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Density of seawater

F. J. Millero and F. Huang

The density of seawater as a function of salinity (5 to 70 g kg⁻¹) and temperature (0 to 90°C)

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Abstract

New seawater density measurements were made as a function of temperature (0 to 90°C) and salinity (5 to 70). The measurements ($N=230$) from 0 to 40°C and Practical Salinity from 0 to 40 were found to be in good agreement ($\sigma=0.0036$) with the equation of state of seawater (Millero and Poisson, 1981) made on samples with a known chlorinity (Cl). These results indicate that the Practical Salinities (S) are in agreement to within ± 0.003 with the values calculated from the Chlorinity, $S_{Cl}=1.80655 Cl$. The measurements from 25 to 90°C were used to extend the equation of state to high temperatures and salinities. All the relative densities ($\rho-\rho^0$, where ρ^0 is the density for pure water) were fitted to equations of the form

$$(\rho - \rho^0)/\text{kg m}^{-3} = AS_A + BS_A^{0.5} + CS_A^2$$

where A , B , and C are functions of temperature and S_A (g kg^{-1}) is the absolute salinity, $S_A=(35.16504/35)S$. The fitted results from $S_A=0$ to 50 and 0 to 40°C ($N=247$) gave standard errors of 0.0037 kg m^{-3} . The fitted results from 25 to 90°C ($N=271$) gave standard errors of 0.0063 kg m^{-3} and all the results ($N=501$) from 0 to 90°C gave standard errors of 0.0062 kg m^{-3} . The earlier density measurements used to determine the equation of state of seawater were combined to derive equations that are valid from 0 to 40°C and 0 to 90°C. The standard errors of these fits are, respectively, 0.0038 kg m^{-3} ($N=713$) and 0.0063 kg m^{-3} ($N=962$). These new measurements expand the equation of state of seawater to a wider range of temperature (0 to 90°C) and absolute salinity (0 to 70).

1 Introduction

The original one atmosphere density measurements used to determine the equation of state of seawater (Millero and Poisson, 1981) were made on seawater of a known

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Chlorinity (Cl). The salinities of these samples were determined using the relationship

$$S_{Cl} = 1.80655Cl \quad (1)$$

This relationship may or may not be valid at the present time (Millero et al., 1976a). For example, the differences in the Practical Salinity (S) and Chlorinity salinity (S_{Cl}) calculated from Eq. (1) may vary by as much as 0.0055 (Fig. 1). This difference is equivalent to an error in density of $\pm 0.0041 \text{ kg m}^{-3}$.

The present one atmosphere equation of state for seawater is limited to salinities from 0 to 40 and temperatures from 0 to 40°C. The equation was derived from the measurements of Millero et al. (1976b) and Poisson et al. (1980). A summary of these measurements are given in Table 1. The equation of state derived from the studies of Millero et al. (1976b) and Poisson et al. (1980) had a $1\sigma = 0.0035$ similar to the individual studies. Poisson and Badhouni (1993) have extended the range to higher Practical Salinities ($S=50$) from 15 to 30°C. They give equations that represent this data with standard errors close to those of the equation of state (Millero and Poisson, 1981). Reliable measurements to higher temperatures are not available at the present time. As the physical chemical properties of seawater are known to higher temperatures (Millero and Pierrot, 2005; Feistel, 2008) there is a need for density measurements at higher temperatures and salinities.

In this paper, measurements of the density of seawater on the Practical Salinity Scale (S) have been made from 0 to 42°C and are compared to those calculated from the equation of state (Millero and Poisson, 1981). New measurements of the density of seawater to 90°C as a function of absolute salinity, S_A from 0 to 70 g kg⁻¹ are also reported. This study is part of a work to extend the equation of state of seawater over a wider range of temperature and salinity (Feistel, 2008). The results will be useful in examining the use of ionic interaction models (Pierrot and Millero, 2000) to estimate the density over a wide range of temperatures and ionic strength and in the future to examine the PVT properties of hydrothermal waters.

