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MARGARET TIVEY: Today, we're going to finish up talking about some of the inputs from rivers and hydrothermal vents. So what we're going to talk about today, we discussed the generation of vent fluid and the generation of rivers. So today, we're going to talk about what happens when these enter the oceans. So when rivers enter the oceans. And this is in terms of estuaries. So I'm going to spend the first third of the class on that.

Then I'm going to talk some about groundwater. And how groundwater input can also affect estimates of fluxes from the continents into the oceans. And then finally, we're going to look at vent fluid entering the oceans, and this includes both formation of deposits, as well as of plumes.

And while the deposits are left on the ocean floor and are a near-source issue, the plumes actually can rise 200 to 300 meters above the sea floor, and you're at about 2,500 meters' depth in the oceans, and you actually create a lot of mixing in a part of the ocean where you wouldn't normally suppose that you were going to have a large driver of mixing. So it has a lot of implications for physical oceanography and for chemical processes that are at a depth that we didn't really consider that important 30 years ago. OK. All right.

So before I start, well, the first thing I want to talk about is that when rivers enter oceans, and when vent fluid enters oceans, you have contrasts. And you're going to have different contrasts for different ones of the fluids. For rivers, your dominant contrast versus the oceans is the change in salinity. So that's the key one for rivers.

And the key one for vent fluids-- or there's two, really, is temperature, which actually creates a large buoyancy, and I'll get to that. So it's temperature and pH are your key differences.

So going back, I want to remind you of what the rivers were like or how rivers were generated. We started with rainwater, and rock. You have weathering. You have congruent dissolution, discongruent dissolution. And the key thing is, you create a fluid that's carrying both dissolved ions, but also, you have particles. And on those particles, you have adsorbed metals.

And you also have clays, iron oxyhydroxides, and humic matter. Put that up there. And those all have negative charges, and so those have ions associated with them as well, and we'll get into that.

And we went briefly through-- at the very end of the river lecture, we went briefly through trace metal release when you have pH changes. So you can have subtle changes-- the pH of river water is going to vary from about 5 to about 7, is that right? Probably? Maybe a little more.

And depending on what its pH is, that can have some effect, but those aren't the dominant ones. It really is this change in salinity. And then the last thing for the rivers was on top of all of this, you have the cyclic salts So that's just a review. OK.

Hopefully you have your notes today. If not, you'll have to remember them because it's much easier to show these pictures as we go through the different types of estuaries.

So essentially what you're doing is the river's coming down to the oceans, and it's going to enter, and any of you who've been near a river mouth, there's multiple different types of estuaries. And the key things that are going to affect the type of mixing in that estuary have to do with the discharge rate. If you've got a very high rate of discharge, you're going to have one style of mixing. And it also has to do with the depth that the estuaries at.

And so we're going to discuss four different types of estuaries briefly. And in these figures-- and my apologies for the quality, they were Xeroxed initially I think about 15 years ago and have been written on and Xeroxed again.

The first type is type A, and here, you have-- and it's where you have a shallow estuary with a small river. So you have a small discharge coming into a small estuary. You have a lot of these around here.

And on this figure, what we have, you have four stations, 1, 2, 3, and 4. And then this just shows the mixing. So you have a station-- I mean the surface. What is that? I don't even know what that's supposed-- this is station 1, 2, 3, 4. But this is the surface, this is the bottom of the estuary, and this is simply showing the type of mixing that's going on.

So when you have low discharge into a small estuary, you have a well-mixed-- well-vertically-mixed processes going on. So you're basically bringing fresh water out, and then you're going to have some tidal sloshing back and forth.

But you end up-- what you want to do is take-- if you look at what the salinity profile is at each of these stations, you go over to the next side of your figure, and pretty much the salinity is not stratified at all.

So these estuaries are-- they're dominated by tidal mixing. They're vertically well-mixed. And this is all in your notes. Probably not as bulleted as this, but they're vertically well-mixed. There's a net outward flow at all depths. And there's a seaward increase in salinity that's similar at all depths.

Now you can also have the same thing going on, but you can end up with-- also in a shallow estuary, but you can end up with a two-layer system. And for this two-layer system, we have the same thing going on. First, let's look at what's happening with the flow. The low-salinity river water is flowing out on the upper part, seawater is flowing in on the lower part, and this is dominantly density-driven, but then you still have fairly-- you do have some mixing, some vertical mixing.

And you end up-- if you take a look at the profiles across each of these stations, you end up with a slightly stratified salinity gradient.

AUDIENCE: And what happens if an estuary is type A or type B? What would cause the inflow of seawater?

MARGARET TIVEY: I think it has to do with the discharge-- a lot of it has to do with the discharge rate. If you have a-- correct me if I'm wrong if anybody-- I mean, if you have a high enough discharge, it's simply a mass-- you're pushing flow out, you're going to draw fluid back in. It's more of a physical-- you'd have to look at the physics of the system.

AUDIENCE: Also, if you have a really shallow estuary, it gives you more turbulent mixing, and so you have better vertical mixing.

MARGARET TIVEY: Right. But these were both for small-- for shallow. Both of these have fairly good vertical mixing, but you do have the-- but you can also-- and this is the other thing. You can also have the same estuary, have the different types at different times of the year.

In fact-- so now I'm going to jump to the-- there's a type D, which I really think should be type C, because it's a variation on type B. And this is when you have a large river entering a shallow estuary. So again, this has to do with discharge rate. And here, you end up with a salt wedge. And as in the case before the surface waters have low salinity, seawater intrudes underneath as a wedge.

And again, here's what the flow looks like. You have a higher rate of discharge, so the flow is coming out here, and this draws in, seawater is coming in here. And it's a mass balance of what's going to happen as the fluid flows.

