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Measuring salinity and TDS of seawater and brine for process and environmental monitoring—which one, when?

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ABSTRACT

Seawater and brine salinity in reverse osmosis applications are commonly determined in the desalination industry by the following methods; evaporation, summation of ions or salinity-conductivity relationships. Results from these methods are often abbreviated as "TDS" irrespective of whether the measurement is actually referring to "solids" or "salts". Although, these methods should yield the same result, often they do not. Differences in the results are explained in this paper, following a review of the methods. Examples of seawater and brine salinity determined as salinity and TDS are given highlighting the advantages and limitations associated with each method. Summation of ions yielding Total Dissolved Salts (TDSalts) is recommended for discrete sampling to provide a breakdown of constituent ions for process design and monitoring. While the Practical Salinity Scale (PSS-78) used in oceanography is recommended as the method of choice for both continuous and discrete sampling for process and environmental monitoring. PSS-78 allows consistent measurement of seawater and brine salinity on land and at sea.

Keywords: Desalination; Seawater salinity; SWRO brine salinity; Practical Salinity Scale; TDS; Salinity monitoring

1. Introduction

Salinity variation is critical in process design and operation of a seawater reverse osmosis (SWRO) desalination plant for the three main process streams; seawater, concentrate (or brine) and treated water. A standard rule of thumb in the industry is an increase in seawater salinity of 1000 mg l^{-1} at a fixed temperature increases the osmotic pressure of seawater by approximately 0.8 bar. Therefore, to determine RO system recovery, pump pressures and ensuing energy requirements, an understanding of seasonal changes in seawater salinity (and temperature) are a prerequisite. Similarly, for environmental purposes, salinity is essential in brine dispersion modelling, ecotoxicity testing and marine monitoring to assess marine impacts from brine discharges and compliance with water quality guidelines. While salinity as an aggregate parameter, is a fundamental SWRO design parameter, the concentration ranges of constituent ions such as boron, bromide and chloride are also required to tailor the RO design to meet drinking water quality targets.

Various methods are commonly used in the desalination industry by process engineers to estimate true salinity, defined as the mass fraction of dissolved salts in seawater or brine (e.g., 35 g kg^{-1} or ppt for normal seawater). Typical salinity methods include; (i) evaporation and

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weighing of a filtered sample, (ii) summation of major ions in a discrete sample and (iii) conductivity salinity relationships to allow on-line monitoring and/or for discrete samples. While all may be abbreviated as "TDS" and ideally they should produce a similar result, they fundamentally differ. The first method measures Total Dissolved Solids (TDSolids) which includes any colloids passing through the filter and non ionised species in addition to dissolved salts. Whereas, the latter two methods measure Total Dissolved Salts (TDSolids) which is of more interest in desalination, yet these two methods may provide quite different results. In contrast, monitoring at sea for environmental purposes often is based on the UNESCO Practical Salinity Scale (PSS-78), long used by oceanographers to determine salinity from conductivity at different seawater temperatures and pressures in continuous salinity monitoring and vertical profiling.

Consequently, salinities used by process and environmental engineers may not be directly comparable and errors can occur, for example, when comparing salinity of brine at the outlet based on TDS by summation of ions to salinity determined at sea by a standard conductivity temperature depth (CTD) probe to assess brine dilution. Therefore, this paper reviews the advantages and limitations of these salinity methods used in process and environmental monitoring for seawater and brine.

2. Background

2.1. Seawater salinity and composition

The chemical analysis of seawater began with Bergman in 1779 [1]. Although, some 80 elements have been found in seawater, 99.9% of the mass of solutes in seawater is comprised of only eleven elements of which sodium and choride account for almost 86% (Table 1).

Moreover, it was suggested by Marcet as early as 1819, that the composition of sea salt was nearly constant from analysis of seawater samples from Arctic, Atlantic, Black, China, Mediterranean and White Seas [1]. This was supported by Dittmar in 1884 from the chemical analysis of 77 seawater samples, representative of all oceans, collected at various depths during the landmark Scientific Voyage of the H.M.S. Challenger (1872–1876).

Dittmar's work showed that while salinity might vary with location, there were no significant regional differences in the relative composition of seawater (for the major ions). The average ratios of the major ions determined by Dittmar, updated in 1940 by Lyman and Fleming [2] for modification of atomic weights since 1884, are given in Table 1 compared to more recent measurements using more sophisticated analytical techniques reported [3].

