temperature of 1.5 °C and salinity as the average practical salinity computed from UNESCO equations from conductivities measured at approximately 1.5 °C and 25 °C (see Methods sections); circles – densities measured at 1.5 °C with Anton-Paar density meter. Salinity profiles: squares – average of practical salinities computed with UNESCO equations from conductivities measured at approximately 1.5 °C and 25 °C; circles – salinities (as grams salt/kilogram solution) computed from conductivity and temperature using Hewitt's (1960) data for NaCl. Conductivities: triangles – conductivities (adjusted to 1.5 °C) measured using Radiometer conductivity meter with samples at approximately 1.5 °C; inverted triangles – conductivities (adjusted to 25 °C) from samples at approximately 25 °C; circles – average of the 1.5 °C and 25 °C conductivities after both had been adjusted to 18 °C. Panels A, B, C, refer to west lobe data; D, E, F refer to east lobe data.

water, and the loss of certain species by precipitation as a result of concentration by evaporation and freezing, particularly in the east lobe.

Table 3. Ionic ratios (g:g) from samples collected on 28 November 1989 (east lobe) and 14 January 1990 (west lobe) of Lake Bonney. All ratios are from concentrations presented in Table 2. Depth is in meters.

Depth	$\dfrac{Br^-}{Cl^-}$	$\dfrac{Na^+}{Cl^-}$	$\dfrac{K^+}{Na^+}$	$\dfrac{Na^+}{Mg^{2+}}$	$\dfrac{Na^+}{Ca^{2+}}$	$\dfrac{K^+}{Ca^{2+}}$	$\dfrac{K^+}{Mg^{2+}}$	$\dfrac{SO_4^{2-}}{Cl^-}$	$\dfrac{Mg^{2+}}{Ca^{2+}}$
East Lobe									
1	0.00469	0.510	0.0600	5.21	3.73	0.224	0.3120	0.3060	0.716
5	0.00479	0.521	0.0600	6.10	3.42	0.205	0.3660	0.3330	0.562
10	0.00625	0.469	0.0573	4.84	9.38	0.538	0.2770	0.0938	1.940
11	0.00672	0.469	0.0500	4.48	11.50	0.577	0.2240	0.0766	2.580
12	0.00742	0.517	0.0403	4.43	14.80	0.595	0.1780	0.0817	3.330
13	0.00679	0.443	0.0468	3.88	12.90	0.604	0.1810	0.0678	3.330
14	0.00733	0.413	0.0548	3.10	12.60	0.694	0.1700	0.0573	4.080
15	0.00900	0.365	0.0630	2.52	14.30	0.902	0.1590	0.0410	5.690
16	0.00967	0.313	0.0681	1.81	14.50	0.985	0.1230	0.0367	8.000
18	0.00973	0.274	0.0650	1.43	19.20	1.250	0.0928	0.0329	13.500
20	0.00990	0.260	0.0640	1.25	17.80	1.140	0.0800	0.2920	14.300
22	0.01000	0.267	0.0656	1.28	21.30	1.400	0.0840	0.2330	16.700
24	0.00929	0.278	0.0641	1.44	24.40	1.560	0.0926	0.0200	16.900
25	0.01000	0.278	0.0667	1.44	26.00	1.730	0.9630	0.0193	18.000
30	0.00938	0.262	0.0667	1.50	26.20	1.750	0.1000	0.0181	17.500
33	0.01000	0.287	0.0674	1.48	26.90	1.810	0.1000	0.0193	18.100
35	0.01000	0.333	0.0540	1.78	33.30	1.800	0.0964	0.0207	18.700
West Lobe									
5	0.00400	0.500	0.0560	6.58	3.85	0.215	0.3680	0.3000	0.585
10	0.00531	0.469	0.0507	5.56	9.38	0.475	0.2810	0.0938	1.690
15	0.00481	0.481	0.0384	4.38	13.20	0.458	0.1530	0.0808	3.000
20	0.00492	0.474	0.0357	4.31	14.00	0.500	0.1540	0.0729	3.250
25	0.00486	0.459	0.0382	4.20	16.20	0.619	0.1600	0.0594	3.860
30	0.00469	0.444	0.0361	4.19	16.40	0.591	0.1510	0.0543	3.910
35	0.00465	0.453	0.0359	4.38	17.00	0.609	0.1570	0.0546	3.870
39	0.00454	0.477	0.0357	4.42	18.30	0.652	0.1580	0.0545	4.150
Seawater ratios @ $S = 35$									
	0.00348	0.556	0.0371	8.35	26.13	0.968	0.3090	0.1400	3.130

