DIERDRE TOOLE: Today we're going to be talking about the global phosphorus cycle. And I'm going to start out by saying I think that it's actually probably the simplest of the biogeochemical cycles, because there isn't really a gaseous form of phosphorus. So a nutshell, what the cycle is, is this first slide. I mean, we can't just leave it here, obviously. But basically, what happens is we have phosphorus minerals and varied phosphorus in the continental crust.

This is leached and eroded. It ends up in the terrestrial biosphere where it's processed a variety of different ways. Once you have the different components in the terrestrial biosphere they're transported by rivers to estuaries and then in the oceans. There's also some physical transport via wind into the ocean. It gets to the ocean. It's cycled by the marine biota. It's buried, becomes part of the marine sediments, and then those sediments are subducted and then ultimately uplifted to continental crust. So that's it in a nutshell, small little nutshell, the phosphorus cycle.

But what I'm going to do today is I'm going to go through each of the biogeochemical cycling and the different reservoirs and look at some of the inventories, just so we get an idea of the different scales we're talking about and some of the timescales in terms of turnover times and reservoirs, and then a little bit at the end, interactions with other biogeochemical cycles.

So why phosphorus? Why phosphate? Why do we care? And what I'm showing here these are world ocean atlas surface distributions of phosphate in millimoles of phosphate per cubic meter, and sea surface nitrate in millimoles of nitrogen per cubic meter. And what some models have suggested and various individuals have suggested is that phosphate is a limiting nutrient on geological timescales. It's also really a limiting nutrient for biology. Without it, they can't do primary production.

And so given that, we really need to constrain the phosphate budget globally. And to do that, we need to understand the factors that influence its oceanic inventory. And so just to address the age-old question are oceanic phytoplankton phosphate or nitrate limited. And that's something you'll hear people argue about ad nauseam. I think the jury's still out. It depends on timescales and it depends on environments.

But there's two general viewpoints I would call them. And the first is the geochemist viewpoint. And essentially this consists of the fact that nitrogen, your loading of nitrogen, it can be topped off. If you don't have enough nitrogen, you can have diazotrophs, which can fix inorganic dianitrogen into organic forms, which are bioavailable. And phosphorus doesn't really have a comparable source like that because we don't have any gaseous forms and there aren't really the same of biological pathways. So geochemists tend to think of it as phosphate limitation.

But the biologists' viewpoint, which is primarily observationalist and experimentalist, when they go out in the field and they look at field data and they do nutrient addition type experiments and bottle additions on deck at sea, they generally find when they're working with these natural assemblages that phytoplankton are more nitrogen stressed than phosphate stressed, and they respond better to nitrate additions than phosphate additions.

And so to give a little bit of information on why some of these hypotheses started, this is the Levitus climatological data. And we have phosphate at the surface, at various depths. You can see the depths of the different colors indicated with these, I guess brownish spots being the shallowest, and then the pink being the deepest, versus nitrate concentrations. And this is the Redfield ratio line, the 16-to-1 ratio line.

And you can see that in a lot of cases they do fall below that line. So that actually the nitrate is drawn down before the phosphate. And so there have been various modeling exercises that have been trying to address this. And one of the ones that I particularly like is Tyrrell 1999, where their final conclusion was that nitrate can be limiting. When you look at the ocean right now, nitrate can be limiting. But on the longer time scales, phosphate is ultimately limiting.

Because when you change the amount of nitrate through nitrogen fixation, you also are going to change the comparable pathways, the loss pathways. Whereas phosphate, you can't do that. So if you change the amount of phosphate loading, you're going to directly change the amount of oceanic productivity. So it's really important for us in long term carbon dioxide, organic carbon export, to understand the inventories of phosphate and how it cycles.

And so this is a figure that's going to come up a lot today. I'm going to say right off the bat that there's a lot of uncertainties in the numbers in this figure. Right now, if you look at it, import balances export, and it looks very clean. But we do have, and I'll talk about this a little bit today, estimates that don't make these estimates look as clean as they do in this figure. So that's just something to keep in mind. These are just estimates at the time this figure was made.

And so again, just to reiterate that the atmosphere is not a significant reservoir of phosphorus at all. We do have an atmospheric box here. But that will correspond to aeolian dust input, which I'll talk about later. And we should know that phosphate only occurs in one oxidation state. And that's the +5 oxidation state which is orthophosphate which is PO4 3-minus.

And so as far as this figure is concerned, all the inventories are in 10 to the 12th moles, and they tend to be in the bold where the arrows correspond to fluxes which are 10 to the 12 moles per year. And so we're going to start out with the lithosphere and follow the cycle all the way around.

And so what we know right now is that, as with carbon, the lithosphere is the largest reservoir of phosphate. It happens to be about the 10th most abundant element in the lithosphere, and is about 0.1% by weight of the crust. And within this reservoir, most of the phosphate is in these phosphate minerals known as apatites. And this is their chemical formula. And they're either a fluorine, which is a fluorapatite, an OH ion which is hydroxyapatite, or the chlorine ion, which is the chlorapatite. This is their pure form.

But their most common form when you look in the lithosphere, actually is this carbonate fluorapatite in which carbonate partially substitutes for phosphate. And the way this works is that just rather than having the phosphate ions, the ortho phosphate ions, you have carbonate ions substitute in their place in their crystal structure. But the one thing that's of interest is that the more carbonate ions you have, the more fluorine ions you're actually going to need relative to the phosphate ions to balance out the charges. And so these are just examples of what some really nice pure apatites.

But they're really interesting because these apatites are not only in these rocks. There's actually quite a bit cycled biologically and cycled anthropogenically at this point. So it's important to know those. And the first is the hydroxyapatite, which is the OH version. It's produced by biota. So we have it in our teeth and we have it in our bones. So there's a lot of it around.

There's also this fluorapatite, which is currently used in fluoridated water in toothpaste. And basically the reason the way that works is that you can exchange any OH ions in your teeth for the fluorine ion. So if you think about the amount of residential cities that are fluoridating their water, there's actually a fair amount of this stuff floating around. They also mine a lot of the sedimentary deposits of these apatites, and they get phosphorite out, which can be 18 to 40% of phosphorus by weight. And they use that in fertilizer.

So a lot of tobacco fields are fertilized with this because I guess it changes the way it tastes, but essentially, as with most fertilizers, there's always that runoff issue, which is going to change the input to the ocean. So we have to be aware that there are some significant anthropogenic sources here.

AUDIENCE: There's also a large anthropogenic-- there's a lot of phosphorus in detergents.

DIERDRE TOOLE: Yeah, detergents have a lot. There's just a lot of phosphorus floating around anthropogenically, these are just in terms of the apatite minerals. But yeah, there's a huge influx from just urban runoff.

AUDIENCE: Has there been a push to get rid of the phosphorus in detergents? I thought I heard--

AUDIENCE: Well, it's hard to do residential. People have been pushing it. The environmental groups are pushing a lot for using non-phosphorus detergents when you go camping and out in the wilderness. But I don't think it's been very successful for replacing it for industrial and residential usage.

DIERDRE TOOLE: Yeah. Yeah, I mean, camping ones exist. I mean, there's all those camp suds.

AUDIENCE: But for a lot of freshwater bodies, phosphorus eutrophication is a big problem.

DIERDRE TOOLE: It's a huge issue.

AUDIENCE: I know that local councils and stuff are trying to push it to that's a really small--

DIERDRE TOOLE: Yeah, it's just like anything. I mean, it takes a lot of momentum and development of actual good products to replace our current ones. But again, it's just something to be aware of that it is a very significant source of phosphorus to the ocean. And it's also going to very much throw all our nice inventories, which are a nice balance right now in these figures, out of whack.

So once we have all this phosphate in the lithosphere and it's uplifted, so it's on land and it's exposed, it's going to be subjected to weathering processes, which is what we talked about on Tuesday. And the weathering and erosion of these uplifted rocks produce dissolved, reactive phosphorus phases, and particulate inert forms of phosphate. And this is when those phosphate minerals are acted on by the acidic compounds. And a way to think about it is that the particulate, really the inert forms of phosphorus, they're not going to be cycled by biology. They're just going to be subjected to physical transport processes, which will ultimately deposit them in the ocean.

