

Salty Seas – Video Tutorial

Everyone knows that seawater is different than freshwater most noticeably because it tastes salty. But is all ocean water equally salty? How do we measure it?

Salinity is a ratio of the total number of grams of dissolved ions present in a set number of grams of seawater. If we measured the number of grams of dissolved ions per 100 grams of seawater, the ratio would be parts per hundred or a **percent**. For seawater, we typically measure salinity as a number of grams per thousand grams of seawater. That makes it parts per thousand or **permil**. Notice the unit designation for permil looks very similar to the one for percent. It just has two zeros in the base instead of one. Note: mil here does not mean “million”, it means “thousand” like in the SI system of units.

Let's see what that looks like for the average salinity of seawater, which is 3.5 grams of dissolved ions per 100 grams of seawater – 3.5%, which is exactly the same as saying 35 parts per thousand or 35 permil. So 35 permil = 3.5 percent. Why use one over the other? The standard for the oceans is to use permil, so we can minimize the use of decimal places. -

Let's review the chemical reaction that takes place when a solid with ionic bonds is dissolved in water. Here we see a block of rock called **coquina**. It is made entirely of shells that have cemented themselves together in a nearshore beach environment. The shells are made of **calcium carbonate** – and the bond that sticks the calcium ion to the carbonate ion is an **ionic bond**, as discussed in last week's tutorials. Water's hydrogen bonds can attack the outer ions in this mineral and draw them off, breaking the ionic bonds and surrounding the ions in hydration spheres. When ionic bonds are broken, one of the ions is left with extra electrons, so it has a net negative charge. The other is missing electrons that it gave away originally to form the bond. That ion has a net positive charge. We call the positively charged ion formed during dissolution a **CATION**. The negatively charged ion is called an **ANION**. When salt crystals dissolve, we end up with a sodium cation and a chloride anion.

Pause now.

This image shows you 1 kilogram of water (1000 grams), and what 35 pieces of that look like in comparison. You can see here that for average seawater of 35 parts per thousand salinity, 19.10 of those 1000 grams are dissolved chloride ions – Cl-minus. 10.62 are sodium ions. 2.66 grams are the sulfate ion. 1.28 the magnesium ion. 0.40 grams calcium ions. 0.38 grams potassium ions. And all other dissolved ions in the ocean make up less than 0.25 grams of every 1000 grams of average seawater.

We talked in the last week's tutorials about how these ions are dissolved by water. Now they are present as ions hydrogen bonded to water molecules that trap them in hydration spheres, so they can't rebond, form a solid, and settle out, which we call precipitation. Notice from a review of the major dissolved ions in seawater that the highest is chloride, and sodium is lower in concentration. Why is that? If chloride came only from dissolving salt, sodium chloride, the two should be equivalent. But in fact there are many solid chloride minerals in the world including magnesium chloride and potassium chloride. When all these minerals dissolve they release chloride. But there's also another reason: residence time.

Here is a table of the **residence times** for a few ions that can be found dissolved in the oceans. Remember from the first part of this class, we defined residence time as the length of time an ion, atom, or molecule resides in a reservoir on average before it is removed. In this case, the reservoir is the ocean. Ions arrive through a variety of sources and are removed primarily through precipitation and sedimentation. So you can see from this list that the ion with the longest residence time is chloride, followed by sodium, magnesium, potassium, sulfate, and calcium. What do you notice about this list so far? It's almost exactly identical to the list of major ions in the ocean, in the same order. So the primary reason that chloride is found in the highest abundance in the oceans is because it has the longest residence time. That makes it very hard to change its composition! And that's also the explanation for why these ions are found in the same proportion throughout the oceans. The mixing time of the ocean is only 1,000 years. If something has a residence time of 1 million years, it will have been well mixed everywhere! We call ions that are found in the same proportion or percentage everywhere in the oceans **conservative**.

Ions that have short residence times and that are readily and easily removed from certain locations of the ocean are called **nonconservative**. Nonconservative constituents have short residence times, so they are found in low abundance. We can see that iron has a residence time of only 140 years – much less than the ocean’s mixing time. Manganese has a residence time close to the mixing time. Both iron and manganese are considered trace constituents. Their composition can change quite substantially due to local phenomena, such as industrial waste dumping or overuse by marine organisms. Once the existing algae are eaten or die and rain down to the bottom of the seafloor, they take their iron with them, and the surface waters are left with no iron until mixing brings in more.

Pause now.