Conductivity–salinity–density relations

Use of the UNESCO equations (see appendix for summary) to predict density from data for conductivity (C), temperature (t) and pressure (p) involves two separate steps: first, calculation of salinity (S) from values of C, t, p using the 1978 Practical Salinity Scale (Eq. A1), and second, the calculation of density (ρ_{UN}) from the equation of state ($\equiv$ $p(S,t,p)$ from Eq. A11, or $\rho(S,t,0)$ from Eq. A9 for atmospheric pressure). The salinity calculation is valid for $2 \leq S \leq 42$, $-2 \leq t \leq 35$ and pressures well in excess of 1000 decibars; the density calculation is valid for $0 \leq S \leq 42$, $-2 \leq t \leq 35$ and $0 \leq p \leq 10000$ decibars.

Salinities for most of the work in and below the chemocline in both basins of Lake Bonney fall outside the ranges specified above. Application of the UNESCO relations to the Lake Bonney samples yields excellent results for salinities less than 42 but results in serious underestimation of density for larger salinities. Figure 4 summarizes the results of applying the UNESCO relations to the entire water column, regardless of the salinity and temperature restrictions. Measured conductivities are also shown, for the 1.5 °C and 25 °C measurements, as well as the average of

both measurements when adjusted to 18 °C. All adjustments to conductivity for temperature are based on the tables and equations of Hewitt (1960). Hewitt's data are for NaCl solutions only but are valid for concentrations that range from those of very dilute solutions to saturation. Comparison in Fig. 4 of practical salinities predicted by the UNESCO equations, with salinity as parts per thousand by weight (grams NaCl per kilogram of solution) from Hewitt's data, shows that there is negligible difference for salinities less than 42, while at higher salinities the UNESCO values are slightly higher. Hence, it appears that application of the UNESCO conductivity-salinity relation beyond its proposed range results in smaller relative errors than for the density-salinity relation (compare the sets of profiles for density and salinity in Fig. 4). This was taken into account when developing a strategy for modifying the UNESCO relations to extend their range of applicability.

