12.742 Marine Chemistry
Problem Set 3 Answer Key

1. This question requires you to do a 'back of the envelope'-type calculation. This means assumptions galore! But you have to support them…

a) For all the calculations see the Excel file. The assumptions that I made to solve this problem are as follows:

- pure solids precipitate
- DIC species are always in equilibrium with the atmosphere, and so are never limiting (acid/base reactions are extremely fast, and I think that relative to evaporating the entire Med. Sea, the gas exchange reaction will be also be fast)
- Density of seawater = 1025 kg/L
- Med. Sea is well-mixed/homogenous
- about half the Ca^{2+} precipitates as $CaCO_3$ and half as $CaSO_4$ (really determining this would be exceedingly difficult, involving rates of precipitation and changing equilibrium balances – this approximation will give us a good guess, but any good guess will work)
- the rest of the SO_4^{2-} will precipitate as $MgSO_4$, and the rest of Mg^{2+} will precipitate as $MgCl_2$

Remember that $MgCl_2$ has 2 Cl- ions! Mg^{2+} is still limiting, but this still needs to be checked!

b) This estimate will inevitably be complicated by impurities in the salts, inhomogeneity, non-conservative behaviors (especially in areas of anoxia, rivers, etc.), the actual kinetics of precipitation (especially for Ca-species).

c) To answer this question we need to know some basic facts about the Med. Sea:

Surface Area: 2.5×10^6 km^2 = 2.5×10^{12} m^2
Volume: SA*depth = 6.25×10^{15} m^3 = 6.10×10^{12} kg

Every time the Med. Sea evaporates about 6.10×10^{12} kg of seawater is removed. The salts precipitate and form salt beds (up to almost 50 m thick!), but the water is basically distilled out into the rest of the ocean. So, evaporating the Med. Sea is like diluting the oceans with additional freshwater. The rate of the additional freshwater input will equal the rate of Med. Sea evaporation.

We need to understand the rate of 'output' (the dilution due to Med. Sea water) and the rate of input (rivers) of Cl- and Na+ to the oceans. If we know that the residence time of Cl- and Na+ is 70×10^6 years and the volume of the oceans is 1.35×10^{18} m^3, we can then calculate the input by:

Input (i) = $[i]*V_{ocean}/\tau_i$

And we can calculate the total of moles removed of Na+ and Cl- by knowing the volume of the Med. Sea and the concentration of Na+ and Cl- within it. In order to get an output rate, however, we need to know the rate of evaporation. According to Matsoukas et al. (2005) that rate is approximately 3.75 x 10^{12} m^3/y, which means that it takes 1600 y to evaporate the Med. Sea.

i	$[i]_{ocean}$ (mol/m^3)	Input/year	$[i]_{Med.}$ (mol/m^3)	Output/year	Out/in
Cl-	560	1.08 x 10^{13} mol	575	2.14 x 10^{12} mol	20 %
Na+	458	8.84 x 10^{12} mol	495	1.84 x 10^{12} mol	21 %

On a yearly basis the output rate is about 20%, which is definitely significant! Once the Mediterranean was isolated the salinity of the oceans would start to fall. Once the Mediterranean was completely evaporated the salinity would stabilize. Also, what would the new ocean concentration of Cl- and Na+ be? Well, we removed 3.43 x 10^{15} mol of Cl- and 2.94 x 10^{15} mol Na+ with one evaporation of the Med. Sea. In the oceans (at the concentrations and volume used above) there exists 7.56 x 10^{20} mol Cl- and 6.18 x 10^{20} mol Na+, so the new inventories would be 7.56 x 10^{20} mol Cl- and 6.18 x 10^{20} mol Na+. So the overall change would not be very much. To change the Cl- and Na+ by 1 psu we would need to evaporate the Mediterranean about 6150 times (see excel workbook).

2. a and b) see excel workbook

c) This part is graded individually for each of you. There are obviously more than 2 circumstances where the ions do not behave conservatively.

3. a) The Arabian Sea is a famous example of wind-driven seasonal upwelling. The problem was based on a paper from Deep-Sea Research (Lee et al., 2000). It has been suggested that Eckman Pumping was the main feature, but this paper provides a different viewpoint. Remember: Eckman pumping refers to when differences in windstress cause up- and down-welling, coastal up- or down-welling occurs when Eckman *transport* moves water laterally off or towards shore.

Eckman Pumping

During the SW monsoon Eckman pumping drives upwelling to the N of the windstress maximum, and downwelling to the S of that point, resulting in shallower mixed layers to the N and deeper to the S. During the NW monsoon the windstress gradient is much smaller and Eckman pumping is much less important.

Non-Eckman Influences: Turbulence and Coastal Up/Down-welling

However, turbulent mixing can have additional, and sometimes contradictory, effects. The turbulent mixing can deepen a shallow mixed layer, or enhance an already deep mixed layer, and turbulent entrainment can overwhelm the effects of Eckman pumping. The strongest vertical effects are the upwelling and downwelling that occur as a result of the alongshore winds. The lateral advection of coastal upwelled waters can influence mid-basin areas and drive primary production in a much great area than expected.

NE Monsoon

Convective overturning (driven by differences in windstress and surface cooling) and horizontal advection are the most important factors. Eckman pumping drives weak downwelling and modulates wind-driven (turbulent) mixing.