Table 1
Dittmar's values from 1876 for the major constituents of seawater calculated by Lyman and Fleming [cited in 2] and recent measurements [3]

Ion	% mass fraction of total ions [Lyman and Fleming, 1940]	% mass fraction of total ions [Millero Halics, 2008]
Cl^-	55.04	55.03
SO_4^{2-}	7.68	7.71
HCO_3^-	0.410	0.298
Br^-	0.19	0.19
F^-	0.003	0.004
Na^+	30.61	30.66
Mg^{2+}	3.69	3.65
Ca^{2+}	1.16	1.17
K^+	1.10	1.13
Sr^{2+}	0.04	0.022
$H_3BO_3^\circ$	0.07	0.055
Total	99.99	99.91

The relationship between major ions is commonly referred to as Marcet's Principle. Essentially Marcet's Principle shows that the major ions shown in Table 1, are conservative, that is, unreactive. Changes are due to addition or loss of water, for example, evaporation or rain. Conservative elements occur because they have low chemical reactivity and the rate at which seawater mixes through the oceans is sufficiently great with respect to the chemical processes acting to add or remove the major ions. As analytical techniques have improved over time some debate whether calcium, carbonate, magnesium and strontium are indeed conservative [4].

Seawater salinity is the combined result of the concentrating effect of evaporation and freezing with dilution from rain, river run-off and melting ice. The salinity of most seawater, free from land influences, varies between 31 and 38 g kg^{-1}, with average seawater around 35 g kg^{-1}. In the Arabian Gulf, salinity is up to 45 g kg^{-1} in areas due to an evaporation rate 8–22 times higher than the precipitation rate and the shallow nature of the Gulf [5].

Desalination plants established on the Eastern Seaboard of Australia, treat seawater of moderate salinity from the South Pacific Ocean. For instance, the Gold Coast Desalination Plant (GCDP) is desiged to treat seawater based on a TDSalts content in the range of 34,000–39,000 mg l^{-1}. Whereas, the Adelaide Desalination Plant will be treating seawater from the Gulf of St Vincent, an inverse estuary (evaporation exceeds freshwater input from rivers and precipitation, resulting in more saline water than the adjacent open ocean), where salinity may be up to 42,000 mg l^{-1}.

2.2. Brine salinity and composition

The SWRO desalination process typically concentrates seawater by a factor of 1.5–2.0, depending on the design of the RO system and the system recovery that can be achieved for source water salinity. The composition of the concentrated seawater, commonly referred to as brine, is similar to seawater as most ions in Table 1, with the exception of boron, are rejected by SWRO membranes in the range of 99.4–99.8%.

The actual salinity of brine discharged back into the receiving seawater may be reduced by mixing prior to discharge through the addition of seawater bypass, other process streams such as treated seawater backwash, as is the case for many Australian desalination plants, or by cooling water for SWRO plants located alongside power plants, for example, the Ashkelon Plant in Israel.

2.3. Determination of salinity

Absolute salinity was originally conceived as a measure of the mass of dissolved salts in a given mass of seawater [6,7]. The only reliable way to determine true or absolute salinity is to make a complete chemical analysis. However, this method is time consuming and cannot yield the precision necessary for accurate work. Thus, to determine salinity one normally uses indirect methods involving the measurement of a physical property such as conductivity, density, sound speed, or refractive index [1].

2.3.1. Development of PSS-78

Historically, oceanographers determined chloride in seawater by titration with silver nitrate which reacted with all halogens giving chlorinity (Cl%). Salinity (S) was then calculated using relationships such as that recommended by the Joint Panel on Oceanography Tables and Standards (JPOTS) in 1966:

$$S = 1.80655\ \mathrm{Cl}\% \tag{1}$$

By the early 1970s, accurate conductivity meters could be deployed from ships to measure conductivity (major ions are conductive) with depth. Consequently, the JPOTS sponsored by UNESCO and other oceanographic organisations developed the PSS-78, abbreviated as PSS-78, using conductivity (C) of a seawater sample relative to a potassium chloride (KCl) solution, instead of chlorinity. A standard seawater of salinity 35.000 has, by definition, a conductivity ratio (Rt) of unity at 15°C atmospheric pressure with a KCl solution containing a mass of 32.4356 g in a mass of 1 kg of solution [1,6]. The salinity dependence of Rt was determined measuring the Rt at various temperatures of Sp = 35.000 seawater weight evaporated or diluted with water [1].