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2 Experimental methods

The seawaters used in this study were Standard Seawater ($S=35.00$) and surface Gulf Stream seawater ($S=36.10$). Both waters have low nutrient concentrations. Solutions at low salinities were obtained by adding water by weight and the high salinities by slowly evaporating the samples. The Practical Salinities were measured with an Autosal salinometer calibrated with Standard Seawater. The absolute salinities of the evaporated samples were back calculated from the weight of the added water needed to dilute it to a salinity range that can be measured by conductivity and density at 25°C . The densities were measured on a Paar 500 densimeter at a fixed temperature ($\pm 0.003^{\circ}\text{C}$) determined with a Platinum thermometer in the instrument. The measurements made at high temperatures were made on degassed samples heated to 90°C to avoid bubble formation in the instrument. The measurements were then made from 90 to 25°C . Densities made on Standard Seawater were reproducible to $1\sigma=0.003\text{ kg m}^{-3}$ from 0 to 50°C and agree with values calculated from the equation of state (Millero and Poisson, 1981) to $\pm 0.0035\text{ kg m}^{-3}$ from 0 to 40°C . All of the measurements were made relative to the density of water which is based on the equations of Kell (1975) adjusted to the 1990 temperature scale (Spieweck and Bettin, 1992). The measured water values from 0 to 90°C agreed to the calculated values to $\pm 0.002\text{ kg m}^{-3}$. Since the density of water (ρ^0) in the original equation of state of seawater is based on the less reliable water equations of Bigg (1967) and the values used in the instrument, all of our measurements are reported and compared to the equation of state of seawater (Millero and Poisson, 1981) in terms of the differences in the density of seawater and water ($\rho - \rho^0$) kg m^{-3} .

A number of density measurements on deep waters in the Atlantic (Millero et al., 1976b, 1978), Indian (Poisson et al., 1980; Millero et al., 2008a), and Pacific oceans (Millero et al., 1978, 2008c) and the Red (Poisson et al., 1980) and Baltic Seas (Millero and Kremling, 1976) are higher than the values determined from the equation of state (Millero and Poisson, 1981). This is attributed to the added salts to seawater from

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the dissolution of $\text{SiO}_2(\text{s})$ and $\text{CaCO}_3(\text{s})$ and an addition of CO_2 and nutrients from the mineralization of organic matter (Brewer and Bradshaw, 1975; Millero, 2000). Since the conductivity salinity does not respond to all the components in seawater, it is useful to examine the physical properties in terms of the absolute salinity (Millero et al., 2008b; Feistel, 2008). The absolute salinity (g kg^{-1}) is defined (Millero et al., 2008b) by

$$S_A = S_R + \Delta S \quad (2)$$

where the Reference Salinity (S_R) is related to the Practical Salinity (S) by

$$S_R = (35.165\ 04/35) \text{ g kg}^{-1} \times S \quad (3)$$

and ΔS is the increase due to added salts (Brewer and Bradshaw, 1975; Millero et al. 2000). The values of ΔS can be estimated by determining the added Si, Ca, NO_3 , PO_4 and TCO_2 to seawater (Millero et al., 2008b, c) It can also be estimated (Millero et al., 2008c) from the differences between the measured densities and the values determined from the equations of state using the approximate equation (Millero et al., 2008c)

$$\Delta S = \Delta\rho/0.751 \text{ g kg}^{-1} \quad (4)$$

where $\Delta\rho = \rho$ (measured) $-\rho$ (calculated from the equation of state). For seawater with no added salts the values of S_A are equal to the Reference Salinity S_R and can be estimated from the Practical Salinity using Eq. (3).

3 Results and discussion

The densities made in this study are given in Appendices I and II. <http://www.ocean-sci-discuss.net/6/153/2009/osd-6-153-2009-supplement.pdf> Two sets of measurements were made from 0 to 40°C and $S_A=4$ to 50 and from 25 to 90°C and $S_A=4$ to 70. The first series of density measurements were made on Standard Seawater ($S=35$) and Gulf Stream seawater evaporated and diluted from $S_A=4$ to 42 g kg^{-1} and

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from 0 to 40°C. The measured densities ($N=230$) are compared to the values calculated from the equation of state (Millero and Poisson, 1981) as a function of temperature and salinity in Fig. 2. The standard error between the measured and calculated values was 0.0036 kg m^{-3} . This is similar to the errors in the density measurements ($\pm 0.003 \text{ kg m}^{-3}$) and indicates that the salinities calculated by conductivity (S) and Chlorinity (S_{Cl}) are in agreement to $\pm 0.004 \text{ g kg}^{-1}$. It should be pointed out that measurements made at salinities from 40 to 48 from 15 to 30°C are in reasonable agreement (± 0.006) with the measurements of Poisson and Badhouni (1993).