The criteria we used to modify the UNESCO relations were two-fold: that the modifications be as simple and involve as few extra parameters as possible, and that the results should merge smoothly with the unmodified UNESCO results as salinity approaches 42. In keeping with these criteria, and in view of the narrow ranges of temperature and pressure encountered in Lake Bonney, no modifications were made for pressure or temperature, it being felt that, over the small temperature range observed in Lake Bonney, interactions between salinity and temperature and pressure represented higher-order effects which in any event could not be resolved with the experimental data available. Further, since the density-salinity relation appeared to be the source of the largest errors, and because no simple methods are routinely available in the field to measure salinity in a way that could be related directly to the UNESCO practical salinity scale, it was felt that modifications should be made only to the density-salinity relation, with the salinity-conductivity relation left unaltered. Finally, by fitting a curve to the deviations from the UNESCO density, versus the difference in salinity from 42 (S − 42 for S > 42), the condition for a smooth transition to the UNESCO values can be satisfied. Our approach differs from that developed for saline lakes in the Vestfold Hills, Antarctica (Gibson et al., 1990, for example). Gibson et al. (1990) derived sets of separate temperature-density, temperature-conductivity and conductivity-density relations, over a wide range of temperatures; their equations are unrelated to the UNESCO formulas.
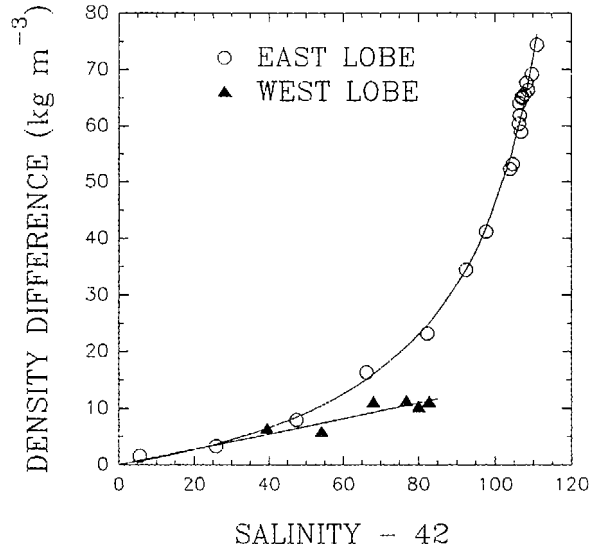

Fig. 5. Density difference (between measured density and density predicted by UNES) versus salinity excess (salinity minus 42). Salinity is that predicted by the UNESCO practical salinity equations as a function of conductivity and temperature; each value represents the average for conductivities measured at two temperatures: approximately 1.5 °C and 25 °C, as explained in the text. Circles are for east lobe data, solid triangles for west lobe data. The solid curve and line represent Eq. 2 and 3, respectively.

Figure 5 shows plots of density differences versus salinity differences, together with the fitted curves for both east and west lobes. The curve-fits were done using a nonlinear least-squares (Marquardt-Levenberg) algorithm. Several options were tried for the east lobe data before settling on the version shown in Fig. 5. The equations and statistics for the curves are

East Lobe:

$$\rho - \rho_{UN} = a(S - 42)/[b - (S - 42)], \quad S > 42, \quad (2)$$

where ρ = density (kg m^{-3}), ρ_{UN} = density (kg m^{-3}) predicted by unmodified UNESCO equations at specified S, t, p (see appendix), $a = 133.36$, $b = 15.299$, and S = practical salinity predicted by the UNESCO equations for specified C, t, p. The statistics for the curve fit were: number of points = 20, standard errors $s_a = 1.605$ and $s_b = 0.9410$, and square root of the sum of squares of the residuals = 7.719, giving an overall standard error of the curve fit of 1.819 kg m^{-3}.

West Lobe:

$$\rho - \rho_{UN} = a(S - 42), \quad S > 42, \quad (3)$$

WEST LOBE   EAST LOBE

DENSITY (kg m^{-3})
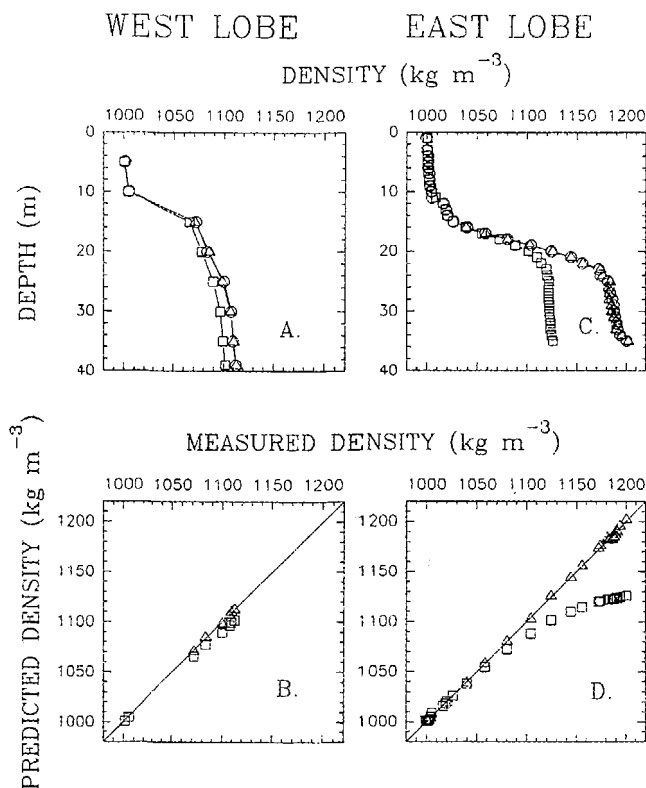
MEASURED DENSITY (kg m^{-3})