Salinity is calculated through the PSS-78 algorithm as follows:

$$S_{\mathrm{p}} = a_{\mathrm{o}} + a_1 R_{\mathrm{t}}^{1/2} + a_2 R_{\mathrm{t}} + a_3 R_{\mathrm{t}}^{3/2} + a_4 R_{\mathrm{t}}^{2} + a_5 R_{\mathrm{t}}^{5/2} + \Delta S \tag{2}$$

where

$$\Delta S = \left[\frac{t_{68} - 15}{1 + 0.0162(t_{68} - 15)}\right] \times (b_0 + b_1 R_{\mathrm{t}}^{1/2} + b_2 R_{\mathrm{t}} + b_3 R_{\mathrm{t}}^{3/2} + b_4 R_{\mathrm{t}}^{2} + b_5 R_{\mathrm{t}}^{5/2}) \tag{3}$$

$a_0 = 0.0080$	$b_0 = 0.0005$
$a_1 = -0.1692$	$b_1 = -0.0056$
$a_2 = 25.3851$	$b_2 = -0.0066$
$a_3 = 14.0941$	$b_3 = -0.0375$
$a_4 = -7.0261$	$b_4 = 0.0636$
$a_5 = 2.7081$	$b_5 = -0.0144$

$$0^\circ\mathrm{C} \le t_{68} \le 40^\circ\mathrm{C}$$

and

$$R_{\mathrm{t}} = \frac{C\ (S_{\mathrm{p}},\ t_{68},\ P = 0)}{C\ (35,\ t_{68},\ P = 0)} \tag{4}$$

where pressure (P) is atmospheric and t_{68} is temperature measured according to the International Temperature Practical Scale from 1968 used at that time. Conversion to the revised International Temperature Scale introduced in 1990 used by CTD instruments is through the following Eq. (8):

$$t_{68} = 1.00024\, t_{90} \tag{5}$$

The result is a dimensionless salinity measure but practical salinity units (psu) are often (incorrectly) added. Supplementary equations were also established for converting Rt measured at pressures greater than atmospheric such as CTD measurements at depth (refer Ref. [1] and APHA 2520D in Ref. [9]). In general, these equations do not need to be applied for monitoring at sea at depths typical of RO intakes and outlets, for example, 20 m (2 bar). However, PSS-78 is not valid at the salinities corresponding to brine from a SWRO plant, being limited to the salinity range of 2–42.

More recently, relationships (Eq. 6) have been developed to relate practical salinity (Sp) to absolute salinity (S_A) taking into account added salts (δS_A) in *deep* water resulting form the dissolution of $CaCO_3$ and SiO_2, and CO_2, nutrients like NO_3 and PO_4 from the oxidation of plant material [3,10]. As this study, is in compatatively shallow water only Sp is used:

$$S_A = \text{Sp}\ (35.165/35) + \delta S_A \qquad (6)$$

2.3.2. Total dissolved solids

Total Dissolved Solids (abbreviated herein as TDSolids) is often determined according to APHA 2540C [9]. This involves pipetting a fixed volume of a well mixed sample (magnetic stirrer) and filtering it through a standard glass fibre filter under vaccum. The filter is then washed by three 10 ml volumes of reagent grade water. The filtrate (including washings) is evaporated to dryness at 180°C for at least 1 h in a similarly prepared (clean dish is heated for 1 h at 180°C) and weighed evaporating dish. The dish is cooled in a dessicator and weighed. The increase in dish weight represents TDSolids. Cycles of drying, cooling, dessicating and weighing are repeated unitl a constant weight is obtained. The volume to be pipetted is chosen to yield between 2.5 and 200 mg of dried residue.

2.3.3. Total dissolved salt

Each major anion and cation presented in Table 1 is determined analytically and the results of the individual ions summed giving Total Dissolved Salts (abbreviated herein as TDSalts). Cations such as sodium, magnesium are typically determined by Inductively coupled plasma-atomic emission spectrometry (ICP-AES), for example, USEPA6010 or APHA 3120B [9]. Whereas, chloride the major anion is typically determined spectrophotometrically from a colourimetric reaction of ferric ions with thiocyanate released through the reaction of chloride with mercuric thiocyanate (APHA 4500 –Cl E [9]).

3. Experiment

An experiment was conducted at the GCDP to validate that PSS-78 could be applied to measure the salinity of brine (Sp > 42) discharged at the GCDP using weight diluted solutions as recommended by Millero [1] and APHA 2520B [9].

The following samples were collected on January 21st 2010 at the plant and allowed to equilibrate to the temperature of the plant laboratory (24°C) overnight:

- seawater from intake;
- brine from first pass SWRO
- permeate (first stage of second pass) and
- brine released at the plant outlet (containing supernatant from backwash treatment).

The GCDP operates at various capacities 33%, 66% and 100%. At reduced capacities, seawater is added to the brine at the outlet to maintain exit velocities of the diffuser ports at sea. The seawater bypass further dilutes the salinity of the brine discharged. Therefore, various dilutions of brine were prepared (by weight) in duplicate corresponding to these scenarios.