About **nutrients**. We first mentioned these back in the chapter on sediments, when we discussed how nutrients, like nitrate and phosphate ions, need to be dissolved in abundance in the water in order for autotrophic plankton to survive. Heterotrophic organisms get their nutrients from their food. Autotrophic organisms make their own food, so they need another way of gathering in their bodies’ building-block material. In the oceans, autotrophs are surrounded by water, and they can absorb the nutrients they need from this water directly. However, the nutrients need to actually be IN the water. Rivers are a major source of nutrients, especially around urban and agricultural areas where the fertilizers (or nutrients) used to help plants grow are carried into the streams by rainwater. Once the marine algae take up these nutrients, the water becomes depleted. When the organisms die, they fall to the bottom of the seafloor, where decomposition returns the nutrients back to the water. However, these nutrients are now trapped in the deep water layer. Last week we discussed the process whereby deep water is formed by high-density cold polar water descending and spreading across the world’s oceans. The surface waters that are warmed by the sun created a separate layer that sits atop. These two layers don’t mix, and the boundary that sits between them is called the pycnocline. Bottom line: the nutrients are trapped at depth and can’t return to the surface until a process called upwelling occurs. We’ll talk in a future chapter about that process. Without upwelling, the surface water is depleted in nutrients, and no more autotrophic organisms can grow until new nutrients are added (like during large rain storms that fill rivers with more fertilizer). Nutrients, therefore, are nonconservative constituents of seawater’s salinity. Their concentration can change rapidly and thus varies greatly from one location to another in the ocean. Nutrients are a limiting factor in the growth of marine algae. Without nutrients, there are no phytoplankton or seaweeds, and that location can be viewed as a marine desert.

Pause now.

So where do the ions in the oceans come from? The primary **source** is rivers. Secondary sources include atmospheric droplets of acid rain, waves, weathering coastal rocks, and hydrothermal circulation at seafloor spreading centers. Of these, the primary source is rivers. Once within the ocean **reservoir**, these ions are moved around through various processes. Currents mix them. Marine organisms take them up for their own needs and then return them back during decomposition. And small particles in the ocean, including microorganisms, can act as precipitation surfaces. The ions will adsorb to these surfaces and precipitate solid mineral layers atop the grains (like minerals coating the inside of plumbing). The **sinks** of this system – the ways to get ions out – are to do the opposite of dissolution – remove the hydration spheres that surround the ions and allow the ions to get back together and bond. This precipitation process happens wherever seawater is evaporated in shallow seas in warm climates – like in South San Francisco Bay’s salt ponds – or where the water becomes supersaturated with ions. When that happens, the water molecules have trapped too many ions and there aren’t enough water molecules left to separate them, so the ions come back together and bond. We call the concentration at which there’s no more room for new ions the **saturation concentration** (the water is saturated with ions and can’t hold anymore). As more ions are added to this water usually by an outside source adding them directly, the water is considered **supersaturated**, and precipitation will occur on any available solid surface. The precipitate minerals will collect as sediment on the bottom of the seafloor, where they get buried over time and are removed from the reservoir. Precipitation is the main way to remove dissolved ions. We discussed this process previously in the chapter on seafloor sediments, specifically when discussing hydrogenous sediments precipitated from seawater. Another precipitation location also previously mentioned is hydrothermal circulation at seafloor spreading centers. As the seawater descends through cracks around rift valleys, salts precipitate and are left behind in the cracks, while new metals are leached out of the rocks and enter the water.

Let's return to the surface. Interestingly, if you look at the salts that precipitate when seawater is evaporated in shallow lagoons, you can see that the salts are made out of the major elements in the ocean. The salt we use on food, NaCl, represents 70% of the precipitates. Other salts include Mg and K sulfates and chlorides. Gypsum, a calcium sulfate, is an important product mined for its use in making drywall. And calcium and magnesium carbonates are important ingredients in cement. Again, these salts are all mined in South San Francisco Bay. You can see the colored evaporation ponds that were created by the corporations that first used the South Bay for this purpose. The colors come from bacteria that live in these ponds. While few of these are still active, most are still kept separated from the rest of the South Bay. The water down there is close to the salinity of seawater – it's 30 parts per thousand – primarily because of the low river input, but also because of the shallow depths and the high evaporation rates. The waters in the salt ponds, however, are many times greater in salinity and are toxic to the organisms that live in the surrounding waters. Billions of dollars are necessary to reclaim these areas of the environment, and wetland restoration is already in process in many of them.

This table shows the main ions dissolved in seawater, their concentration in the oceans, their residence times, and their concentrations in their primary source: rivers. Notice how low their abundance is in the freshwater of rivers. Yet, they ARE present there, even if in low abundance. Remember, the oceans have been around on this planet for 4.4 billion years. During that time the rivers have carried small amounts of ions to the oceans, then the water has evaporated, gone back to the land, and picked up a few more. It's like adding pennies to a bank. One penny in your pocket doesn't seem like a lot. But if you carry it to your bank and leave it there every hour of every day for your entire life, you'll never be accused of being someone with lots of money in your pocket. But at the age of 70 there will be \$6,132 in your bank account. Imagine you could do this for 4.4 billion years! You'd have \$385 billion dollars!

Consider visiting the salt ponds of San Francisco's South Bay, where you can get up close and personal with the salts produced by seawater evaporation. Closest entry from San Francisco? Bedwell Bayfront Park, at the north end of Marsh Road in Menlo Park.

Pause now.

For more information and more detail, continue on to the next video in this series.

[End credits]

Seawater Chemistry Series:

Part I: Salty Seas

Part II: Measuring Salinity

Part III: Carbonated Oceans

Part IV: Salinity's Impact on Marine Life

Salty Seas

Geoscience Video Tutorial

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City College of San Francisco

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