The internal consistency of the measurements was examined by fitting the relative densities to an equation of the form

$$(\rho - \rho^0)/\text{kg m}^{-3} = AS_A + BS_A^{0.5} + CS_A^2 \quad (5)$$

The variable A , B and C are functions of temperature (t °C)

$$A/(\text{g/kg}) = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a^5t^5 \quad (5a)$$

$$B/(\text{g/kg})^{0.5} = b_0 + b_1t + b_2t^2 \quad (5b)$$

$$C/(\text{g/kg})^2 = c_0 \quad (5c)$$

The parameters needed to fit the seawater measurements ($N=247$) from 0 to 40°C and S_A from 5 to 50 are tabulated in Table 2 along with the standard error of the fit ($\sigma=0.0037 \text{ kg m}^{-3}$). This standard error of the 0 to 40°C fit is similar (Fig. 2) to the differences between our measurements and those calculated from the equation of state of seawater (Millero and Poisson, 1981). The parameters needed to fit the seawater measurements ($N=271$) from 25 to 90°C are also tabulated in Table 2 along with the standard error of the fit ($\sigma=0.0063 \text{ kg m}^{-3}$). All of the measurements from 0 to 90°C ($N=501$) have also been fitted to Eq. (5). The parameters for the fits are given in Table 2 along with the standard error of the fit ($\sigma=0.0062 \text{ kg m}^{-3}$). The differences between the measured and calculated densities from these fits are shown in Fig. 3. Most of the differences are with 2σ , where σ is the standard error of the fit. Somewhat

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larger errors occur at high temperature and low salinity. These measurements extend the equation of state to seawater as a function the absolute salinity S_A over a wide range of temperature and salinity.

The measurements made in this study from 0 to 40°C and 0 to 90°C have been fitted to Eq. (5) with all of the measurements used to determine the International Equation of state of seawater (Millero et al., 1976b; Poisson et al., 1980). The results of these fits ($N=713$ from 0 to 40°C and $N=962$ from 0 to 90°C) are tabulated in Table 3 along with the standard errors, respectively $\sigma=0.0038 \text{ kg m}^{-3}$ and $\sigma=0.0063 \text{ kg m}^{-3}$. It should be pointed out that the earlier measurements made on the 1969 temperature scale were converted to the 1990 temperature scale (Preston-Thomas, 1990). Changes in the temperature scale do not significantly affect the values of $(\rho - \rho^0)$ which do not vary significantly with temperature. The results of this study can be used to determine the properties of seawater and most estuarine waters over a wide range of Absolute Salinity and temperature. These results will also be useful in extending the ionic interaction model for seawater (Pierrot and Millero, 2000) to 90°C. Future work on the density of seawater above 100°C at applied pressure are needed to extend the temperature range to the levels available for the thermochemical properties of seawater (Millero and Pierrot, 2005; Feistel, 2008).

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Table 1. Summary of the 1 atm density measurements made on seawater.

Author	Number	Std Error (1σ)	Temperature	Salinity
Millero et al. (1976b)	122	0.0035	0 to 40°C	1 to 40
Poisson et al. (1980)	344	0.0035	0.3 to 30°C	5 to 41
Poisson & Badhouni (1993)	79	0.0043	15 to 30°C	35 to 50
This Study (0 to 40°C)	247	0.0037	0 to 40°C	5 to 50
All Combined	713	(0.0036)		
This Study (0 to 90°C)	501	0.0062	0 to 90	4 to 70
All Combined	962	(0.0063)		

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Table 2. The coefficients for the densities measured in this study fitted to Eq. (2).