Conductivity (normalized to 25°C) of all GCDP brine samples were measured with a conductivity meter calibrated using a 58.6 mS cm^{-1} (25°C) standard and the weight of each sample measured. Temperature compensation of the conductivity meter had been confirmed prior using a reference thermometer. Permeate was then slowly added to the solution, mixed by a magnetic stirrer, until the conductivity of the solution equaled that of the seawater feed. The final weight of the solution was measured. The salinity of the original brine samples (corresponding to 33–100% plant capacity) was determined by correcting the salinity of the diluted sample (equal to seawater) back to the original value using the weight ratio of dilution. A calibration check was made on the conductivity meter following completion of the test. The experiment was repeated on October 5th and included dilutions of seawater to extend to lower salinities.

4. Discussion and result analysis

4.1. Comparion of TDSolids to TDSalts

During commissioning of the GCDP, grab samples were taken from the seawater intake and TDS determined by both evaporation and summation of ions. TDS results are shown in Fig. 1 along with the average

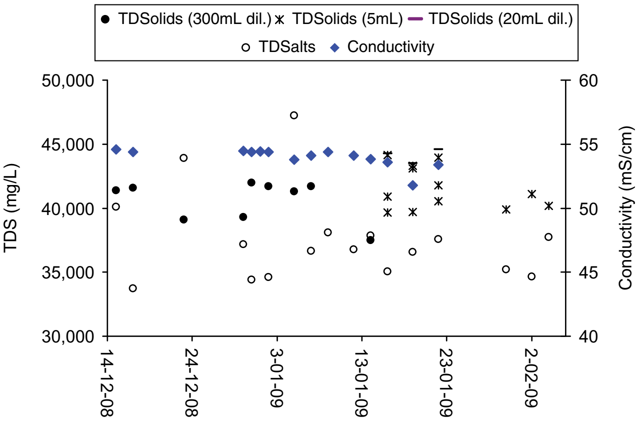

Fig. 1. Comparison of TDS determined by evaporation (20 ml and 300 ml prediluted by 1 in 10, and 5 ml samples) and by summation of ions.

conductivity from the on line seawater intake analyser corresponding to the time when the grab samples were taken.

Conductivity remained quite stable over the six weeks of testing, ranging from 51.8 to 54.6 mS cm^{-1} with a difference of only 2.8 mS cm^{-1}. Problems were encountered during commissioning with air in the sampling lines, resulting in zero conductivity as air passed through the sensor. While this issue was being resolved, conductivity data was not available from the on line analyser and hence the data gaps in Fig. 1.

In contrast TDS measured by evaporation and summation or ions showed much greater variability, ranging from 33,720 to 47,250 mg l^{-1}. In general, TDS measured by evaporation overestimated salinity with a median TDS of 41,300 mg l^{-1} which is more consistent with seawater found in parts of the Arabian Gulf than the Pacific Ocean. While the median TDS determined by summation of ions was lower, 36,700 mg l^{-1}, it showed the greatest variability yielding the highest and lowest TDS results. This is most likely due to an error in dilution of the sample prior to analysis for sodium and/or chloride. However, a breakdown of the constituent ions was not available.

The higher TDSolids results are not surprising as a 30 ml sample diluted to 300 ml with deionised water was filtered in the test for the initial period from December 15th 2008 to January 16th 2009. At the maximum design TDS (39,000 mg l^{-1}) for the plant, this would have yielded 1170 mg of dry residue in the evaporating dish, far exceeding the recommended weight in APHA 2540C of maximum 200 mg l^{-1}. At this level, the residue could have formed a water trapping crust and TDSolids would include some mechanically occluded water despite drying at 180°C. The sample volume was therefore decreased to 5 ml (undiluted), to fall within the desired range of 2.5 mg to 200 mg l^{-1} dry residue, albeit at the high end of the range. TDSolids was determined in triplicate for the next three sampling dates and in addition, a 2 ml sample was diluted to 20 ml with deionised water prior to filtration. For the latter, TDSolids was even higher than previously measured by evaporation and 7000 to 9000 mg l^{-1} higher than the corresponding TDSalts results. Triplicate TDSolids measurements for 5 ml were not reproducible, showing a difference of 3400 to 4500 mg l^{-1} between results for a given sampling date.

The above results illustrate the difficulty involved in obtaining reliable TDSolids results for highly saline water such as seawater. As noted in APHA 2540C [9], highly mineralised water with considerable calcium, magnesium, chloride and sulphate may be hygroscopic and require prolonged drying, proper dessication and rapid weighing. Moreover, with the high sulphate concentration, some water of crystallisation may remain increasing the TDS measured. On the other hand, at the temperature necessary to evaporate off the water, the bicarbonates and carbonates are decomposed, with the loss of CO_2, Br_2, Cl_2, and boric acid [10] which may reduce the overall TDS. However, typically this effect has less effect on the TDS than the aforementioned.