Fig. 6. Comparison of predicted and measured densities. For the depth profiles, circles give measured densities, squares the densities predicted by the (unmodified) UNES, and triangles the densities predicted by the UNES with the corrections of Eq. 2 and 3 for salinities $S > 42$. For the graphs of measured vs. predicted densities, the squares are for the unmodified UNES values; the triangles include the corrections from Eq. 2 and 3.

The complete procedure for calculating density for a sample with specified C, t, p would be to first calculate salinity S and then density ρ_{UN} from the (unmodified) UNESCO equations (see appendix). Then, for samples with $S > 42$, a correction can be made to the density using Eq. 2 or 3.

Discussion

Measurements from samples taken in late November 1989 and early January 1990 show that the concentrations of salts in both the east and west lobes of Lake Bonney have changed very little since the work of Angino *et al.* (1964) in 1961–1962. An apparent downward shift in depth of the salt profiles can be explained by increased lake levels; the rise in lake level has been caused by addition of relatively fresh meltwater entering the lake just under the ice-cover, leaving the saltier, deeper water undisturbed. Temperature profiles differ among various investigations conducted in the early 1960's, but the main structural features of the temperature profiles have been preserved since then. Because temperature is far less conservative than salt, the temperature profiles have adjusted to the increased lake levels and do not show the apparent downward shift characteristic of the salt profiles. Aside from this apparent downward shift, profiles of dissolved salts do not appear to have changed significantly. This is consistent with the very long time-scale associated with diffusion, H^2/k_s where H = water depth and k_s = molecular diffusivity of salt. Unlike temperature, (which is affected by solar radiation) diffusion is probably the main process affecting salt concentrations. Turbulence is nonexistent within and below the chemocline (unpublished microstructure data; Spigel *et al.*, 1991) and meltwater inflows are relatively fresh. For $H = 40$ m and $k_s = 10^{-9}$ m^2 s^{-1}, the diffusion time is greater than 50,000 years. Ionic ratios still indicate a possible seawater origin for Lake Bonney.

Our modifications to the UNESCO equation of state to compute density when salinity exceeds 42 have standard errors on the order of 1 to 2 kg m^{-3}. These may seem large in terms of absolute accuracy, but inspection of Fig. 6 shows that relative densities are well represented. The main purpose of the equations we derived was to compute water-column stability, a calculation based on relative density differences. Owing to a unique ionic composition, our modifications to the UNESCO equation of state are specific to the east and west lobes of Lake Bonney. Although derivation of

where ρ, ρ_{UN} and S are as defined for Eq. 2, and $a = 0.13696$. The statistics of the fit were: number of points = 6, $s_a = 0.007277$, square root of sum of squares of residuals = 2.735, and overall standard error of the fit = 1.223 kg m^{-3}.

Sources of the residuals include errors in measured densities, conductivities and temperatures, as discussed earlier. The adequacy of the choices of shapes of the curves can best be assessed with reference to Fig. 6, which shows comparisons of predicted versus measured densities; the results of the unmodified UNESCO result are also shown. The shapes of the curves appear satisfactory and the simple modifications represented by Eq. 2 and 3 clearly provide and improved fit to the measured densities.

the equations is straightforward, application to other Antarctic lakes will require that similar measurements and curve-fitting be done for those lakes.