But it's really the dissolved phosphorus that we're more interested in the reactive form. And basically dissolved phosphorus, it occurs almost exclusively in this tetrahedral phosphate ions, and it has an acid base equilibria that it undergoes depending on the pH of the environment it's in. And so it cycles between four primary phases which range from phosphoric acid, dihydrogen phosphate, hydrogen phosphate, and then orthophosphate. And so what I have here is a diagram of the percent of total inorganic phosphate, and as a function of its chemical form, as a function of pH.

So if we look, for example, at freshwater systems, which we were just talking about, their pH generally tends to range from about 6 to 7. So you can see that the primary phosphorus form is going to be the dihydrogen phosphate. And that's in contrast to the ocean, which has a slightly higher pH on the order of 8.2. But there we're going to have primarily the hydrogen phosphate ions.

The dissolved phosphate is very reactive and it's taken up and cycled by the terrestrial biota. And it's extremely key for some of the most key functions of higher life forms, and life forms in general. I mean, it produces these organophosphates and phosphate esters. And the most important of those are things that are very obviously we know that are DNA and RNA or ATP in the phospholipids.

And just to stress how important phosphate in these, for example, DNA, the backbones of the chain, which is what the nucleotides actually connect to, are these alternating chains of like deoxyribose with a phosphate. And so these form the backbones of the chains of DNA. RNA is the same. It's just a ribose and then the phosphate ion. So they're pretty key to life. I mean you can't have primary production, and reproduction, and higher life forms without these.

It's also a key element in ATP, just so you guys know, it's a chemical currency of energy in life forms. And you see you have your sugar group and your ribose group. But then you have your three adenosine triphosphate. You have your three phosphates at the end. They're also really important in phospholipids, which are an important constituent of cell membranes. And basically, you have these phosphate esters which are produced with fatty acids. They're these hydrophobic phobic carbon chains.

And then on the end, they have polar head groups. I think if you've seen pictures of cell membranes, you have the polar head groups, and then you have the fatty acid chains all pointing in. And phosphates is a key element in the polar head group.

But just trying to understand what they happen to, and we're still going back to where we were talking about in terms of we have the uplift and erosion. And so we have these exposed minerals. And then they've been by various weathering processes turned into dissolved phosphate concentrations. We need to know what happens to that dissolved phosphate. And we know that actually the dissolved phosphate concentrations in soil are really low. And that's because there's a lot of iron and aluminum in soil. And the dissolved phosphate will actually adsorb onto these, forming iron and aluminum oxides, which will essentially it traps them and precipitates them out so they're no longer available for biology.

And because of this, the terrestrial systems are often phosphate limited. But terrestrial plants have a way to get around this. They can increase the availability of that phosphate. They have these chelating compounds in their roots. What they do is they leach these chelating compounds, which can actually dissolve the iron oxides and aluminum oxides of phosphate and other salts to return that phosphate to a dissolved form that can then take up.

And so we know that the carbon-to-phosphate ratio, the moles-to-moles ratio in marine organisms is often around Redfield. That's a whole other lecture in itself. But it's on the order of 106. But in terrestrial plants, we find that this ratio is much greater than 106. And so they're able to survive with much less phosphorus because of this availability issue. And terrestrial plants contain less phosphate per mole carbon due to the high proportion of structural, carbon-rich and phosphate-poor molecules, and examples of those are just carbohydrates, and ligands, and that type.

So going back to our original figure, again, we want to try to get an idea of the turnover times and retention times in the land, the land soil reservoir for phosphorus. And so looking at the turnover time, we know that our inventory is 100 times 10 to the 12th or 10 to the 14th moles of phosphorus in that land biota, and that it recycles with the back and forth between the biota, to the land, to the biota, on the order of times 10 to the 12th moles per year. So that gives you a turnover time of about 50 years for phosphate in a terrestrial environment.

And if we want to think about the retention time of the reactive and eroded phosphate on land, so basically, once it's reactive, how long will it stay there? We have our inventory again, which is 6.5 times 10 to the 15th moles. And then if you want to consider, and again, this is a rough estimate because we're trying to consider the various export pathways. You can have this pathway, which is just to the deep ocean and burial. And that's for the particulate, the inert forms of phosphate. And we also have the pathway to the surface ocean, and that's the more biologically labile forms of phosphate.

You get a flux on the order of 0.7 times 10 to the 12 moles per year, which gives you a retention time on the order of 9,000 years. So once they're in the sediments, they tend to stay there. The phosphate tends to stay there for a fair amount of time.

So given this turnover time of 50 years and the 9,000-year retention time, we need to understand the processes by which these the phosphate actually makes it to the ocean, because that's obviously what we're primarily concerned about because of the nutrient limitation. And there's two primary processes, the aeolian input of dust, which I'll talk about first which is a small input, and then fluvial inputs, which is really the primary input which I'll talk about second.

And again, just to reiterate the point, there's no gaseous forms of phosphate. So this small source due to aeolian dust is the only atmospheric source. This is the only non-river source of phosphate to the ocean. And so if we want to estimate the total aeolian phosphate flux, we basically take an estimate of the total dust flux. And this is a map here from Natalie Mahowald's paper in 2005. And it's just a dust deposition estimate in grams per meter squared per year.

So if we take this overall estimate of dust deposition, and then a mean concentration we expect a phosphate in those aerosols, and then an estimate of solubility, that will tell us how much actual aeolian phosphate flux makes it to the ocean in a reactive form. If we get things that are completely not soluble, they're just going to sink out and they're never going to be bioavailable.

So in terms of this source, it's to remember that dust input to the ocean is highly variable in space and time. It varies seasonally with rainfall and transport patterns. Like we talked about last week, there's huge glacial interglacial cycles. And it's also very episodic based on wind speed or other physical processes. So again, bringing our equation along, we can use some literature values for solubility. Current estimates are that the solubility of dust phosphorus ranges from 21% to 51% which is actually enormous compared to iron. If you remember, it was a very small percentage. So there's quite a bit of soluble phosphate.

And these are literature estimates of the actual input of phosphate in 10 to the ninth grams per year, and so if you just convert that you get 0.01 to 0.02 times 10 to the 12th moles per year. And so you can see this is small input relative to the fluvial and relative to a lot of the turnover. So again, it's a fairly insignificant pathway. And it's important to know that even though the solubility of phosphate is so high, that even in the oligotrophic gyres, which are extremely nutrient limited, that the estimates of the input account for less than 1% of new production. The rest is attributed to upwelling of phosphate or vertical mixing. And again, this is in contrast to iron, where a small influx of iron can really increase your productivity fairly rapidly.

So going back to the primary source of transfer to the ocean, it's fluvial processes, so transport and incorporation of these phosphate minerals in the particulate in dissolved forms to rivers via estuaries to the ocean. And what we do know is that a huge percentage, probably 90% to 95%, of the phosphorus in rivers is in particles. Very little of it's in the actual dissolved bioavailable form. And these are, again, the inert minerals which are eroded directly from the continental crust.

And some of those iron and aluminum oxides where the reactive P was actually adsorbed onto the clay, those come too. But what happens is when these rivers dump into the estuaries, you can start having chemical changes within the estuaries themselves. You can think of them as being processing areas. And so in these estuaries, You can actually have the reactive P desorb from the iron oxides. And so then it becomes bioavailable. It can be processed, taken up by the Marine Freshwater biota, and turned into organic phosphorus compounds such as the DNA, the RNA, a lot of the intracellular components.

And this can be removed from estuaries via sinking out, or also there's some salinity-induced flocculation with humics and irons in the river. But the important thing to know is that because the reactive P pool is so small relative to the particulate pool, a really small change amount in the partitioning between these two pools, so the amount of P adsorbed to the clays, it can greatly change our estimates of the fluvial input of bioavailable phosphate. And again, right now our estimates have a pretty large range, but currently they're about 0.03 to 0.15 times 10 to the 12 moles per year.