Finally, while TDSolids is designed to measure "dissolved solids", the test uses a filter with a nominal pore size in the range of 1.2–2 µm whereas, the common division between particulate and dissolved is filtration using a 0.45 µm pore size membrane. Even 0.45 µm pore size membranes have been shown to allow the passage of small colloids [11]. Consequently, TDSolids will certainly include any colloids passing through the test filter and non ionised species not just dissolved salts.

According to APHA 2520A, TDSolids and TDSalts should be similar after drying at 180°C. This may be the case for fairly clean water with a low salinity such as desalinated (and potabilised) water but was not found to be the case for seawater at the GCDP plant or other plants the Author has been involved with. To obtain a final dried residue closer to the lower end of the recommended range of 2.5 mg l^{-1} without predilution would require a volume of only 70 µl for seawater. This is expected to produce inconsistent results with repeated cycles of drying and weighing. From the above, TDSolids is not recommended to determine seawater salinity nor more concentrated brine samples where these problems would only be exacerbated.

4.2. Determination of TDSalts

TDSalts is routinely determined for seawater in the early stages of SWRO design. Depending on site location and source seawater variability, TDSalts may be analysed over a full year to provide the seasonal range in salinity, as an aggregate parameter. In addition, it will provide the range of important design ions such as boron, bromide and chloride to tailor plant design to meet drinking water quality targets.

However, to accurately calculate TDSalts by summation of ions, requires analysts experienced in saline water analysis and chloride and sodium in particular (86% of total ions in seawater). Such laboratories are not always located close to site, necessitating other laboratories to be used which is reflected in the results obtained. An illustrative case of the Author's experience in this regard, is presented in Table 2 where replicate seawater samples were analysed by three different laboratories (A, B and C).

Chloride measured by Laboratory B was unrealistically high for one replicate, 31,500 mg l^{-1} while the other replicate was 1.7 times lower. Determination of chloride (and sodium) typically involves one or more sequential dilutions of the seawater (or brine) sample. Therefore, a small error for either chloride or sodium will yield a

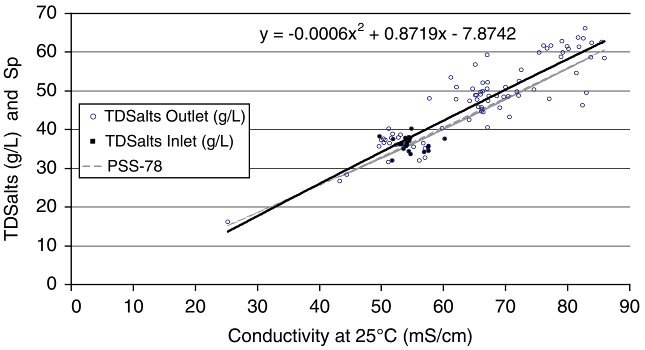

Fig. 2. TDSalts measured for seawater from the GCDP intake and brine from the outlet with polynomial fit to data compared to salinity (Sp) calculated by PSS-78.

large error. The final "total" result represents the combined errors in determining each ion. Hence, TDSalts for this replicate was close to 50,000 mg l^{-1}. Disregarding this result, the TDSalts concentration measured by the three laboratories ranged from 36,090 to 37,748 mg l^{-1}.

The ionic balance of all samples was checked for electroneutrality, whereby, the sum of anions and cations, expressed as milliequivalents per litre (meq l^{-1}) should be within 5% for the anion sum range of 10–800 meq l^{-1} to be deemed acceptable according to APHA 1030E [9]. Only Laboratory A met this criteria and therefore, the percentage contribution of each ion to TDSalts was calculated (Table 2). The % contribution of chloride, sodium and other major ions were found to be similar to that expected from Table 1, further confirming TDSalts results measured by Laboratory A are more likely to be closer to the real salinity of seawater from this location.

Ionic balance results in Table 2, demonstrate that not all laboratories check the overall cation–anion balance for a sample. Often times, an analyst is dedicated to a particular technique or suite of analytes. Consequently, sodium and chloride may not be determined by the same analyst. Apart from a conductivity check of the sample prior to testing to determine the required dilution, the analyst might not be aware the sample is seawater nor of the final TDSalt result. Notwithstanding, it should be noted that ions present in smaller percentages in seawater, for example, boron may be accurate in a seawater analysis despite the overall ionic balance exceeding 5%. Moreover, unrealistic TDSalts results may still be returned even if ions balance for a sample, if both sodium and chloride results are both too high or too low.

