

Elemental composition of commercial seasalts

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ABSTRACT

Eight different, commercially available, synthetic sea salt mixes were analyzed for some thirty-five elements and ions and other chemical parameters. The results are compared to those of water from typical tropical oceans.

Synthetic mixes of seawater salts are commonly used to make seawater for marine aquaria. Coral reef organisms are maintained in closed aquaria for recreation, education, public displays, propagation, and research. Our research interests involve the effects of water chemistry on coral reef metabolic rates, particularly the relationship between saturation state of calcium carbonate, alkalinity and pH. We are interested in the possibility of mixing synthetic seasalts to create seawater with differing pH buffering systems. Despite the widespread use of a variety of salt mixes, the relative composition of elements and ions in these salts are not reported to the consumer. The large variety of salt brands makes it difficult to determine which salt mixes are appropriate for a given saltwater application. In this publication we report on some 35 different elements and ions for eight different commercial salt mixes. We also compare the composition of the synthetic seawater to ocean water, typical of tropical oceans.

Eight salt mixes were purchased from That

Fish Place, Lancaster PA, 17603, USA and shipped to the Hawaii Institute of Marine Biology, Kaneohe HI, 96744, USA. The salt mixes were opened, the “dry” salts were mixed manually and sub-sampled 10 times. The sub-samples (~300 grams) were placed in zip-lock bags, and then sealed. Samples were analyzed for the “major” cations and anions, nutrient compounds and “trace” elements. Two sub-samples of each salt in the zip-locked bags were analyzed. The above mixing and sub-sampling were the best practical methods for a typical consumer of minimizing inhomogeneties in the salt mixes. Thirty-five grams of each salt sample were mixed into highly purified water (18 milliohm cm^{-1} water from a milli-QRG Millipore ultra-pure water system) and brought to one liter. If salts are thoroughly dried, their salinity should be approximately 35 parts per thousand; however, salt mixes usually contain water of hydration. Salinity was measured on freshly prepared synthetic seawater sample. The major cations Na^+ , K^+ , Ca^{+2} , Mg^{+2} , Sr^{+2} , and B^{+3} were measured with a Perkin Elmer Atomic Absorption Spectrophotometer. The major anions Cl^- and SO_4^{-2} were determined by ion chromatography (2010 Dionex in chromatograph with AS-4 column). The anions F^- and Br^- are in relatively small concentra-

tions, and are included in the measurement of Cl^- . Total CO_2 was measured by acidifying a prepared seawater sample, then measuring CO_2 gas by infrared detection (OI model 700 Analytical TOC Analyzer).

The inorganic nutrients, PO_4^{3-} , NO_3^- , NH_4^+ , SiO_3^{3-} , were measured with a Technicon II Autoanalyzer using slightly modified Technicon Industrial methods (Walsh, 1989.) Total nutrients were measured by oxidizing water samples with UV light and peroxide and then measuring inorganic nutrients again. The difference between total nutrients and inorganic nutrients is considered “dissolved organic nutrients” as dissolved organic phosphate (DOP) and dissolved organic nitrogen (DON). pH was measured with a Senorex S-100C pH probe with an Orion model EA-940 ion-analyzer. Total alkalinity was measured by an addition of 0.01N HCl to bring a 20 ml water sample to pH's between 3.0 and 3.8. The remaining elements, Li, Si, Mo, Ba, V, Ni, Cr, Al, Cu, Zn, Mn, Fe, Cd, Pb, Co, Ag, Ti, were measured by Inductively Coupled Plasma emission spectroscopy (ICP). All results were adjusted to 35 ppt salinity and a temperature of 25°C, density 1.023 kg L⁻¹. Values for duplicate samples were averaged and then rounded off to the average error of duplicate analysis. The dissociation constants used to calculate borate alkalinity and species of inorganic carbon in seawater were taken from a readily available text, Stumm and Morgan (1981).

The results are summarized in Table 1, and are ranked from highest concentration to lowest. Molecular weights are listed in the Table so one can easily convert from mmol kg⁻¹ to ppm by multiplying the value in the Table by the molar mass (molecular weight, g mol⁻¹), giving mg/kg⁻¹ which is parts per million (ppm); similarly $\mu\text{mol kg}^{-1}$ times the molar mass is parts per billion (ppb). Concentrations of the elements and ions in tropical surface ocean water are also listed for comparison.

Some generalizations are apparent. The salinity of all mixtures is 2-6 parts per thousand

(ppt) lower than 35 ppt, because of water of hydration. The major cations are within about 10% of seawater, except salt #8, which has a Mg^{+2} value only 70% of seawater. The major anions, Cl^- and SO_4^{2-} , are also within about 10% of seawater, except a low SO_4^{2-} value for salt #7 and a high value for salt #8. Salt #8 has an equimolar value of Mg^{+2} and SO_4^{2-} . A possible explanation is that MgSO_4 is the sole source of Mg for this salt.