And so once we have this and we have the estuaries draining out to the ocean, and some of this reactive dissolved phosphate making its way to the ocean, we need to understand some of the turnover processes and chemical components of it in the ocean. And so again, just going back to this figure, which we saw earlier, which is the percent of inorganic phosphate in the various chemical forms as a function of pH, remember in the ocean that the primary dissolved inorganic phosphorus form is hydrogen phosphate.

And what tends to happen is that ion pairs are formed with a major cations in seawater. So you have a lot of these. You have some of your free hydrogen phosphate, but you also have sodium, calcium, and magnesium versions of these floating around.

And so just to take a step back, because if you guys do any reading, I'm going to post some additional readings to do on this. There's a lot of jargon out there in terms of how people refer to the different phosphorus pools. And right now most of the dissolved phosphorus or the bioavailable bioreactive phosphorus, it's fairly much operationally defined. So basically we run these experiments and the results tell us which reservoir they should be put in.

For example, the soluble reactive phosphorus, which people call SRP, is measured in filtered seawater, and it's a fraction of the phosphate that can be measured directly by the colorimetric phosphomolybdate method. And so basically we're not saying that it's just the particles. It's basically the results of this colorimetric method are what we're going to deem the soluble reactive phosphorus. And this fraction is believed to consist mostly of the inorganic phosphate. But it also encompasses a few acid labile organic compounds. So again, the partitioning isn't as clean as we'd like.

There's also the total dissolved phosphate. And that's measured by the same method in filtered seawater after treating it with a strong oxidizing agent. And then there's the soluble non-reactive phosphate. And it's calculated by difference between these two methods. And it's generally thought to consist mainly of the dissolved organic phosphates and polyphosphates.

So essentially your soluble reactive phosphorus can be considered your dissolved inorganic phosphate. Your total dissolved phosphate is obviously your total dissolved inorganic and dissolved organic phosphate, the sum of the two. And your soluble nonreactive phosphate can be considered first order approximation your dissolved organic phosphate. So just so if you see some of these terms floating around in the papers, people are going to use different nomenclature depending on the problem they're actually looking at.

And so the soluble nonreactive phosphate or the dissolved organic phosphate, it's a large percentage of the total dissolved phosphate in surface oligotrophic waters. So a lot of it's in the organic form. But again, because it is bio-limiting and the concentrations are almost undetectable in some of these oligotrophic gyres in the subtropics, most of this is found as components within phytoplankton cells, so the DNA, RNA, the phospholipids. But as with carbon, we know that this dissolved organic phosphate can be converted back to inorganic phosphate via enzymatic and microbial remineralization processes. So it's going to cycle through the biota, the phytoplankton. and the bacteria loop, fairly much like carbon cycles through.

So again, going back to this figure, we can see that the ocean biota reservoir is much smaller than the land reservoir by maybe a factor of 25. But the fluxes between the reactive people and the biota are much larger. You see, if you see here we have fluxes on the order of 2 times 10 to the 12. Here we have fluxes on the order of 33. I mean, they're not balanced with the difference being export to the deep ocean. We don't have that same lack of balance on the land side.

So we want to look at a turnover time. Again, you can take the reservoir size, 4 times 10 to the 12th, and divide it by the flux. And it gives us a turnover time on the order of 0.12 years. And if you remember, the turnover time we had on land was 50 years. So there's a significantly faster cycling of organic phosphorus in the ocean than on land. And this tends to be due to the dominance of single-cell organisms with really short lifetimes. So they're just they're processing it through their lifetime really rapidly, so the growth-death bacterial processing.

So it hasn't been easy to measure phosphorus cycling in seawater. A method that people have used and was published recently, I guess not so recently, in 1999, is that they tried to study phosphorus cycling using two natural radioactive phosphate isotopes. And this is P32 and P33. And these are cosmogenic isotopes from argon. So basically argon gets hit with cosmic rays. It forms these secondary isotopes. And the way that these are delivered to the ocean is that they're rapidly removed onto aerosols in the atmosphere, which are rained out via wet deposition processes. So again, that's something that's going to be subjected to a fairly spatially and temporally variable distribution.

But what we do know is that P33 to P32 in rainwater varies very little. If you look at the activity ratio, the measurements. They have done, it's within a very small range. And that the P33 to P32 ratio actually will increase with time, and that's a function of their different half lives. So if you see P33 has a half life in the order of 14 days where that of P32 is 25 days.

So what we know is that when we take in a sample of organic matter and look at this ratio, the higher the P33-to-P32 ratio, the older the phosphate pool, and older being essentially when the biota take up, assuming there's no isotopic fractionation, when the biota to take up these isotopes, they're essentially fixed within them, and then they're just subjected to radioactive decay. So you can see how long it's been since they've taken up isotopes.

AUDIENCE: That ratio seems to go the wrong way given the half lives. P33 has a faster half life.

DIERDRE TOOLE: Faster half life, so that should go down.

AUDIENCE: I don't have those two. I don't have those two in my brain.

DIERDRE TOOLE: Yeah, I might have mistaken the 32 is 14. Oh, I put the half lives backwards. I'm sorry. P32 is the 14 days and P33 is 25.3 days. Sorry. So, yeah. But it is the higher, so P32 is going to disappear faster for a given time. You're going to have less P32 than P33. So then you'll know that it's an older phosphorus pool. Thanks, Scott. Sorry.

And so, again, what they did in this study, this is Benitez-Nelson and Buesseler in *Nature* in 1999. And what they did is they measured the phosphorus isotopic ratio in the different pools. So again, the inorganic phosphorus, the dissolved organic phosphorus, but then also within different size fractionations of the seawater. So you can get the phytoplankton class zooplankton. And from this they were able to estimate the age of the phosphorus. And they also could estimate the turnover of phosphate within the pools and the pathways through the various levels of the food chain.

The crux of all of this, is that you need to be able to constrain the P33-to-P32 ratio of rainwater, because essentially, that's your starting point. And everything is going to be leveraged and compared to that starting point, so you need to know that. And so it's really crucial to understand the variability of that. And they found, again, that it's not very variable spatially. And preliminary results from these studies is that the DOP turnover rates vary widely in space and time, suggesting that there's a pretty large range of bioavailability of these DOP that it's not all considered the same.

So going back to the same figure again, I should just put it up on the board somewhere. Surface seawater, phosphorus turnover time, again, taking the inventory divided by the flux. We have a turnover time on the order of 2.7 years. And so we do know that a relatively small fraction of this is exported. But again, there's very few direct measurements. They primarily consist of the isotopic ratio type measurements that I was just discussing.

The current estimates are that the mean residence time and surface waters for phosphate is on the order of 9 years. And so because we don't have these direct estimates of P export flux, we're often left estimating it with quantities that we feel like we have a better understanding of and ability to constrain. And one of those is carbon export.

And there's a lot of different ways, and people obviously use sediment traps and the like. But you can get global estimates based on satellite observations. So if you want to calculate your rate of your organic phosphorus export, what you could do is you can take some of carbon export data set and then a mean phosphate-to-carbon ratio in the organic matter that's being exported to calculate your export of organic phosphate.

And so literature values from Laws et al, suggest that the global carbon export production is on the order of 10 to 15 moles of carbon per year, and that the average-- we'll get back to this a little later these C-to-P ratios. But the average C-to-P ratio is on the order of 117. And so this would suggest an average export of phosphate from the surface waters on the order of 10 to the 13th moles of phosphate per year.

And I just want to address this so there's not any confusion later that this number is 10 to the 13th. So 10 times 10 to the minus 12th is significantly different than this 0.3 that we have in the original figure we're discussing. And as with anything, we're constantly updating estimates as we have better constraints on the different parameters. Again, there's a lot of uncertainty by factors of 2 to 3, up to factors of 10, obviously, within our flux estimates. So it's just something to keep in mind. I mean, we're looking at broad-scale comparisons between the various turnovers and the various reservoirs.

So once we know that we have this export, this particulate organic that's leaving, again, if we want to divide it to first order approximation into our surface ocean, our deep ocean box, once we have this organic phosphorus that's leaving that box, the surface ocean, we need to understand how much of that's actually making it to the sea floor. Because that's what's going to help us complete our loop and get it back available to land.

