A pinch of **salt**

If oceanographers could distinguish by taste the various salts and minerals in the ocean, seawater would be a great deal easier to analyse. The scientists would sip from their sample jars, swish the water across their palates then spit the water back overboard, licking the residual salt from their lips as they nodded in agreement and exclaimed, 'Ah, yes, a fine example of North Atlantic 35.' Or would they? Perhaps the flavour of dissolved carbon dioxide might linger a moment in their mouths, or the tips of their tongues would find a bit of calcium carbonate chalking the back of their teeth. Such oddities would tell them that the water was not like the usual North Atlantic vintage[6]

Rather than taste seawater to determine its salinity, oceanographers electrocute their samples and measure how easy it is for the electricity to flow through the water. This measurement of conductivity accounts for the electrolytes from dissolved salts but misses other dissolved material in seawater. The conductivity method, or 'Practical Salinity Scale,' has been used by marine scientists since 1978. UNESCO incorporated the scale into the 1980 equations for calculating the density of seawater.

Now, a more accurate way of identifying 'Absolute Salinity' everywhere in the ocean has been devised and incorporated into a Thermodynamic Equation of Seawater. The new equation is set to become the next oceanographic standard as of 2010, after becoming an industrial standard last year. Any company interested in providing drinking water for desert cities near the coast, for example, will use the new method of calculation in building seawater desalination plants. The thermodynamic equation will also make climate models even more accurate than at present. On 24 June, experts attending the 25th assembly of UNESCO's Intergovernmental Oceanographic Commission (IOC) in Paris recommended that the entire oceanographic community adopt the thermodynamic equation and the use of Absolute Salinity.

'I was not familiar with seawater 20 years ago,' says Rainer Feistel of the Leibniz-Institut für Ostseeforschung in Warnemünde (Germany). But the mathematician and physicist had a good handle on energy conservation, thermodynamics and the maths behind complex systems. In the late 1980s, after nearly a decade in Berlin, Feistel moved back home to the Baltic Sea region and started applying his skills to oceanography. The equations he found himself navigating worked fine for the open ocean but developed inconsistencies in regions that were strongly influenced by river drainage, evaporation, precipitation or extremes in temperature. 'As you go to points where there are sensitivities, it's a real mess,' Feistel says. The Baltic Sea was one such region. 'I was surprised,' he says. 'There was a missing mathematical component, a "Gibbs function" which physicists had determined for all sorts of various fluids, except apparently seawater. 'Named after American mathe-matician Josiah Willard Gibbs (1839–1903), the 'Gibb's function' defines a fluid in terms of its energy and heat transfer, or thermodynamics.

Water warmer than that above it will rise, just like a hot air balloon rises above the cooler, denser air surrounding it. That is why freshwater from rivers and rain will float on a calm surface and why cold or salty water tends to sink

What's in a salt?

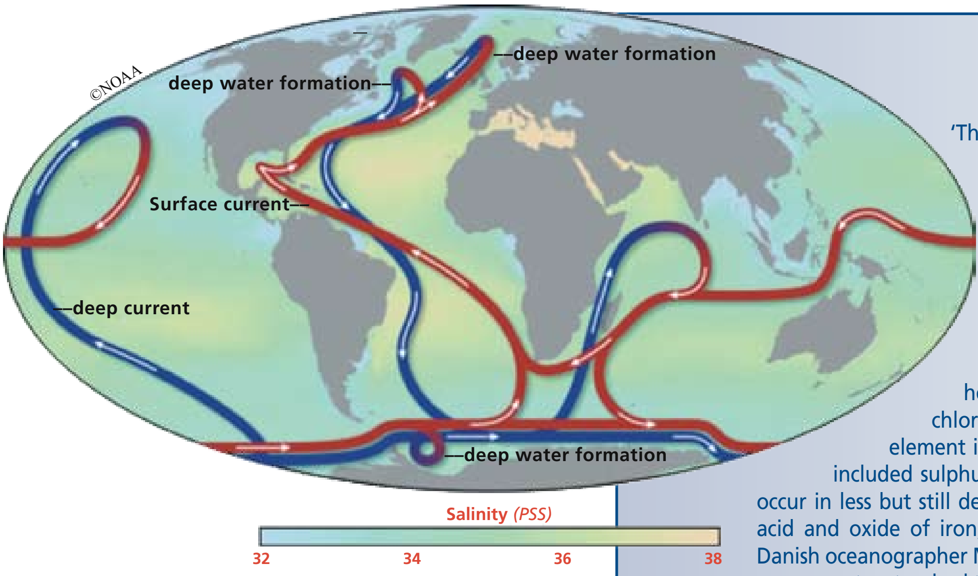
'In chemistry, any positive and negative ion bound together is called a salt,' explains molecular geneticist and chemosensation (taste and smell) expert Hiroaki Matsunami of Duke University in the USA. In the ocean, salts dissolve into free-floating negative and positive ions, also known as electrolytes. These charged particles are what make it possible for electricity to flow through water. The same ions that make up the salt used in foods – sodium (Na^+) and chloride (Cl^-) – account for more than 86% by weight of the 11 major ions in the sea and are what gives the ocean its salty taste. Dried, these ions form table salt and get sprinkled over food.