Included in Table 2 are TDSalts results from seawater and brine at another plant from a different location using a laboratory skilled in saline water analysis. Ionic balance is well within the required 5% demonstrating

Table 2
TDSalts in replicate seawater samples determined by three laboratories from location A and for seawater and brine at location B

Analyte	Unit	Seawater location A								Location B (lab D)	
		Lab A				Lab B		Lab C		Seawater	Brine
		Rep 1	% Total	Rep 2	%Total	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 1
Chloride	mg l^{-1}	20,170	53.43%	20,170	53.68%	18,200	31,500	17,000	17,000	19,700	35,500
Sulphate	mg l^{-1}	2809	7.44%	2806	7.47%	3010	3020	2900	2800	2650	4800
Bicarbonate	mg HCO$_3$ l^{-1}	118	0.31%	120	0.32%	150	155	70	70	134	220
Fluoride	mg l^{-1}	0.49	0.00%	0.49	0.00%	1	1	0.8	0.8	0.9	ND
Bromide	mg l^{-1}	74	0.20%	74	0.20%	ND	ND	ND	ND	ND	ND
Sodium	mg l^{-1}	12,000	31.79%	12,000	31.94%	12,900	12,300	13,700	13,900	11,100	21,600
Magnesium	mg l^{-1}	1560	4.13%	1460	3.89%	1480	1420	1380	1370	1210	2260
Calcium	mg l^{-1}	486	1.29%	451	1.20%	447	428	420	420	433	662
Potassium	mg l^{-1}	501	1.33%	465	1.24%	534	520	580	550	560	1220
Strontium	mg l^{-1}	9.62	0.03%	8.99	0.02%	8.71	8.33	7.1	7.1	7.4	ND
Boron	mg l^{-1}	4.42	0.03%	4.17	0.01%	3.8	3.7	5.9	5.9	5.7	ND
TDSalts	mg l^{-1}	37,748		37,574		36,736	49,357	36,090	36,150	35,801	66,262
Sum cations	meq l^{-1}	688		677		719	687	745	753	618	1190
Sum anions	meq l^{-1}	631		631		579	954	542	540	613	1105
Ionic balance	%	4.3		3.5		10.8	–16.3	15.8	16.4	0.4	3.7

ND = not determined.

TDSalts can be used equally well for seawater and brine for discrete sample analysis. A check of the % contribution of each ion to total ions is also similar to Table 1.

4.3. Conductivity salinity relationships

While TDSalts may be suitable for determining salinity for discrete samples, it does not lend itself to continuous real time salinity monitoring at a plant or at sea. Therefore, relationships between TDSalts and conductivity are often developed. At its simplest it may be the ratio of TDS/conductivity, which normally falls somewhere in the range of 0.55 for freshwater to 0.7 for more saline water (APHA 1030E [9]).

To develop such a relationship, particularly for the brine discharged at the GCDP, composite 24 h samples of the brine from the plant outlet are routinely determined on a weekly basis and monthly for seawater at the intake, by an external laboratory. TDSalts for analyses from March 2009 to October 2010 as a function of conductivity are presented in Fig. 2. The polynomial fit to the TDSalts data for inlet and outlet (107 samples) is given in Fig. 2. As salinity monitoring at sea, conducted with a standard CTD probe, is based on PSS-78, salinity was also calculated by PSS-78 as per Eq. 2.

Assuming PSS-78 to be more accurate despite being limited to Sp < 42, TDSalts results showed a wide spread around salinity calculated by PSS-78, overestimating salinity up to 30% on one occasion to underestimating salinity up to 20%. This is most likely associated with the difficulties in analysing each individual ion of a sample and the combined errors thereof as previously discussed. Despite the variability in TDSalts evident in Fig. 2, the resultant equation yields salinity results only 5% higher than PSS-78 for seawater and brine salinities expected at the GCDP. Therefore, PSS-78 or the equation specific to the GCDP (yielding a small error) could be used to allow continuous monitoring of either seawater or brine, allowing salinity variation to be more closely monitored by a relatively simple method compared to the collection and analysis of discrete samples.

4.4. Validation of PSS-78 for brine

Ideally one method is used to determine brine and seawater salinity that can be universally applied for process and environmental monitoring. PSS-78 has been used by oceanographers for more than 30 years to convert conductivity to salinity at different seawater temperatures and pressures. Consequently, PSS-78 is the most commonly used salinity parameter and is reported directly by CTD.

Dilutions of GCDP brine samples by weight were prepared to within the valid range of PSS-78, in this case the seawater feed as described in the experimental section. Salinity calculated by weight was compared to PSS-78 to confirm if PSS-78 was valid at the salinity range corresponding to brine at the GCDP. Results for 100% brine, dilutions of brine at various ratios including salinity corresponding to brine plus supernatant, seawater bypass flows and intake seawater are presented in Fig. 3. A regression analysis of the data showed an excellent correlation between salinity calculated by PSS-78 and salinity determined by weight for the salinity range 18 to 62. PSS-78 results were only 0.3% higher on average than salinity based on weight dilutions. The R^2 coefficient, measuring the goodness of fit, was very close to 1 ($R^2 = 0.9997$) validating that PSS-78 could be used to determine salinity of GCDP brine in addition to seawater. Consequently, PSS-78 is recommended to allow continuous monitoring and as a check for TDSalts results.