So literature estimates suggest that the global organic carbon delivery rate to the sea floor below 1,000 meters is estimated to be equivalent to an oxygen consumption of 54.4 times 10 to the 12th moles per year. And so again, we don't have direct measurements of the phosphorus delivery to the sea floor. So we're going to use carbon and oxygen estimates, and try to back it out from those. And again, another literature estimate demonstrated that in this organic matter that below 1,000 meter, the ratio of oxygen and phosphorus in the organic matter, this is of the particles sinking to the deep sea, is on the order of 170.

So again, if we want to estimate the phosphorus delivery to the sea floor, we can just do a simple conversion. And using the ratio and the flux, and we come up with 0.32 times 10 to the 12th moles of phosphorus for a year. And so just to put that into perspective, that's about 3% of the export flux. So I mean it's what you'd expect. It's a reasonable number. But let's just to keep in mind then that most of it, 97% of it, is remineralized and recycled within the ocean. And so the actual getting delivered to the sea floor for some of the next processes we're going to talk about is fairly small.

And so again, now we have that 3% of the export flux from the surface hitting the sea floor. And we need to figure out how much of that that hits the sea floor is actually buried and how much of it is actually rereleased out into the water column. And so the degradation of organic phosphorus and sediments, it decreases with the amount of organic phosphorus buried. And this is because there's extensive phosphorus recycling due to remineralization processes within the oxic layer in the sediments.

And what this serves to do is it actually increases the pore water phosphate concentrations, which can actually end up that you have as a diffusive flux out of the sediments where the sediment concentration is higher than the concentration in the overlying water. So you'll actually have a flux out. And again, this is from the literature. But deep sea sediment flux extrapolated to the global ocean actually suggests, like I said, that you do see an efflux of phosphate from the sediments that's greater than or equal to the rate of delivery of P from the surface export.

So again, just to bring home the point here is that much of the organic carbon and the organic phosphorus is going to be remineralized in the water column. And that the actual thing we're trying to estimate at this point, which is burial, is it's the difference between the delivery to the seafloor and the efflux out, both of which are pretty poorly constrained. And again, it's an issue where we're subtracting two large numbers. So we need some more work done on that before we can be entirely quantitative.

To do the same type of thing that we did with export, but rather just with burial in this case, we can estimate the rate of organic burial as a function of a measured or estimated organic carbon burial rate times the mean carbon-to-phosphate ratio in the buried sedimentary material, and the organic carbon burial rates at depths greater than 1,000 meters, are approximately 1.25 times 10 to the 12th moles per year. And so that's less than 3% of the delivery.

So we have 3% of the surface export reaching the sea floor, and then 3% of that actually getting buried. So you can see most of it is going to be recycled within the biota within the ocean. We do know though, if we're not going to look at such deep depths, if we want to focus more on the continental margins or the shallower regions, that there's much larger amounts of phosphorus are actually buried. So when we want to do global estimates, we have to keep in mind that the processes are going to be a little different in terms of their magnitude depending on where you are.

But if we assume a Redfield ratio, again 106-to-1, in sediments deposited at depths greater than 1,000 meters, the maximum burial rate of organic phosphate is about 1.25 times 10 to the 12 moles per year divided by 106, which ended up as 1.1 times 10 to the 10th moles per year. So that's a very small flux overall in the phosphorus cycle. But these flux estimates, they are getting adjusted upwards over the last decade. And a lot of that is because people, the investigators, are starting to take into account the shallower sediments and the higher deposition rates and burial rates in these continental margin regions.

And so now, the current understanding is that these estimates actually range from 4.1 to 18.5 times 10 to the 10th moles per year. And so, once these organic materials land in the sea floor and start to get buried, we need to understand the effect of the organic matter degradation. So any bacterial processes within the sediments of the overlying waters, how that's going to affect the C-to-P ratio. Because I mean, all of our budgeting so far we've done based on these ratios.

And so we don't really have a good assessment of how the bacterial processing will change these ratios, which are key to understand. What I have plotted here is from the literature. It's a mole-to-mole plot of phosphorus to carbon in organic matter. It's times 10 to the third because we've done rather than carbon to phosphorus, phosphorus to carbon, as a function of the percent of organic carbon in the sediments.

And what you can see, a couple of things are immediately obvious that coming up with an average C-to-P, it's a pretty hard task. And it's obviously something that's going to vary spatially. It's highly variable. But you do see that the P-to-C ratio, C-to-P, it varies systematically with the percent of organic carbon in the sediments. And you often see that it is greater than Redfield. And so when that tells us is that there's a preferential release of phosphorus over carbon to the bottom water before this final burial actually occurs.

But just like many studies, there's other studies, later studies, not necessarily better studies, but later studies that contradict these results. And this later study suggested, this study is from 1999, suggested that 1990, excuse me, systematic changes in this ratio, the C-to-P ratio, of the buried organic matter and thus the preservation or the organic matter, actually varied with the sedimentation rate. And so that gives us a clue as to how this is going to vary over the different regions of the ocean floor.

And so this is a plot from their paper, which is sedimentation rate centimeters per year. This is a log scale as a function of the asymptotic organic C-to-P. And what that means is if you look at pore water concentrations they often have an exponential asymptotic type shape. And they took that value as the C-to-P to represent the sediment column. But what they found is that the C-to-P ratio of organic matter was actually close to Redfield, with Redfield being 106, and low. They classified everything less than 200 as low. So it was actually close to Redfield and low at really high sedimentation rates, which is greater than 1 centimeter per year, or at the really low sedimentation rates, so less than .002 centimeters per year.

But it's in this intermediate range of sedimentation rates that we get these very high C-to-P ratios. And so what they took this to mean is that under oxic respiration conditions, they assume that the phosphorus is remineralized preferentially to the carbon. And so their interpretation was that at very high sedimentation rates, so in a coastal upwelling region or a delta type region, there's actually really excellent preservation of organic material when it hits the sea floor. And that's because there's such a large flux of organic matter, and you have a fairly small depth that you're talking about. So your actual time available for remineralization is much less.

And so in that case, you'd expect the C-to-P ratio to be close to Redfield. And in contrast to that, in these very low sedimentation rates, so these are the really deep sea, 5,000, 6,000 meter pelagic-type environments that by the time that organic material hits the sea floor, that remineralization is complete. I mean, everything that can be remineralized is and what's left is just the refractory organic material. So again, you'd expect that to have that near Redfield ratio because it's going to reflect the initial values.

And what they interpreted the mid-range sedimentation rates is that these are what they consider corresponding to the real continental margins type areas. And they this reflects the preferential regeneration of phosphate. So what you're going to see is you're going to see detrital compounds that are enriched in phosphate relative to carbon. Or what you're going to see are the remains of bacteria within the sediments that have a high C to P because they reflect what they're consuming.

And so what this would do is this would actually decrease the importance of margin sediments as a sink for phosphate. And if we saw in the last slide that a lot of our estimates of burial have been of creeping up because people are starting to think that a lot more phosphate, I just said sulfate, but a lot more phosphate was buried on these shelf slope areas. And this type of phenomenon would actually start to actually decrease the importance of the margin areas.

AUDIENCE: I haven't seen the [INAUDIBLE]. You said it's they're basing on this asymptotic--

DIERDRE TOOLE: Yeah.

AUDIENCE: What about authigenic precipitation of particulate phosphate in those sediments?

DIERDRE TOOLE: I'm going to talk about that in one minute in the next couple slides. But this is just in terms of--

AUDIENCE: But that would counter that argument. You could get very high dissolved carbon to phosphorus in the pore waters because phosphorus has been stripped out.

DIERDRE TOOLE: Yeah in like apatites.

AUDIENCE: Kathleen Ruttenberg would argue that counters that.

DIERDRE TOOLE: Yeah. Yeah. No, that thing, again, one of the main points that I really do want to make is that there are a lot of different processes occurring simultaneously, and there are different people that have different opinions in terms of which is the dominant process. And this is just trying to understand the C-to-P though of the buried organic matter, this plot. They're not trying to tease it apart the total amount of carbon or phosphate, which we'll talk about in a second is the formation of those phosphate minerals.