SW Monsoon

Wind-driven entrainment, coastal upwelling and horizontal advection are the main players in this regime, overwhelming any effects of Eckman Pumping.

b) Coastal upwelling will occur in the SW monsoon. The upwelling brings deep, cool and nutrient-rich waters to the surface, and then removes them to the mid-basin. This results in an area of extremely high productivity and low temperatures.

4. a) (A great place for review of the concepts covered in this question is Chapter 2 of Sarmiento and Gruber.)

Just as with wind, water flows along lines of constant pressure, which in water is density. It is much easier for water to flow along an isopycnal than across isopycnals. Eckman transport drives the large scale surface circulation patterns: the western boundary currents, equatorial upwelling, gyre rotation are all the effects of the large scale wind patterns that we spoke about in class. The combination of the Trades and the Westerlies results in the gyres. Eckman transport piles water up in the subtropics, and then, as it tries to flow down the slope, the earth's rotation forces the water to travel at a right angle to the slope. That is how the rotation is established. The earth's rotation also results in the strengthening of the current on the west of the gyre (the western boundary currents). The opposing action of the N and S Trades results in equatorial upwelling. These are the major features that we can see in the given figures.

On the density plot the flow of water is not back and forth along the single dimension that we see, rather it is in and out of the page. In the northern hemisphere the gyre rotates to the right, and the southern gyre rotates to the left. Therefore on the density plot we are given the water is flowing out of the page at the northern half of the northern gyre, into the page at the southern half of the northern gyre, into the page in the northern half of the southern gyre and out of the page in the southern half of the southern gyre. I think this is an example of when a picture is worth a thousand words – and your drawings are far better explanations than my insufficient words.

In the far south is the Antarctic Circumpolar current, which flows from west to east all around Antarctica (yes, I realize the description is a bit redundant given the name, but I wanted to get in the west to east part).

The other thing that we can see is where upwelling occurs at the equator. On the density plot you can see where the isopycnals deepen in the gyres (diffuse downwelling) and bend upward at the equator. At the equator is the equatorial counter-current. Think about this – the wind drives the flow of water towards the west. But there must be a 'resupply', and if flows eastward along the equator, between the two tradewind-driven westward-flowing currents.

b) The different water masses are surface water, Antarctic Bottom Water (AABW) and Antarctic Intermediate Water (AAIW). AABW flows along the bottom of the Pacific, eroding as it moves northward. It is composed of Circumpolar Deep Water (CDW) and North Atlantic Deep Water (NADW), which gives it a very high salinity. It returns to the south as North Pacific Deep Water (NPDW), never having come in contact with the atmosphere, and flows above AABW. Above the NPDW, AAIW appears as a salinity mid-depth low from about 500-2000 m through out much of the Pacific. In the North Pacific there is some intermediate water formation (see the outcrop of intermediate depth isopycnals, and lines of constant S and T) which is termed (yes, you guessed it) North Pacific Intermediate Water (NPIW). Finally, we have surface water that has higher temperatures and salinities due to heating, mixing, evaporation, etc. We can make out the mixed layer depth as areas of high gradients: density, salinity, temperature, etc.

c) (Thanks to Naomi for some clarification on one models bomb radiocarbon penetrates in the Pacific! And for general editing and comments.) The anthropogenic tracers that we use to discriminate water masses have only been present for about half a century. This is a very small amount of time relative to thermohaline circulation (a few thousand years). Therefore, both ^{14}C and CFC's are primarily only in surface water. However, in the high latitudes you can see how they are beginning to be incorporated into intermediate and deep waters. Radiocarbon is especially interesting. Tracing the bomb-spike allows us to identify waters that have been influenced by anthropogenic activity; this is particularly easy in the surface waters. The radiocarbon age of the deep waters, unaffected by anthropogenic activity, reflects the time since these waters were last at the surface (this is one way to calculate the turn-over time of the oceans). Unfortunately, mixing between 'hot' surface waters and 'cold' deep waters complicates the ^{14}C signal of intermediate waters and makes it very difficult to interpret. In highly convective regions, such as deep and intermediate water formation regions, bomb radiocarbon penetrates much deep than it does in stratified regions For example, in the gyres, where there is high stratification, the surface waters have a $\Delta^{14}C > 0$ due to the input of bomb carbon. In comparison, weak stratification in the Southern Ocean results in deep convection that mixes surface and deep waters. This mixing 'ages' the S. Ocean, resulting in the $\Delta^{14}C < 0$. If you compare the Δ14C figure with the Salinity figure you can clearly see that 'hot' surface waters have been incorporated into the AAIW. This is because AAIW forms from surface waters in the S. Ocean. The rapid mixing in this region between surface and deep waters results in an AAIW ΔC^{14} signal that is less than the value of stratified surface waters. We can see the 'oldest' $\Delta^{14}C$ water is NPDW, which makes sense, since it has never 'seen' bomb radiocarbon. Therefore, while most of the bomb radiocarbon is present in surface waters, a small fraction has mixed into AAIW and AABW. Separating bomb radiocarbon from natural abundance radiocarbon requires numerical models. This is a calculation that many oceanographers make when trying to determine the age (since formation) of a water packet.