4.5. Comparison of PSS-78 with AWQC equation

The Australian Water Quality Centre (AWQC) in South Australia developed the following empirical equation to determine TDSalts from conductivity (25°C) for a variety of water it tests:

$$\text{TDSalts} = 0.548C + 2.2 \times 10^{-6} \times C^2 - 2.06 \times 10^{-12} \times C^3 \tag{7}$$

The equation was based on the TDSalts and conductivity analysis of hundreds of samples covering an extensive range of source water types and salinities conducted over 10 years Source water types included; River Murray, brackish groundwater, Pacific and Indian Ocean seawater typically found off the Australian coast to more saline seawater estuaries such as the Gulf Saint Vincent and brines from the highly saline

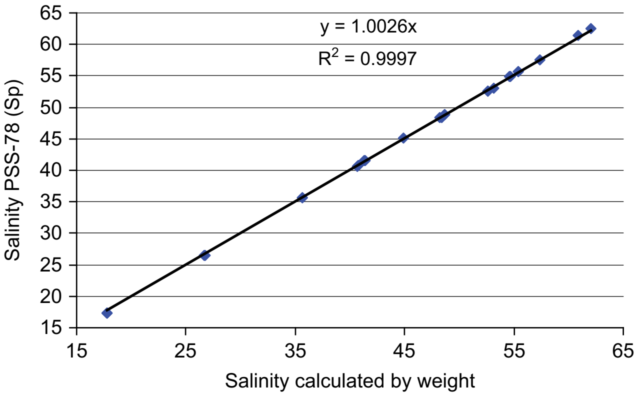

Fig. 3. Comparison of salinity determined experimentally from weight diluted brine and seawater to salinity calculated by PSS-78 (Sp).

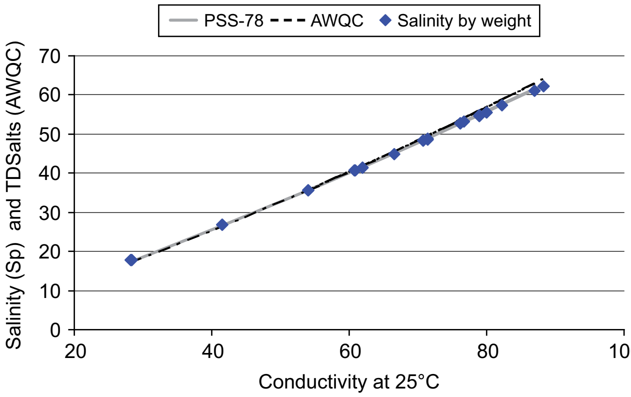

Fig. 4. Comparison of salinity determined from weight diluted GCDP brine and seawater to salinity calculated by PSS-78 and AWQC equation.

inland Lake Eyre and Coorong with a TDSalts of up to 165,000 mg l^{-1} [12].

Salinity calculated by the AWQC equation was compared to PSS-78 and from salinity calculated from weight dilutions of GCDP brine for the salinity range 18–62 (Fig. 4). Excellent agreement was found between PSS-78 and AWQC, with the latter salinity on average only 0.7% higher than PSS-78, demonstrating that either could be used to determine salinity of discrete samples or for continuous monitoring based on conductivity corrected to 25°C.

4.6. Vertical profiles of salinity

A distinct advantage of PSS-78 is that in addition to allowing continuous salinity monitoring at a plant, salinity as a function of seawater depth can also be examined. Prior to construction of the GCDP plant, baseline monitoring was conducted for 2 years in the Kirra-Tugun embayment where the seawater intake and outlet are located. Temporal and spatial variation in salinity was investigated using a CTD probe at the diffuser site and at two control sites, 500 m north and south, remote from the diffuser mixing zone. Significant natural variation was found in the water column on occasion. Illustrative examples at the control sites obtained during operational monitoring are presented in Figs. 5(a) and 5(b). A subtle difference in Sp of 0.5 at the surface between the two sites is observed in Fig. 5(a). Whereas, in Fig. 5(b) an abrupt halocline, defined as a strong vertical gradient in salinity, is observed which extended 4.6 km further south to Point Danger. Such phenomena could not be observed to this degree of accuracy using discrete sampling of the water column for TDSalts analysis.