Again, they're specifically trying to just tease apart the ratios in the organic material and biological processing of that, and how that changes our interpretation of the importance of the slope as a loss mechanism. And so perfect segue, Scott.

But what we do have to understand before we can take all these things to heart is the actual chemical nature of the buried phosphate in sediments, how much of it is going to be in the organic form versus how much is going to be tied up into secondary authigenic phases. And so basically at your bottom water, sediment pore water interface, there's going to be a great deal of organic matter decomposition.

And what happens from this is this organic matter decomposition releases different forms of phosphate. In this case, I have hydrogen phosphate. And most of this is actually able to diffuse back out to the bottom water above. But some of it does precipitate with some of the iron and aluminum oxides in the sediment itself to become a phosphate mineral, essentially being trapped, and no longer available to be considered part of the organic pool.

And so the fates of this released phosphorus from this organic matter decomposition in pore waters, it's ultimately going to dictate the C-to-P of the organic matter in the marine sediments. So we know that the phosphorus can be buried as the refractory organic phosphorus, but it can also be buried as these carbonate fluorapatite formed in sediments, so the sediment minerals, or it can be buried as absorption of dissolved phosphorus to iron oxides or aluminum oxides in hydrothermal plumes. And I'll get to in a second, but low temperature basalt interactions with the hydrothermal vents.

Just kind of as an aside to think about, because there are oxic basins, anoxic basins. It depends on where you are. The extent of phosphate burial, it also seems to depend on the presence of oxygen in the bottom waters. So it's going to depend on the structure within your pore waters of your oxygen anoxic boundary. So in the presence of oxygen, the preservation of organic carbon decreases because there's more opportunities for remineralization, while that phosphate actually increases.

And the reason for that is that due to the presence of this iron oxide layer near the sediment water interface, you're actually going to trap the phosphate release from the organic matter decomposition. So if you don't have this layer, this oxide layer, because you have low oxygen, the preservation of P is going to change. And so if no little or no oxygen is present, you're going to have more organic carbon preserved, but you're going to have more phosphate released from the aromatic, but the phosphate released from this organic matter decomposition by the bacteria in those pore waters, it's more likely to diffuse to the overlying water layer rather than getting trapped or adsorbed onto those oxides. And that'll give you a C-to-P that's greater than Redfield.

So going back to, this is what Scott was starting to allude to, is we need to understand the formation of these phosphate minerals to understand ultimately how the phosphate released from organic matter decomposition, its ultimate fate, and the carbon-to-phosphate ratios that we use for all these flux calculations.

And so basically I'll try to go through this. Is we have an iron oxide layer. And again, phosphate can adsorb onto this. And this is going to be subjected to burial within the sediments. And as these iron oxides are buried and reduced, once you get below the oxide layer and the anoxic layer of sediments as they're reduced, the adsorbed phosphate is going to be released to the pore water. And so you're going to have phosphate in the pore water. And you're actually going to have iron too.

And once this phosphate is released in the pore waters, it can do one of two things. It can either slowly diffuse upward to get back out into the water column, or it's going to get trapped in these carbonate fluorapatites, in which case it's buried, it's deposited, it's there. And we also see simultaneously that as the organic phosphate materials, any refractory organic phosphate materials, if you're in the pelagic area or any organic materials, really it hits the sediment layer, a coastal slope, that those are also going to be subjected to burial and decomposition processes which will release phosphate again.

And so that phosphate is subjected to the same processes. So either it can be diffused out or you can make these phosphate minerals. But essentially, it's pretty well-documented now that in sediments underlying upwelling and most margin regions that these fluorapatites, the CFAs, are very often observed. And so what they think is that these CFAs tend to precipitate from pore waters where the phosphate concentrations near the sediment water interface are high.

And so what you have is you have a consistent recycling of this iron. Iron forms iron oxides. It's buried down in the sediment where it's reduced. And then it diffuses up to form the oxides again. And every time it goes through this recycling loop, it can actually scavenge phosphate, either the phosphate within the pore water column that's diffusing up or phosphate from the water column itself. And so what it does is as it scavenges more and more phosphate as it goes through these recycling loops, you're actually having phosphate building up at each cycle.

And so when you end up with this loss of phosphate, this phosphate is replaced by phosphate being pulled out of the water column where the iron in this recycling is actually replaced by iron containing detrital materials. So when the iron is precipitated out to things such as pyrite, you can get iron from some of the detrital materials.

So this CFA precipitation, it's been pretty widely documented, and it's moved beyond just being observed in the continental shelves, slope type areas. I mean, it's actually they've been observed pretty ubiquitously in the deep sea water. And so the way they've done this is they use a leaching procedure that's actually able to differentiate between the different forms of phosphate and sediments. And so what I have shown a plot here is its depth in centimeters of the sediment, and then weight percentage of phosphate.

And you can see that the organic phosphate, which is represented by the open symbols and the authigenic phosphate, which is primarily these carbonate apatites. They tend to have an inverse relationship. So basically as the P organic, the organic phosphate decreases with depth. So as more and more of that is being remineralized with depth that the CFA concentration actually is increasing. So that means that most of the phosphate from these organic materials that are buried within the sediments are being recycled through the sediments and ultimately ending up being precipitated as these CFAs. And so this has been termed the phosphorus sink switch.

They were also able to document the precipitation of phosphate released from the organic matter. It was also confirmed during a couple pore water modeling studies. And I know this figure speaker is small, but what we have again is depth in terms of centimeters from 0 to 300. And then we have the open circles or observations where the line is a model fit, the best model fit, and the first plot is ammonia in micromoles, and the second plot is hydrogen phosphate in micromoles.

And what they were able to do is based on a stoichiometric ratio, it's a stoichiometric model for oxidation of sedimentary organic materials. You know that for x amount of moles of ammonia there's going to be x amount of moles change in phosphate. They were able to estimate what the expected pore water profile of phosphate would be. And the estimates is this black solid line where the open symbols are the actual organic observed, actual observations of observed phosphate.

And what you can see is that the estimates of what should be there organically are far in excess of what actually are in the organic form. And so what that suggests is that there actually is this large precipitation of the authigenic phosphate materials. That's what's making up the difference between the expectation of how much dissolved phosphate should be there versus how much phosphate is actually there.

And CFAs are now seen as the main form of phosphate present in deep sea sediments. That's a pretty wide held belief. So if we're going to look just at organic phosphate burial and remineralization, that's going to significantly underestimate the total reactive phosphate that's actually buried in these sediments, because there's a lot of it precipitated in these lithogenic materials.

And so just of as an aside to something that you should know is that there also is phosphate removal at hydrothermal vents, hydrothermal processes. And it's the same type of reaction. But there's that scavenging of phosphate from the seawater by iron oxides. And these are just iron oxides found in the plumes of hydrothermal vents.

Again, using element ratios, if you want to look at the iron fluxes at these hydrothermal vents, times a mean phosphate-to-iron ratio in the plume particles, you get a relatively small scavenging of phosphate out of the water column relative to the inventory of phosphate in the overlying waters, and it's on the order of 0.8 times 10 to the 10th moles per year.

At these same locations, you also have phosphate being removed via, again, the formation of these same, the authigenic apatite minerals and absorption on secondary iron oxides, and this is primarily during low-temperature interactions between basalt and seawater, and it's a larger removal process in the order of 3 times 10 to the 10th moles per year, but that's still significantly smaller than the other removal processes.

Ultimately, we want to understand the residence time and the turnover time of phosphorus in seawater because of its role as a limiting nutrient. And this recognition of the widespread distribution of these lithogenic phosphate materials has led to significant revision of our phosphate residence times in the ocean and downward revisions. And from the literature, the previous estimates of phosphate burial in 10 to the 10th moles per year was on the order of 3.8. But once we start taking into account the importance of the continental margin regions and the burial of these apatites, the modified estimates range from 8 to 18.5 times 10 to the 10th moles per year.