After chloride and sodium, the ocean's next most common ions are sulfate (SO_4^{2-}) and magnesium (Mg^{2+}). How would the ocean taste if these ions were more common? 'I tasted magnesium sulfate and it tasted really bad but I wouldn't call it bitter,' Matsunami says of the ingredient used in bath salts.

For a century, oceanographers calculated salinity based primarily on measurements of the most common salt ion: chlorine (*see box overleaf*).

The shortfalls of the conductivity method

The conductivity method established in 1978 improved accuracy, as it tracked all the ions in the sea and not



This map measures the equivalent parts of salt per thousand parts of water in the world's oceans, using the Practical Salinity Scale. It also shows the path followed by the ocean conveyor belt, with the warm surface currents in red. The ocean conveyor belt is driven by differences in seawater density

The search for salinity

'The exact chemical composition of seawater is unknown at the present time,' says Frank Millero of the Rosenstiel School of Marine and Atmospheric Science at the University of Miami in Florida (USA). It is not for want of trying. Marine scientists have been searching for the 'magic formula' for measuring salinity for over 150 years.

As early as 1865, Danish marine geochemist Georg Forchhammer found 27 different substances in seawater he sampled from different regions of the ocean. 'Next to chlorine, oxygen and hydrogen, sodium is the most abundant element in seawater,' he wrote. Other major substances he found included sulphuric acid, soda, potash, lime and magnesia. 'Those which occur in less but still determinable quantity are silica, phosphoric acid, carbonic acid and oxide of iron,' he concluded. His tables were used until 1902 when Danish oceanographer Martin Knudsen filtered and distilled North Atlantic water as a seawater standard that all marine scientists could use to calibrate their instruments easily and compare their samples from around the world with a control.

In the 1930s, the introduction of instruments that could measure seawater's electrical conductivity set sailors scrambling to determine whether chemical analysis or the new physical analysis worked better to determine salinity. Conductivity won and by the mid-1950s, deploying a rosette of sampling tubes equipped with conductivity, temperature and depth recorders (CTDs) was becoming a routine part of oceanographic cruises. To maintain consistency, a change to the international standard for seawater was made in 1978 that allowed oceanographers to compare conductivity to a Practical Salinity Scale.

Unlike the Practical Salinity Scale, which accounts only for ions, the new Absolute Salinity will incorporate non-electrolytes using tables that account for how these additional substances vary region by region. Once again, the latitude and longitude at which the seawater samples are taken will play an important role in calculating salinity.

just chloride. But calculating salinity from conductivity, as opposed to old-fashioned chemical analysis, required sacrificing the definition of salinity. This is because conductivity measures only free-floating ions or electrolytes, the same dissolved salts that are found in power drinks. In fact, any non-conductive material, such as dissolved silicon dioxide and carbon dioxide, 'is simply ignored' when it comes to practical salinity, Feistel says.

The Baltic Sea is a prime example of seawater with an unusual composition, far different from the North Atlantic standard. It has electrolytes that conduct electricity but they are not the typical sodium chloride. The vast rivers of Poland and Russia drain into the Baltic Sea, bringing with them dissolved calcium carbonate ($CaCO_3$) from the limestone river beds. When $CaCO_3$ dissolves, it dissociates into the conductive ions Ca^{2+} and CO_3^{2-}. These ions prefer to be bound together but, if they can't be, they will often bind to other molecules floating in seawater, changing the mass of the molecules and wreaking havoc with conductivity measurements.

The switch to Absolute Salinity

Feistel's re-evaluation of the 1980s equations provided seawater with a 'Gibbs function'. The previous mathematical equations for determining the properties of seawater had not accounted for water's ability to transfer heat from warmer to cooler currents. Nor did the old equations set a standard for comparing how difficult such a transfer of energy might be, based on the water's inherent pressure and volume. The thermodynamic equation of seawater chews up all of the old equations and spits out a neat new bundle of computer algorithms that modellers crave.

In 2010 for the first time, the algorithm for measuring salinity will incorporate more than dissolved salt into the conductivity conversion. Millero, who worked on the 1980 equation of seawater, and Feistel are helping to bring about the change. They have been working with modeller Trevor McDougall of the Centre for Australian Weather and Climate Research in Hobart as part of an international team established in 2005 by the Scientific Committee on Oceanic Research and the International Association for the Physical Sciences of the Ocean. They are incorporating the location of the conductivity measurements with chemical analysis from those regions into the new Absolute Salinity calculation. The team has also redefined how the properties of seawater are calculated using this new Absolute Salinity method and combining it with the principles behind thermodynamics to form a single new thermodynamic equation for seawater.