Typically, for natural seawater the ratio of HCO_3^- and CO_3^{2-} balances the slight excess charge of the major cations over the anions. However, it is apparent from Table 1 that total CO_2 varies about 20 times, from 0.12 to 2.5 mmol kg⁻¹. Total B varies about 13 times from 0.36 to 4.90 mmol kg⁻¹. Thus the pH buffering system of these salts are fundamentally different. pH values are higher for the salts with relatively low total CO_2 .

Phosphate concentrations vary 24 fold from extremely low values, 0.05 $\mu\text{mol kg}^{-1}$ to moderate concentrations of 1.2 $\mu\text{mol kg}^{-1}$. Similarly, NO_3^- varies from 0.79 to 18.4 $\mu\text{mol kg}^{-1}$. Ammonia also ranges 22 fold from 0.55 to 11.9 $\mu\text{mol kg}^{-1}$. None of the concentrations, however, are sufficiently high to be of any concern to the maintenance of reef organisms. Total organic carbon and the dissolved organic nutrients, DOP and DON, are actually lower than typical surface ocean water. Silica concentrations range from 2.7 to 11.5 $\mu\text{mol kg}^{-1}$ by colorimetric assays and from 14 to 46 $\mu\text{mol kg}^{-1}$ by ICP. Most samples contain higher than seawater levels of Si. Discrepancies between colorimetric and ICP assays for silica (Table 1) are common, and usually ascribed the presence of “condensed” forms of silica unreactive to colorimetric assays (Greenberg et al. 1992).

The remaining transition metals are all higher in artificial seawater than in seawater. Only Cr,

Table 1. Elemental composition of synthetic sea salts for marine aquaria. SW = seawater; 1 = Instant Ocean, 2 = Tropic Marin, 3 = Marine Mix, 4 = Reef Crystals, 5 = Rea Sea Salt, 6 = Kent, 7 = Coralife, 8 = SeaChem Reef, MW = molecular weight, g mol⁻¹, TA = total alkalinity (mequiv kg⁻¹).

	SW	1	2	3	4	5	6	7	8	MW
ppt	35	29.65	32.64	29.40	28.91	30.07	28.85	28.39	29.54	
Major Cations (mmol kg⁻¹)										
Na ⁺	470	462	442	467	461	472	460	464	504	23.0
K ⁺	10.2	9.4	9.1	10.1	9.5	9.9	10.1	9.3	10.7	39.1
Mg ⁺²	53	52	46	53	50	55	57	63	37	24.3
Ca ⁺²	10.3	9.4	9.1	10.1	9.5	9.9	10.1	9.3	10.7	40.1
Sr ⁺¹	0.09	0.19	0.08	0.15	0.08	0.10	0.10	0.08	0.21	87.6
Sum	607	594	561	601	589	610	605	620	609	
Major Anions (mmol kg⁻¹)										
Cl ⁻	550	521	497	538	520	537	531	566	516	35.5
SO ₄ ⁻²	28	23	21	28	27	25	24	15	37	32.1
TCO ₂	1.90	1.90	1.10	2.10	0.75	1.08	2.52	0.32	0.12	12.0
TB	0.42	0.44	0.36	0.41	0.65	0.54	0.54	1.26	4.90	10.8
Sum	608	569	541	596	574	588	582	597	595	
Nutrients (μmol kg⁻¹)										
PO ₄ :P	0.20	0.05	1.20	0.46	0.32	0.37	0.16	0.95	0.57	31.0
NO ₃ :N	0.20	1.00	2.20	1.63	5.00	0.79	2.05	6.30	18.4	14.0
NH ₄ :N	0.20	10.2	0.55	9.2	7.8	5.2	11.9	8.4	0.7	14.0
SiO ₃ :Si	5	4.2	3.2	11.5	5.9	4.5	4.1	2.7	11.3	28.1
DOP:P	0.2	0.1	0	0.2	0.2	0.1	0.1	0.2	0.1	31.0
DON:N	10	2.9	5.5	8.2	6.3	1.9	2.4	11.2	3.1	14.0
TOC:C	50	29	32	29	28	29	28	28	22	12.0
pH	8.25	8.35	8.90	8.49	9.28	8.69	8.08	9.17	8.81	
TA	2.3	2.3	1.5	3.1	3.2	1.6	2.7	1.5	2.2	
Trace (μmol kg⁻¹)										
Li	20	54	29	36	62	44	62	1793	117	6.9
Si	5	16	14	29	46	17	37	18	23	28.1
Mo	0.1	1.8	2.5	3.3	2.4	2.8	2.8	2.7	2.6	95.9
Ba	0.04	0.85	0.32	0.71	0.27	0.70	0.39	0.37	0.86	137
V	0.04	2.9	2.8	3.4	3.5	3.4	3.7	3.8	2.9	50.9
Ni	0.004	1.7	1.7	2.3	2.1	1.9	1.9	2.2	1.7	58.7
Cr	0.003	7.5	7.6	8.3	8.8	8.3	8.9	9.7	7.7	52.0
Al	0.002	240	230	250	250	240	290	270	270	30.0
Cu	0.001	1.8	1.9	3.0	2.4	2.3	2.6	2.8	2.4	63.5
Zn	0.001	0.50	0.55	0.75	0.60	0.60	0.60	0.90	0.55	65.4
Mn	0.0004	1.2	0.7	1.2	0.10	1.6	1.4	0.9	1.0	54.9
Fe	0.0001	0.24	0.24	0.34	0.27	0.27	0.30	0.30	0.26	55.8
Cd	0.0001	0.24	0.24	0.34	0.27	0.27	0.30	0.30	0.26	112
Pb	0.00006	2.1	2.3	3.2	2.6	2.7	2.6	2.9	2.5	207
Co	0.00005	1.3	1.3	1.8	1.6	1.5	1.6	1.7	1.4	58.9
Ag	0.00001	2.3	2.7	3.6	4.3	3.7	4.0	3.8	3.9	108
Ti	0.00001	0.67	0.62	0.73	0.79	0.83	1.04	0.97	0.85	47.9