And these estimates are 2 to 5 times higher than previous estimates. So if we increase our burial rate significantly, it's going to give us a reduction in the mean residence time in the ocean. So for example, again going back to the same figure, if we want to look at our inventory divided by our turnover time using the original estimates, the residence time was on the order of 74,000 or 75,000 to 80,000 years. But using these revised estimates, the turnover times are actually on the order of 15,000 to 30,000 years for new burial flux estimates.

And this reduction in time scale is telling us that the phosphorus might actually be able to vary on timescales relevant to interglacial glacial cycling. So that's important to consider. So again, if phosphate is the ultimate limiting nutrient on these longer-term scales, changes in the oceanic inventory are going to make a really big difference in terms of changing the intensity of the biological pump and potentially concentrations of CO2 and oxygen in the atmosphere.

There has been some observations for reduce carbonate fluorapatite burial at upwelling margins during glacial periods. But again, this sink, this margin production of the CFAs, only accounts for about 10% of the total P being removed from the ocean. So if all other phosphorus sinks remain the same, the phosphate phosphorus inventories, it would change very little. Again, we don't have very good constraints on this at this point.

Just as a last thought, how phosphate interacts with the carbon, the oxygen, some of the other biogeochemical cycles, this is a proposed climate feedback. And it is based on the crux that phosphate burial is more efficient when sediments are deposited under oxic conditions. And that's because of that scavenging by the Iron oxide minerals. And what I'm going to present here is just a potential negative feedback mechanism to control oxygen in the atmosphere over the Phanerozoic. And so this is getting back to your million-year timescales.

And so what happens is if an atmospheric oxygen concentrations decrease and this bottom water oxygen concentrations will decrease, we'll actually have a decrease in the burial of phosphate in either form, organic or inorganic. And that seawater phosphate inventory is thus going to increase because it has nowhere else to go.

Export production will increase. Basically, what that's saying is if we have more phosphate in the water, we're going to have more biological primary productivity. So our export production, our production and export production, are going to be able to increase. Hmm?

AUDIENCE: Nothing, you'll find it.

DIERDRE TOOLE: What did I--

AUDIENCE: The arrow for the atmospheric oxygen.

DIERDRE TOOLE: Oh yeah. It's supposed to go the other way. Sorry. OK, so we have an increased production and export production because this increased productivity. We're going to have an increase in organic carbon burial, which is ultimately going to serve to come back around and increase the atmospheric oxygen concentration. So this is a stabilizing feedback loop in a way that the phosphate biogeochemical cycles can play into the climate. And that's all I have for today.

And for August, you can come around here if you want. If this is actually just a fusion going on, and I think this is another case of where it's just the data. It looks a little bit funny. But no, it's not just effusion. You do have-- it looks like the boundary line isn't quite in there. But the reason that it goes down is because it's consumed. So even if there was some of diffusion going on, like the oxygen wasn't being used right at the surface, which is hard to imagine. Yeah something would have to be reducing it or because it's going away. So it is a very steep curve.

AUDIENCE: Just since he was talking, so I understood just that you would see the consumption is lumped in along on the straight line. Or is that not a fair--

DIERDRE TOOLE: It's true. But in this case, the straight line is you would say straight line is like this or something. It is a curve. It's just a really sharp exponential curve.

AUDIENCE: Yeah.

DIERDRE TOOLE: OK. I have a ton of questions. I got a big email from Caron, Andrea, and Abigail that basically said, ah! So I don't know how far everyone has got on question 3. But the key thing to question 3, part B is that it's not asking you to diagram things with depth numbers, or rates, or anything like that. It's asking you to draw idealized cartoons basically.

So one of the questions was how can we interpret the calcium carbonate thing here as depth? And you can't. Well, you can't get an actual depth off of it. That's not going to happen. I mean, you could find out what the exact depths are if you go to some literature or you look at an atlas. That's not what we're asking you to do.

What we're asking you to do is I went through the question a little bit, but I don't want to give you my little answers I came up with because, one, I didn't think about them for very long, so I'm not sure how correct they are. And two, that's not fair.

But what I want you to do is this is about it. Like you're drawing a little mid-ocean ridge and you're drawing the saturation horizon, the lysocline, the CCD. Draw where you think they are based on all the information you have. You don't have to go to outside sources. Based on what you have in these three or four plots, draw where about you think they would be. Does that make sense?

So we know as an example, we know from the drawing here, we're looking at a cross section right here for the Atlantic. This is about the 30 degree point. The mid-ocean ridge is right here. Note, the high carbonate. Why on Earth would there be high carbonate on mid-ocean ridge, you may ask? Hope the answer. That's important.

So you're asked to just draw what this little profile would be. So if you had depth, and you had distance across the Atlantic, the bottom would look something like this, right? And then you can see, OK, this is about 50. And then here's the 25 line. And then here's the 5 line. So from that, you can start to say, remember that plot that Bill put up that looked like this where he had the calcium carbonate? No 2 on that, solid.

I think this was percent of seafloor sediments. And there are all these little plots. It was some percentage here. And then it went like this all the way down to 0. And we said that this would be the lysocline and this would be the CCD. These were all different core tops. Remember that? That's more or less the same information you're getting here. It's the percent carbonate in the sediments on the seafloor.

So using that, you should be able to figure out approximately your lysocline and your CCD, right? I think that was probably the most confusing thing to figure out. The vertical profiles of the rain and the burial, again, we're plotting depth here, but instead of plotting like an actual vertical profile, you're going to be using, knowing the saturation horizon, and knowing about the depth of the CCD. You can say, OK, well, you're going to be plotting a flux of what you think at this 30 degrees North for the North Pacific, North Atlantic, or 30 degrees South for the South, Southern Ocean.

So you're plotting basically a flux, either a burial rate or a rain rate versus depth. And this isn't a single depth. This isn't a single CCD cast. So these are all places, if you put out sediment traps at the bottom of the basin, all over the basin, along this 30-degree horizon line. So you would have, as we talked about just before, the Atlantic one's going to have the mid-Atlantic ridge in the middle. So you're going to have a trap here, here, here, here, here, here, here, here.

You're going to be covering all these different depths. And those different depths are this z-axis. So it's not like you're on the ship, and you throw your cast overboard and collect it from one different depth. You're not doing the burial rate like that, or the burial rates like this. You're getting burial rate information from all of these traps. Does that make sense? Does that help?

AUDIENCE: Thank you.

DIERDRE TOOLE: OK, and the same burial rate, rain rate, same basic idea, two different things, but same basic principle.

AUDIENCE: Are we supposed to do all three of them?

AUDIENCE: Rain rate, isn't the rain rate from the mixed layer at the surface?

DIERDRE TOOLE: So the rain rate, yeah, the rain rate is what's falling into these traps. The burial rate is what's actually going to be getting buried. Yes, no?

AUDIENCE: So how do you get values for z that is greater than-- so there's some minimum depth. I mean do you bring this all the way to the shore, so you get values of z that are really small?

What about z equals 100 meters?

DIERDRE TOOLE: We're not actually looking for specific values. Again, we're looking for a little cartoon. So rather than getting exact values for a burial rate, which I'm not even sure you can get off of this data, what you could do is you could say, OK, well I have three different diagrams. And if we have the same z1, z2, and z3 going across, so we have z1 is here, z2 is here, z3 is here. So how would the flux change differently in the Atlantic, versus the Pacific, versus the Southern ocean?

So it would be relative to the different basins rather than an absolute value. So you would say, oh, it's higher here and then it's lower here. But this one's more like there and there. Do you understand what I'm saying? I don't think you do. Yes, Andrea is not-- really big so.

AUDIENCE: Can I ask a question about the license line versus the calcite saturation horizon?

DIERDRE TOOLE: Yeah.

AUDIENCE: From my understanding, it seems like a lot of the time they're going to be at the same place, but I'm not sure that's right.

DIERDRE TOOLE: Yeah I mean, this is a weird thing. The calcite saturation horizon is very well defined. We have a KSP value, we have an ion activity product. We can know where the calcite saturation horizon is. The lysocline is more looking at a plot of points and going, oh, it's about there. I actually have issues with the lysocline because I don't think it's really all that useful.