Ensuring any climate model is worth its salt

The fundamental properties of seawater – salinity, temperature and pressure, along with the freezing and boiling points, heat capacity, speed of sound and density – are intricately tied together. Being able to measure salinity is important, as salinity levels are indicators of climate change. They indicate how much freshwater is evaporating from the oceans. Parts of the Atlantic Ocean appear to be getting saltier, for instance. A possible explanation could be that trapped heat from higher atmospheric concentrations of CO_2 is causing more seawater to evaporate than before, leaving the salt behind.

Secondly, salinity levels affect water density. Density especially determines whether a current rises towards the surface or sinks towards the seafloor, as the denser the seawater, the deeper it will sink. Density depends on temperature, pressure and the amount of dissolved material in the water. Knowing the density of seawater is crucial to monitoring the Earth's climate. The ocean transports heat via currents collectively called the ocean conveyor belt in a process known as thermohaline circulation. In the Arctic and Antarctic Oceans, cool and salty waters sink to form deep water currents. Over thousands of years, these currents travel around the world until they reach areas of upwelling which bring them to the surface. Once at the surface, the sun-warmed, rain-freshened currents head back to the poles where the formation of ice allows the cycle to continue. A massive input of freshwater, such as from melting polar ice caps, can prevent the surface water from sinking and slow down or even stop the ocean conveyor belt, potentially causing great changes to the Earth's climate. 'Every climate model worth its salt depends on our ability to know if hot water goes up and cold water down, as well as how far and how fast,' observes Keith Alverson, head of the Ocean Observations and Services section of the UNESCO-IOC.

Several factors influence ocean circulation patterns: wind, rain, seafloor topography, the conditions of the surrounding water, as well as the moon and the rotation of the Earth. Ocean circulation models include all of these factors and the computer algorithms that generate the models take weeks to run. Climate change models, which incorporate the ocean's ability to transport heat, take even longer. 'To see what model works best, what fits with the Earth's climate record from the past then run the model forward a century or two can take the best part of a year,' McDougall says. To incorporate non-electrolytes into the equation for salinity then merge the various other equations for different seawater properties into one, McDougall's team has relied on theories from Josiah Gibbs. They are mixing 19th century theory with 21st century computer algorithms.

Based on what they have run so far, McDougall estimates the new equation will show a 3% change in how the ocean circulates heat from the equator to the poles. The other change he is noticing is a 0.5°C difference in the surface temperature of the equatorial Pacific Ocean in both the east and west. Off the coast of Peru, trade winds drive warm surface water away from shore and cold, nutrient-rich, deep water upwells to fill its place. The warm water pools further to the west, warming the air above it and increasing precipitation over Indonesia. During El Niño years, the reduction in the strength of the trade winds allows the warm, nutrient-consumed water to stay closer to the Peruvian shore. The winds push the rain only as far as the central Pacific and Indonesia experiences droughts.

The new thermodynamic equation for seawater allows models to account better for changes in density and for heat transfer as a result of rain falling on the Earth's surface. 'The main reason to do this work is to make these models as accurate as possible,' McDougall concludes.

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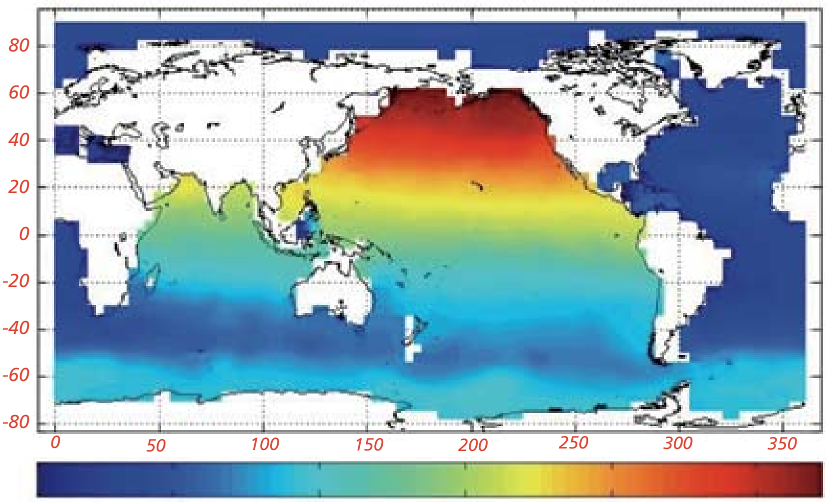

Difference in salinity, in grams/kilogram

Courtesy of Trevor McDougall and David Jacket, CSIRO, Australia

This map shows where the measurement of salinity is most affected by the new Absolute Salinity method (in grams of dissolved material per kilogram of water). Absolute Salinity takes into account all dissolved material and not just salts, unlike the Practical Salinity Scale. The deep red colour is accounted for by additional silicon dioxide in this part of the Pacific Ocean that the Practical Salinity Scale was not picking up. The darkest blue shading indicates little or no change

6. *Water from the North Atlantic with a salinity of about 35 parts of salt per thousand parts of water has traditionally been used as a control for comparing other water samples. It is composed primarily of sodium chloride*

7. *Freelance science journalist working with the UNESCO-IOC. Author of* Marine Science: Decade by Decade (2009), *a history of 20th century oceanography: c.reed@unesco.org*