Table 2. Concentration of carbon dioxide species in mmol kg⁻¹. SW is the seawater concentration of Nozaki, 1994. 1 = Instant Ocean, 2 = Tropic Marin, 3 = Marine Mix, 4 = Reef Crystals, 5 = Rea Sea Salt, 6 = Kent, 7 = Coralife, 8 = SeaChem Reef Salt, CA = carbonate alkalinity (mequiv kg⁻¹), BA = borate alkalinity (mequiv kg⁻¹), TA = total alkalinity (mequiv kg⁻¹).

Compound	SW	1	2	3	4	5	6	7	8
Before equilibration with air									
TCO ₂	1.90	1.90	1.10	2.10	0.75	1.08	2.52	0.32	0.12
CO ₂ (x10 ⁻³)	9	8	0.9	6	0.2	2	20	0.1	0.1
HCO ₃ ⁻¹	1.66	1.65	0.70	1.74	0.34	0.81	2.32	0.16	0.084
CO ₃ ⁻²	0.23	0.24	0.40	0.35	0.41	0.26	0.18	0.16	0.036
After equilibration with air, pCO₂ = 35µatm									
TCO ₂	1.94	1.99	1.55	2.27	1.53	1.42	2.38	1.26	1.82
CO ₂ (x10 ⁻³)	11	11	11	11	11	11	11	11	11
HCO ₃ ⁻¹	1.73	1.78	1.41	2.02	1.40	1.31	2.10	1.17	1.65
CO ₃ ⁻²	0.20	0.19	0.13	0.24	0.12	0.10	0.27	0.08	0.16
CA	2.13	2.17	1.67	2.50	1.64	1.52	2.64	1.33	1.97
BA	0.10	0.10	0.072	0.11	0.12	0.099	0.15	0.21	1.07
TA	2.23	2.27	1.74	2.61	1.76	1.62	2.79	1.54	3.04
pH	8.18	8.21	8.10	8.26	8.11	8.08	8.30	8.04	8.17
Saturation (Ca x CO ₃)	2.06	1.71	1.16	2.16	1.12	0.90	2.81	0.81	1.62
Aragonite 0.89 x 10 ⁻⁶ at 25°C									

Pb, and Ag were near detection limits for the ICP. Note that the concentrations in artificial seawater are all approximately the same, probably reflecting the industrial processing methods for preparation of the salts. The exception is Li, where one sample is nearly 100 times greater than the other, which probably reflects relatively high Li in the source for MgCl₂. Thus the major differences between synthetic seawater appear to be related to their pH buffering system, which will be discussed below.

All salts vary from lot to lot so we only want to discuss and stress some general points about these mixtures. After mixing up salts, the seawater exchanges N₂, O₂, and CO₂ with air. N₂ and O₂ are inert in seawater, however CO₂ reacts readily with water to form bicarbonate (HCO₃⁻), carbonate (CO₃⁻²) and some hydrogen ions. This does not change the overall buffering capacity or “total alkalinity” of seawater, because there is an equivalent amount of anions and cations entering the water. It can however change the buffering

capacity of C species, or carbonate alkalinity. Carbonate alkalinity is an important quantity because it is directly related to the concentration of CO₃⁻². Carbonate (CO₃⁻²) is considered important because the saturation state of CaCO₃ as aragonite (the product of free Ca⁺² times CO₃⁻²) affects precipitation of CaCO₃.

Given the above initial conditions of these salts, what happens after equilibration with air? Generally, CO₂ is absorbed by water, increasing the total dissolved CO₂ in the water and decreasing pH. Hydrogen ions decrease the borate alkalinity and hence carbonate alkalinity must increase. The process continues rapidly until the partial pressure of CO₂ gas in the water is equivalent to the air, or 350 µatm of pressure. We can calculate this equilibrium knowing temperature, salinity, pH and the total C and total B concentra-

tions. Table 2 is a summary of the C species before and after equilibration with air. It is not surprising that most of the salts are less oversaturated with respect to aragonite saturation than surface seawater (Table 2) however it is rather surprising that two of the salts, #6 and #8, are only at saturation. These large differences in the CO₂ species and alkalinities may alter the basic calcification rates of organisms in these waters. We recommend proper addition of carbonate alkalinity, maintenance, and measurement for research use of these salts.

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