	0 to 40°C	25 to 90°C	0 to 90°C
S_A	8.246111E-01	8.055888E-01	8.167896E-01
$S_A t$	-3.956103E-03	-2.588520E-03	-3.602792E-03
$S_A t^2$	7.274549E-05	2.449074E-05	6.310021E-05
$S_A t^3$	-8.239634E-07	3.908917E-08	-6.889045E-07
$S_A t^4$	5.332909E-09	-1.795219E-09	4.865381E-09
$S_A t^5$		8.617570E-12	-1.478197E-11
$S_A^{1.5}$	-6.006733E-03	-4.893389E-03	-5.321919E-03
$S_A^{1.5} t$	7.970908E-05	2.132621E-05	3.205571E-05
$S_A^{1.5} t^2$	-1.018797E-06	-1.907666E-07	-2.823113E-07
$S_A^{1.5} t^2$	5.281399E-04	5.165275E-04	5.275830E-04
Number	247	271	501
Std.Err.Fit	0.0037	0.0063	0.0062

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Table 3. The coefficients for the densities measured in this study and literature data (Millero et al., 1976b; Poisson et al., 1980) fitted to Eq. (2).

	0 to 40°C	0 to 90°C
S_A	8.207423E-01	8.197247E-01
$S_A t$	-4.090059E-03	-3.779454E-03
$S_A t^2$	7.695554E-05	6.821795E-05
$S_A t^3$	-8.284116E-07	-8.009571E-07
$S_A t^4$	5.490137E-09	6.158885E-09
$S_A t^5$		-2.001919E-11
$S_A^{1.5}$	-5.738085E-03	-5.808305E-03
$S_A^{1.5} t$	1.044735E-04	5.354872E-05
$S_A^{1.5} t^2$	-1.758636E-06	-4.714602E-07
$S_A^{1.5} t^2$	4.840416E-04	5.249266E-04
Number	713	962
Std.Err.Fit	0.0036	0.0063

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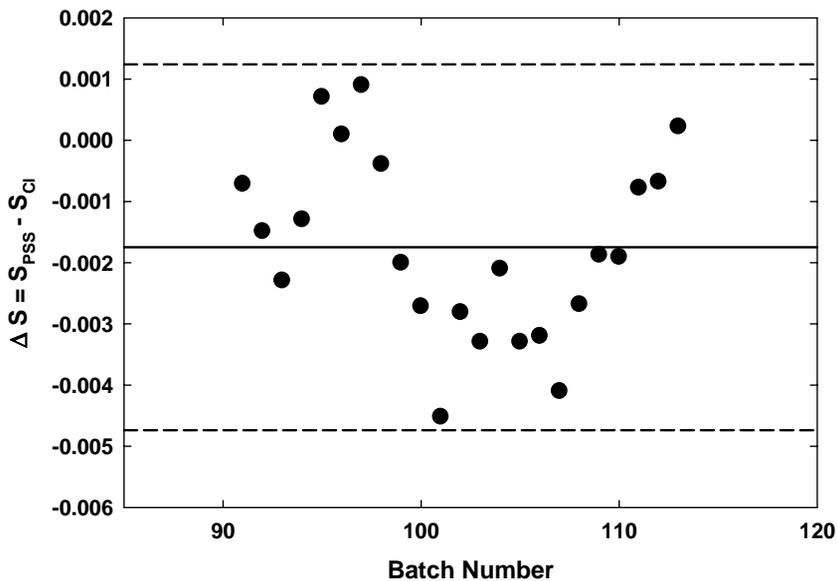


Fig. 1. The differences between the Practical Salinity (S_{PSS}) and the value calculated from the Chlorinity ($S_{Cl}=1.80655$ Cl) for the last series of Standard Seawater where Chlorinity was measured (P91 to P113). The dotted line is 2σ .