Acknowledgements

Appendix

UNESCO conductivity-salinity-density relations (Lewis, 1980; Millero & Poisson, 1981; Millero et al., 1980; Fofonoff & Millard, 1983).

Salinity

Practical salinity S is defined in terms of conductivity ratio as

$$S = a_0 + a_1 R_t^{1/2} + a_2 R_t + a_3 R_t^{3/2} + a_4 R_t^2$$
$$+ a_5 R_t^{5/2} + \frac{(t-15)}{1+k(t-15)}(b_0 + b_1 R_t^{1/2}$$
$$+ b_2 R_t + b_3 T_t^{3/2} b_4 T_t^2 + b_5 R_t^{5/2}) \qquad (A1)$$

where the a_i, b_i and k are constants where values are listed in Table A1, t = temperature in °C, and R_t is the ratio of conductivity of water at salinity S, temperature t, and gauge pressure $p = 0$ (atmospheric pressure) to that of seawater at a salinity of 35, temperature t and atmospheric pressure:

$$R_t = C(S,t,0)/C(35,t,0). \qquad (A2)$$

R_t is the conductivity ratio routinely measured by oceanographic salinometers. R_t is related to R, the ratio of conductivity at salinity S, temperature t and pressure p to conductivity of seawater with salinity 35, temperature 15 °C and atmospheric pressure, by

$$R_t = R/(R_p r_t), \qquad (A3)$$

$$R = C(S,t,p)/C(35,15,0), \qquad (A4)$$

$$r_t = C(35,t,0)/C(35,15,0), \qquad (A5)$$

$$R_p = C(S,t,p)/C(S,t,0) \qquad (A6)$$

Polynomials for r_t and R_p are given in terms of t, p as

$$r_t = C_0 + C_1 t + C_2 t^2 + C_3 t^3 + C_4 t^4 \qquad (A7)$$

$$R_p = 1 + \frac{p(e_1 + e_2 p + e_3 p^2)}{1 + d_1 t + d_2 t^2 + (d_3 + d_4 t)R} \qquad (A8)$$

for pressure p in decibars.

Values of the coefficients in Eq. A1, A7, and A8 are given in Table A1.

To calculate the salinity for a water sample with *absolute* conductivity $C(S,t,p)$ using these formulas, one first needs to compute R, the conductivity ratio to that of standard seawater at salinity 35, temperature 15 °C and atmospheric pressure. For the purposes of this study the value of this reference conductivity was taken as $C(35,15,0) = 4.2914\ S$ m^{-1} (Caulkin & Smith, 1980). Then, given $R = C(S,t,p)/C(35,10,0)$ one can compute R_t from Eq. A3 (with r_t and R_p computed from Eq. A7 and A8) and then S from Eq. A1.

The range of validity of these equations is $2 < S < 42$ and $-2\ °C < t < 35\ °C$.

Density

The density (ρ, kg m^{-3}) of seawater at one standard atmosphere ($p = 0$) is computed from the practical salinity (S) and the temperature (t, °C) with the following equation:

$$\rho(S,t,0) = \rho_w + (8.24493 \times 10^{-1}$$
$$- 4.0899 \times 10^{-3} t$$
$$+ 7.6438 \times 10^{-5} t^2$$
$$- 8.2467 \times 10^{-7} t^3$$
$$+ 5.3875 \times 10^{-9} t^4)S$$
$$+ (-5.72466 \times 10^{-3}$$
$$+ 1.0227 \times 10^{-4} t$$
$$- 1.6546 \times 10^{-6} t^2)S^{3/2}$$
$$+ 4.8314 \times 10^{-4} S^2 \qquad (A9)$$

where ρ_w, the density of pure water reference, is given by

$$\rho_w = 999.842594 + 6.793952 \times 10^{-2} t$$

Table A1. Coefficients in conductivity-salinity equations.