Vertical salinity profiling is also used to detect if a more saline dense layer is present at the boundary of the diffuser mixing zone due to brine discharge, at "impact" sites. If detected, dilution is calculated from the salinity of the brine discharged at the plant and the increase in salinity for the dense layer at the impact site compared to background salinity (average of both control sites for

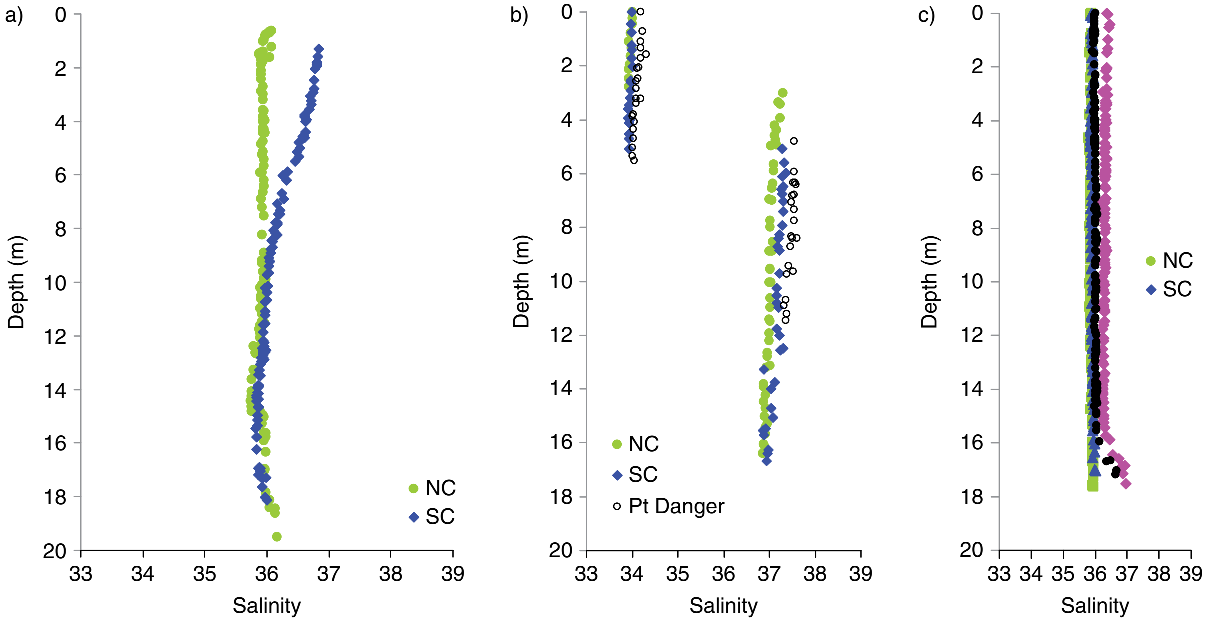

Fig. 5. Vertical salinity profiles (Sp) on September 1st 2009 (a) showing natural variation in salinity with depth at north (NC) and south control (SC) sites, point danger on November 12th 2009 (b) and at boundary of diffuser mixing zone (IN and IS) on September 25th 2009 (c).

the same depth). Fig. 5(c) illustrates a small increase in salinity at around 16 m at two of the impact sites compared to the control sites. To ensure no errors occur in using different methods to estimate salinity, all the aforementioned streams are determined using PSS-78.

Dilution is then compared to the No Observed Effect Concentration (NOEC) determined from direct toxicity testing, also typically expressed as a dilution, at which no ecological impacts are expected. While, it is useful to define NOEC in terms of dilution it should also be characterised in terms of salinity using PSS-78 as elevated salinity is generally the major toxicity concern associated with SWRO brine. Moreover, high salinity brine represents normal operating conditions, other potential toxicants might be present only during RO cleaning and not discharged back to sea.

5. Conclusions

TDSolids is not recommended for estimating salinity in seawater or brine due to potential artefacts such as a water trapping salt crust and inclusion of colloids which inevitably overestimates salinity when evaporating a filtered sample. TDsalts is recommended to estimate salinity of seawater and brine and to provide a breakdown of constituent ions for discrete samples. This is useful in process monitoring of key design ions, for example, chloride, boron. However, TDSalts requires laboratories skilled in saline analysis and the ion balance should be independently checked. Empirical conductivity salinity (using TDSalts) relationships allow continuous real time monitoring and can be very accurate, for example, the AWQC equation.

PSS-78, long used by oceanographers and the basis of CTD probes, was validated for brine salinities up to 62 and can be used for discrete or continuous salinity measurement. Therefore, PSS-78 is recommended for universal use in desalination process and environmental monitoring. This will allow consistent measurement of seawater and brine salinity on land and at sea and reduce errors when different salinity methods are used and compared. Similarly, ecotoxicity results should be defined in PSS-78 salinity in addition to required dilution.

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