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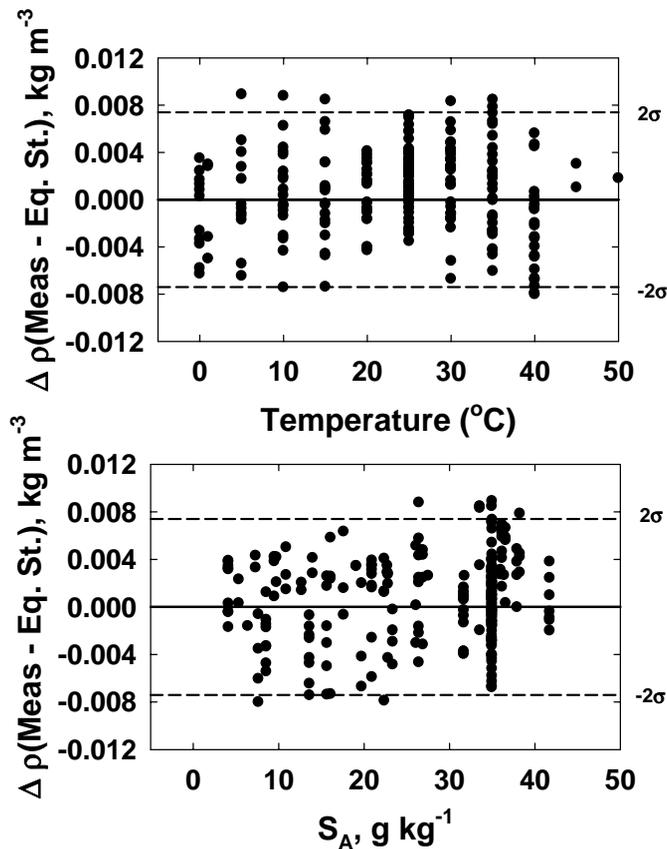


Fig. 2. The differences in the measured ($N=230$) densities ($\rho - \rho^0$, kg m^{-3}) with those calculated from the equation of state (Millero and Poisson, 1981) as a function of temperature and salinity ($\sigma=0.0036 \text{ kg m}^{-3}$).

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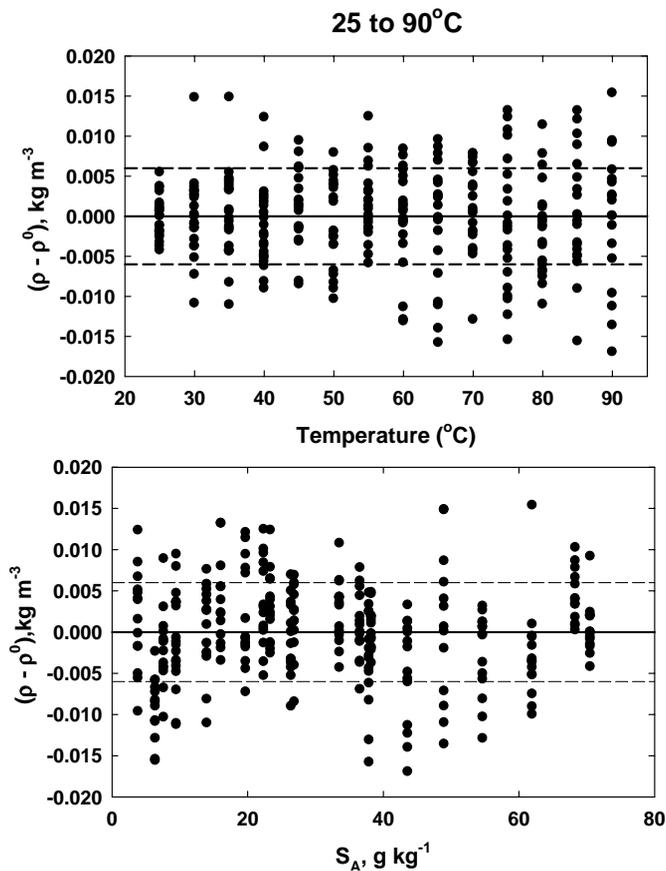



Fig. 3. The differences between the measured ($N=501$) and calculated densities ($\rho - \rho^0$, kg m^{-3}) from 25 to 90°C and S_A from 5 to 70 g kg^{-1} as a function of temperature and salinity ($\sigma=0.0062 \text{ kg m}^{-3}$).