But you're right, they'll probably be somewhere in the same vicinity. But remember, metabolic dissolution could affect that. If there's a lot of metabolic dissolution going on over the calcite saturation horizon in those sediments, the lysocline might creep up above the saturation horizon. However, again, if there's not a lot of metabolic dissolution going on, maybe it's a little bit below. I'll check this, but I'm pretty much certain that there's not a consistent difference between the two. They could theoretically be switched either way. But there are two very different things, and they're measured very differently.

AUDIENCE: That's one of the things I'm confused about is because my interpretation of their definitions is that they're very similar because the calcite saturation horizon is where the saturation state is 1.

DIERDRE TOOLE: Yep.

AUDIENCE: So that means that it is saturated, and below that point, it seems to me that below that point is where you're going to start seeing evidence that it's not completely saturated, which would mean that that's the lysocline.

DIERDRE TOOLE: Right, but remember to see a change in the percent calcium carbonate, you've got to get a lot of dissolution because calcium carbonate makes up so much of so many of these sediments. I mean, it's over 50% in a significant portion of the Atlantic and even the Pacific, which we think of as rather calcium carbonate poor. I mean, there's still areas that have huge amounts of calcium carbonate. So in order to see a drop of even 10%, remember you need over 50% of the calcium carbonate to decline. That's why the lysocline could be below the saturation horizon or above it.

So I'll check on that because it may be that although theoretically it could be either place, it's consistently one or the other. And I can't remember. It's an issue I have with I just don't like the lysocline. I think that's why I don't remember it well. But I'll check on that. But theoretically it could be either. And as for doing part B, decide what you think is correct. Back it up with some evidence and cool.

AUDIENCE: Are we supposed to back up part B with evidence?

DIERDRE TOOLE: No, but if you're saying I think this is where the lysocline is, I guess it might help me to make a note. I probably won't be too harsh on grading the lysocline, given my feelings. I think we'll get into this next week, but there's a lot of trying to interpret paleo data saying, oh, the lysocline changed from here to here. And it's like, OK, maybe it changed, but what if it did? What does that even mean? I mean, it's kind of a-- I guess to me, it's a little bit of a hand-wavy definition of what the lysocline is.

Just remember, saturation horizon determined from water column measurements, lysocline determined from sediment measurements. Are there other questions?

AUDIENCE: I've got one with the question I had about the unit stuff.

DIERDRE TOOLE: I did, yep, I printed this one out too. OK, so I've been looking at this and the question is, I'll write it a little bit bigger so people can see it. Is the fact that we are given on the problem set that, ooh, wow, that's tiny d sed equals dc water times porosity squared. So the units of diffusion in seawater are-- this is hard to do-- centimeters squared per year. That's centimeters squared of seawater per year.

So in sediment, we still want it to be in water. But it's still going through water. But it's going to be in bulk sediment. So we want it to be in centimeters squared of bulk. So let's see here. d sed would be in centimeters squared of bulk sediment per year. Right?

Now this equation doesn't give that to us. The units don't work. You have this in centimeters squared of seawater per year, and porosity is in centimeters cubed of pore water over centimeters cubed of bulk sediment. So what you end up in, is some crazy units of centimeter squared of seawater per year times centimeters to the sixth of pore water, over centimeters to the sixth of bulk sediment. The units don't work.

And the reason for this is that this relationship we use because we can't get better. It's what we can do. We can do a little bit better, but it takes a lot more calculations. And I think people do it. But there was no reason to make you guys go through tortuosity and all these other things. This is a relationship that pretty much works. But of empirical. It's not a theoretical relationship.

So it's just one of those things where you plug and chug, and it spits it out in the right units. And the reason I know this works, your porosity to be less than 1, because remember, you're multiplying it. You have less water there because of the particles. And also with depth, your porosity is going to decrease as your particles are packed together and the pore water is squeezed out. So I guess I'm going to end up giving you a little bit of the answer here.

But your porosity is going to change to something like this. So as you can see at the top it goes from about 0.84. And then it just decreases with depth, and starts to come to pretty consistent value. And that's pretty common with compaction. It only occurs in the top few centimeters. And then it evens out.

And these numbers are less than 1. They look right. This is what we see in sediments. So the equation that you get even though the units are total crap, it is right. And that's what we do. It's just it's not theoretical.

AUDIENCE: I think when I was looking at it, I assumed that it was an empirical relationship, though I wasn't squaring my units. But so I assumed, when I was thinking about it, I was like, well, if I flip the porosity upside down, and I don't end up squaring the units, then the units work out. But I shouldn't do that?

DIERDRE TOOLE: Right.

AUDIENCE: Don't do that.

DIERDRE TOOLE: That's not right. So you want the porosity to be-- you want a number less than 1, because you want your diffusion in bulk sediment to be less than your diffusion in water. Think about this. Not only does it like to go from point A to point B in water, it can just go straight. But in sediment, it's got to go all around the little sediment grains.

AUDIENCE: Yeah, I think that we were happy with their actual number for porosity. It was the converting it into the diffusivity.

DIERDRE TOOLE: No, you're right. The units totally don't work at all.

AUDIENCE: Wait, I'm still confused about units, though.

DIERDRE TOOLE: OK.

AUDIENCE: OK. Can we look at the flux equation and just go through the units. Because when I do that, I still end up with wacky units.

DIERDRE TOOLE: OK, yeah. So the flux-- Yep what?

AUDIENCE: Sorry, the C is going to be in centimeters cubed water per centimeter cubed [INAUDIBLE].

DIERDRE TOOLE: I've got to move this. This can be any d. Just we're using d sed. So I'm using it. So sorry. What were you saying?

AUDIENCE: B is going to be in centimeters cubed water to centimeter cubed [INAUDIBLE].

DIERDRE TOOLE: Yep.

AUDIENCE: The d sediment is going to be in centimeter squared, bulk sediment per year is what we just said.

DIERDRE TOOLE: Yep. Yep.

AUDIENCE: And then the concentration is going to be in micromole per centimeter bulk sediment per year or the concentration dc.

DIERDRE TOOLE: Yep.

AUDIENCE: Why is it centimeter cubed? Isn't it just change in depth?

DIERDRE TOOLE: Well, remember, you want to end up in micromoles per centimeters squared per year.

AUDIENCE: That's c.

DIERDRE TOOLE: Oh, sorry. Hold on. Yeah, I remember what this is. What you have to remember here is this is all getting very ugly. So we're just going to start over here. Your delta c is the key thing here. What are the units on your delta c exactly?

AUDIENCE: Moles per liter.

DIERDRE TOOLE: OK. Moles per liter. And it's actually delta c over delta z, because we're looking at the change in and c over a depth. So what's the z unit?

AUDIENCE: Bulk sediment.

DIERDRE TOOLE: Yep centimeters.

AUDIENCE: Bulk sediment, right?

DIERDRE TOOLE: Right, but let's go with centimeters for the moment. But you're right, yes, bulk sentiment. So what we end up with is if you convert liters to centimeters cubed, this whole thing becomes moles per centimeters to the fourth.

AUDIENCE: OK. Here's my issue with that. Is when we're talking about phi and when we're talking about d sediment, we care about whether the centimeters is in water or sediment or bulk sediment. How can we arbitrarily decide that, well, that's in bulk sediment, but we don't care anymore. We're going to say that it's the same as water because if you convert liters to centimeter cubed. It's going to centimeters cubed water.

DIERDRE TOOLE: Right, you basically have moles per centimeter cubed water and then centimeters sediment. Right?

AUDIENCE: Bulk sediment. It's not even sediment. It's bulk sediment.

DIERDRE TOOLE: Yes, I just if I write everything down, it gets really, really ugly. So I just use sediment as bulk sediment. That's kind of my notation. So what we then have is just making sure that yes, this does work as it should. I've gone through it before. Our d sed is in centimeters squared per year of bulk sediment. And then our phi is centimeters cubed water centimeters cubed sediment. So phi times d, we get centimeters cubed water over centimeters sed per year.

Right? And if we multiply that times delta c, which we have right here, we get the centimeters of water cancel out, and we get moles per centimeter squared of sediment per year.