i	a_i	b_i	c_i	d_i	e_i
0	+ 0.0080	+0.0005	0.6766097	--	--
1	− 0.1692	−0.0056	$+2.005460 \times 10^{-2}$	$+3.426 \times 10^{-2}$	$+2.070 \times 10^{-5}$
2	+25.3851	−0.0066	$+1.104259 \times 10^{-4}$	$+4.464 \times 10^{-4}$	-6.370×10^{-10}
3	+14.0941	−0.0375	-6.969800×10^{-7}	$+4.215 \times 10^{-1}$	$+3.989 \times 10^{-15}$
4	− 0.0261	+0.0636	$+1.003100 \times 10^{-9}$	-3.107×10^{-3}	--
5	+ 2.7081	−0.0144	--	--	--

$\Sigma a_i = 35.0000 \qquad \Sigma b_i = 0.0000 \qquad k = +0.0162$

$$-\ 9.095290 \times 10^{-3} t^2$$
$$+\ 1.001685 \times 10^{-4} t^3$$
$$-\ 1.120083 \times 10^{-6} t^4$$
$$+\ 6.536332 \times 10^{-9} t^5 \qquad \text{(A10)}$$

For pressure greater than one atmosphere, the high pressure modifications to the equation of state are (note that *pressure p is in bars* for the following equations, *not decibars as in Eq. A1–A8*):

$$\rho(S, t, p) = \frac{\rho(S, t, 0)}{1 - p/K(S, t, p)} \qquad \text{(A11)}$$

where $\rho(S, t, 0)$ is given by Eq. A9 and $K(S, t, p)$ is the secan bulk modulus given by

$$K(S, t, p) = K(S, t, 0) \text{ is } Ap + Bp^2 \qquad \text{(A12)}$$

where

$$
\begin{aligned}
K(S, t, 0) =\ & K_w + (54.6746 - 0.603459t \\
& + 1.09987 \times 10^{-2} t^2 \\
& - 6.1670 \times 10^{-5} t^3) S \\
& + (7.944 \times 10^{-2} \\
& + 1.6483 \times 10^{-2} t \\
& - 5.3009 \times 10^{-4} t^2) S^{3/2}, \quad \text{(A13)}
\end{aligned}
$$

$$
\begin{aligned}
A =\ & A_w + (2.2838 \times 10^{-3} - 1.0981 \times 10^{-5} t \\
& - 1.6078 \times 10^{-6} t^2) S \\
& + 1.91075 \times 10^{-4} S^{3/2} \qquad \text{(A14)}
\end{aligned}
$$

$$
\begin{aligned}
B =\ & B_w + (-9.9348 \times 10^{-7} + 2.0816 \times 10^{-8} t \\
& + 9.1697 \times 10^{-10} t^2) S \qquad \text{(A15)}
\end{aligned}
$$

The pure water terms K_w, A_w and B_w of the secant bulk modulus are given by

$$
\begin{aligned}
K_w =\ & 19652.21 + 148.4206t - 2.327105t^2 \\
& + 1.360477 \times 10^{-2} t^3 \\
& - 5.155288 \times 10^{-5} t^4 \qquad \text{(A16)}
\end{aligned}
$$

$$
\begin{aligned}
A_w =\ & 3.239908 + 1.43713 \times 10^{-3} t \\
& + 1.16092 \times 10^{-4} t^2 \\
& - 5.77905 \times 10^{-7} t^3 \qquad \text{(A17)}
\end{aligned}
$$

$$
\begin{aligned}
B_w =\ & 8.50935 \times 10^{-5} - 6.12293 \times 10^{-6} t \\
& + 5.2787 \times 10^{-8} t^2 \qquad \text{(A18)}
\end{aligned}
$$

The high pressure International Equation of State of Seawater, 1980 is valid for practical salinity from 0 to 42, temperature from -2 to 40 °C and applied pressure from 0 to 1000 bars.

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