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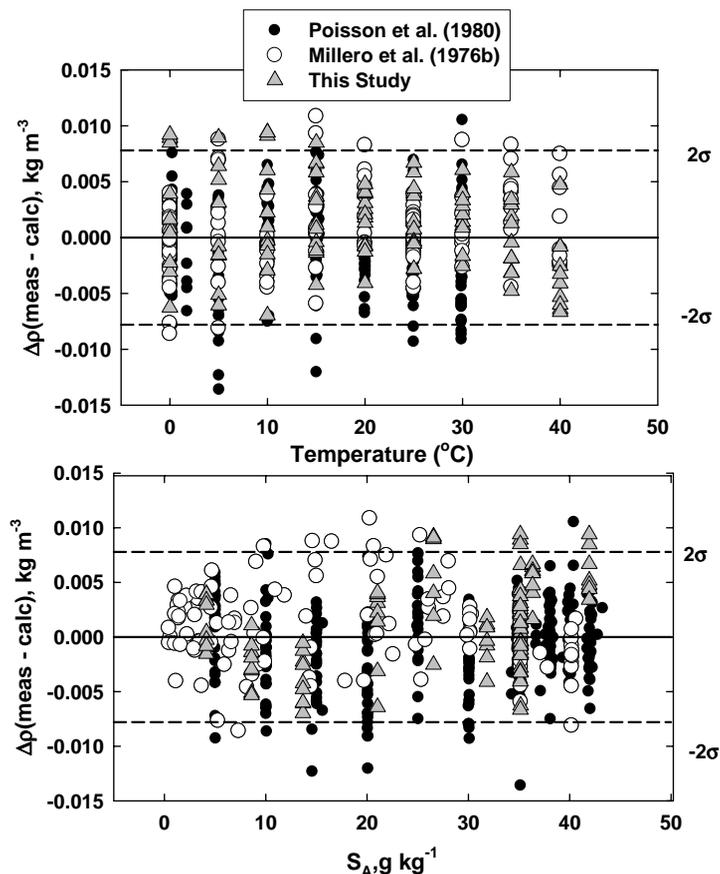


Fig. 4. The deviations between the measured ($N=713$) and calculated values from 0 to 40°C and S_A from 0 to 40 g kg^{-1} of Poisson et al. (1980), Millero et al. (1976b), and this study as a function of temperature and salinity ($\sigma=0.0037\text{ kg m}^{-3}$).

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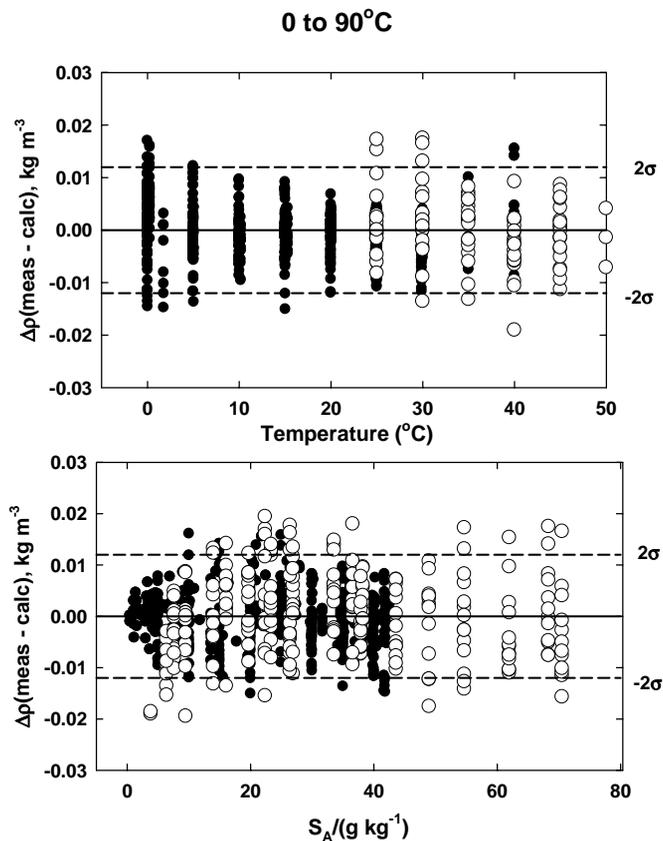



Fig. 5. The deviations between the measured ($N=962$) and calculated values from 0 to 90°C and S_A from 0 to 70 g kg^{-1} as a function of temperature and salinity ($\sigma=0.0062 \text{ kg m}^{-3}$). The closed circles are from studies made from 0 to 40°C and the open circles are from 25 to 90°C. This study.

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