AUDIENCE: And so this again gets to my-- I'm sorry I'm really confused. Isn't the bulk like the centimeters bulk sediment going to be different than centimeters sediment?

DIERDRE TOOLE: Yes. I'm just using sediment. I'm using sed for bulk sediment. It's bulk sediment everywhere here. OK. I think this is your problem. The porosity is water per bulk sediment. It's less than 1. You have so much water in this volume. If you took a liter of mud and you evaporated out the water and you found out how much water was in it, it would be the water over the total mud. So the mud would include that water.

AUDIENCE: I had that definition wrong. You're right. Thank you.

DIERDRE TOOLE: OK. There we go. I was like, I don't understand why she's not getting this. That's why. That's why. That would make it confusing.

AUDIENCE: OK. Thank you.

DIERDRE TOOLE: I did, and I emailed you back right before I came over here. I don't remember what it asked, but I could answer it for you right now, too.

AUDIENCE: I was wondering about the last part of question 1, where we're supposed to calculate the n2 fluxes and the [INAUDIBLE].

DIERDRE TOOLE: Yes. Yes, and you wanted to know if we calculate it at the interface?

AUDIENCE: Yeah are we just doing it that interfaces?

DIERDRE TOOLE: So and that's a good question because you get your numbers from the interface, because that's where the flux actually occurs. You're crossing that boundary. But the flux integrates over the entire layer because it's production. If you have once again our friend the nitrate curve. And this is the anoxic-oxic boundary. The production of nitrate from organic matter happens all over this region. And it fluxes out here and out here. Right? So the flux here, and the flux here together have to equal that production.

So these fluxes are integrated over this entire layer. But you do calculate it from the numbers you get at the interface.

AUDIENCE: So, OK because I calculated it from [INAUDIBLE] far enough, so you can't see it. But like from here to here originally.

DIERDRE TOOLE: So you used a point here and a point here to calculate a slope?

AUDIENCE: It doesn't seem like a great idea to pick the point right next to it because then you're really compounding any measurement errors.

DIERDRE TOOLE: Well. Yeah, that's true. You can do that. I did actually choose the two points closest to the interface, just because that's the steepest point. I was doing it fast. Also, it makes it really easy to just calculate the slope. If you just do the points next to each other, then you just calculate the slopes all the way down like you just compare. Does that make sense?

AUDIENCE: Well, I did that to get the inflection points.

DIERDRE TOOLE: Right. But I'm just saying if you do these points next to each other, it's easier to do in Excel. It's not easier to actually do. It's easier to drag.

AUDIENCE: So should I redo that?

DIERDRE TOOLE: No, that's fine. That's fine. Actually, that may be the way they actually-- I don't remember exactly how they choose their points.

AUDIENCE: Why? Because they don't give you an answer key?

DIERDRE TOOLE: No, no, no, I mean, if they were to go out and make these measurements in sediments.

AUDIENCE: [INAUDIBLE] makes up these questions and doesn't tell you.

DIERDRE TOOLE: No, sometimes I'm as lost as you guys are.

AUDIENCE: Sorry.

DIERDRE TOOLE: That is absolutely true. I don't get answer keys, only the old ones from our TAs.

AUDIENCE: That's very strange.

DIERDRE TOOLE: One second, Caron, I'll get to your question.

AUDIENCE: Oh, I have another one. But she can go ahead.

DIERDRE TOOLE: No, why don't you finish your question?

AUDIENCE: OK, well there's another. So then if you assume it was on the number 2.3A, so it was assuming the oxygen consumption rates. So then if you assume that that's not a diffusion curve and it's a consumption curve, just you use the flux to get the consumption rates?

DIERDRE TOOLE: Yes.

AUDIENCE: OK.

DIERDRE TOOLE: Yep, the same thing as we did. I actually was confused why we're doing the same thing twice, but we're doing the same thing twice.

AUDIENCE: So I got a higher consumption rate on the August and the March doing that. Except from the profiles we looked at in class, I thought the August one looked like a lower production type profile.

DIERDRE TOOLE: Because?

AUDIENCE: I don't remember. But that doesn't sound wrong.

DIERDRE TOOLE: No, I mean, if you think about it just in terms of the biology, at a higher temperature, there'll be more active even in the water column as well as in the sediment. So there's going to be more organic matter. And then if you look at these curves, the oxygen curves, this one goes away really fast, which means that this is a really, really steep flux. So even though it doesn't look like there's a lot, the fact that oxygen is going away really fast means that the organic matter is going away really fast. Caron?

AUDIENCE: This is kind of along a similar line-- or actually, I don't know. This is for 2.4B, where we're calculating the rate of removal of uranium from the core columns. And the way I did it is I looked at like the nitrate curve essentially. And I said, OK, well if we've got-- I don't have my problems with me. Yeah, so if you look at it like the nitrate curves, then you've got the flux at the sediment water interface. And then the flux at the point where around 6 centimeters where the inflection point is. And I calculated the flux at those two points and added them, like we had been doing for the nitrate in order to calculate the consumption.

DIERDRE TOOLE: Yeah, I mean, the uranium profiles certainly go back up. And I can't remember why right now that they do that. But let me just read this really fast. It's not as if uranium here is all of a sudden soluble. It's not like this turns oxic. I don't remember why it goes back up. I will find out, but I don't remember why it is.

But you can just use this consumption curve. OK?

AUDIENCE: OK, so you're just saying ignore the fact that it goes up?

DIERDRE TOOLE: For now.

AUDIENCE: And just flux at the surface.

DIERDRE TOOLE: For now, yes. Because I cannot remember why it goes back up and therefore I can't remember if you should include that or not. And so I'm just going to say right now it goes from oxic to anoxic. That's a consumption term. What's going on down here, sediments are kind of funky. It could be in the past that this was oxic. It could be that there's some of advective force coming through these that's advecting oxic seawater down here. So I don't know what this is. I can't remember if this happens everywhere or perhaps this is just something that's going on in this location.

So for now, just go with this as the consumption term, because that's what we know. We know it's being consumed there. I'll find out what's going on in the lower portions of that graph.

AUDIENCE: I realize that it's just being consumed there.

DIERDRE TOOLE: Well, it could be, I mean if there is an advective force, an advective flow of oxic seawater here for some reason, then perhaps it is being redissolved. But I don't know that that's what's going on. It could be just, I mean, if these are ancient, if this is pelagic, then this is burial. This is old. This is real old. If this is coastal, then this is rather current. And it could still be effectively active. So I just I don't know enough right now in order to answer what's going on deep. Right, just don't worry about it for right now. I'm going to be grading based on this. How's that?

I understand your frustration and I will try and figure it out. But to do this problem set, just worry about this curve here. Well, I can't believe that we didn't cover uranium. I was going to ask you about it, but that's just me.

AUDIENCE: Because there was one thing, use your knowledge.

DIERDRE TOOLE: Of uranium?

AUDIENCE: Yeah.

DIERDRE TOOLE: I'm pretty sure that this came from some old sediments problems that's from the sediments class where we do cover uranium.

AUDIENCE: So can I ask another units question on number two?

DIERDRE TOOLE: You can, but I have to--

AUDIENCE: I can ask you the units question. So am I missing a factor of 1,000 somewhere?

AUDIENCE: Where?

AUDIENCE: Did you switch from micromoles to moles?

AUDIENCE: Where? In the number? I don't what is that, 2, or the one with the porosity and all that.

AUDIENCE: Well in all of those, what I ended up doing is I ended up calculating phi, and then converting phi into liters per centimeter cubed.

AUDIENCE: You're psycho. All right.

AUDIENCE: So that's where I got my factor of 1,000 is because that conversion.

AUDIENCE: Yeah.

AUDIENCE: But I know Louis did it the other way, where he converted his other thing into centimeters cubed instead of liters or something.

AUDIENCE: So you did end up with a factor of 1,000. So your final answer is in micromoles, not moles? No, that doesn't make sense. What's that?

AUDIENCE: For flux?

AUDIENCE: Yeah.

AUDIENCE: Yeah, my final answer is in micromoles.

AUDIENCE: Instead of millimoles?

AUDIENCE: Yeah.

AUDIENCE: All right.