But here, instead of having a very well-stratified-- one of the key differences is you end up with this wedge. So out at station 4, the salinity increases at a much shallower depth, whereas at station 1, it's fairly fresh down towards the bottom. And there's an example in your notes about the Chesapeake Bay where at times of high discharge, you have a salt wedge, and at times of lower discharge, you have a stratified, a vertically stratified--

Now you also have the situation where you have a very deep estuary, and the example we're using here is that of a fjord, And you have a sill located here. And again, this shows the flow. The freshwater is flowing out at the upper levels. You have return of seawater at lower levels, but not at the deepest levels because you have the sill blocking those deep levels.

But then what happens is you end up with higher salinity fluid basically pooling underneath behind the sill and it's not mixing up as often, and so you end up with a very highly stratified salinity gradient. And the reason we're talking about these salinity gradients is it's that-- is that the major change, the key property that is affecting whether or not you have non-conservative processes is this change of salinity. So it's important to know where the major change in salinity is occurring within the estuary.

And so, again, this just shows a picture of the different types, and you'll have a lot of mixing, but you're mixing up in the shallower region because you have a sill which is preventing entrainment down here. All right.

So now we get into what are the processes that are going to occur? The non-conservative processes that occur in estuaries. And we went over this last week. I'm going to show you a lot of diagrams, and most of these are going to be salinity diagrams where you have the seawater salinity here and freshwater salinity here. And if it's-- and you have some element here.

And so if this is seawater salinity and this is freshwater salinity, if it's conservative mixing, you're simply going to have a straight line. And of course, if you have removal, you're going to be coming on this side of the straight line. So that's removal here and this is addition here.

OK, so. You have a number of different things going on. A key one you have going on-- we talked about what's in the water. And one of the main things that's going on is you have particles in the water. So you have river colloids. And again, these are dominantly iron and humic substances.

And what happens is the sea salt-- well, for all of these we talked about them having a negative charge on the outside, and this is described well in your notes. Basically, the colloids are electrically charged submicron particles. There's going to be the clays, the organic material, and some of the humic-- and some of the iron oxyhydroxides.

So they're too small, they're very, very small, they're not going to undergo gravitational settling. And this negative charge on the outside, they're these electrostatic interactions which keep them in solution and help to keep them in solution. What happens is, when you bring in a higher-salinity fluid and you bring in salts, this neutralizes the electrostatic charges, the electric charges. So when the electric charges are neutralized, the colloids clump together, they aggregate, and then they're large enough to gravitate to settle by gravity.

So basically, you are neutralizing salts. If I could write today. Salts neutralize the electric charges. Which allows aggregation, and then settling.

AUDIENCE: You'll sometimes hear it described as flocculate.

MARGARET TIVEY: Right. Which actually drives me crazy because flocculation, to me, is all fluffy and it stays in the water-- and it does for a little while, but then it gradually settles. So I'll put that as flocculation. There's two C's, right? As opposed to flagellate. Flocculation. OK. OK. And then second one.

So that's the first key. The second one that's very important is desorption. And this is what I talked about-- we talked some about this going on within rivers with the pH changes because when the pH gets lower, you can desorb some of that-- when it gets higher, some of the trace metals desorb from particle surfaces.

But the desorption in the river, you sometimes-- and Scott talked about this on an earlier lecture, and I talked about it as well, you can have calcium released from clay surfaces and replaced by sodium. You can also have radium. Can do the same thing.

The third one-- the first two are the key ones that are going on right in the water. If you just took a batch of seawater and took a [INAUDIBLE] or desorption going on in terms of nonconservative processes. But there's a third one. When you can't explain it by these two, the other thing you can have happening are interactions with estuarine sediments.

So basically, you have-- there's poor water gradients, and so you can-- if you actually stir up sediment on the bottom, you release pore fluids that are in the sediment. You also bring up sediments that have ions adsorbed on the outside, so you can release those. So really, the process is one of resuspension and interaction with the resuspended material. And the other one is release of pore waters. It's not just release, it can be released and exchanged. I know. OK. Put them all on one page.

AUDIENCE: What do you guys think of pore waters in an estuary? Have you guys been to any of the little estuaries around here, the salt marshes? There's lots of what in an estuary? Lots of organic matter. So if you dig down into the mud-- it's a good field trip for you guys this weekend. Go to an estuary and dig down in the mud, you very quickly get to anoxic mud.

MARGARET TIVEY: And you'll be able to tell because it'll start to smell really, really bad.

AUDIENCE: And so that's one of the things, in pore waters from estuaries, is you're now releasing anoxic waters, which are going to have very different metal composition. So in some ways, there is some analogy between the pH--

MARGARET TIVEY: Right.

AUDIENCE: pH changes that we're going to talk about at the end.

MARGARET TIVEY: Yeah. Yeah, and in fact, at the very end when I'm talking about the vents, I'm going to talk about the microbial activity, but I'm not going to talk about it for the estuaries.

AUDIENCE: We will talk about microbes more when you guys-- after the midterm.

MARGARET TIVEY: Oh, is that right? OK. OK. All right. And then, speaking of bugs, this is the last one, which is you can have uptake-- did you read the notes this morning so that you could interject that properly when I needed it? Uptake by estuarine--

AUDIENCE: This one's burned into my brain. I think I have this class burned into my brain.

MARGARET TIVEY: You have uptake by estuary and biota. And they can remove elements. Or this can remove elements. Presumably it can also release elements, but I think it's more the-- or not uptake, but the regurgitation. No, the--

AUDIENCE: I guess I'm kind of confused as to what the definition of conservative mixing is.

MARGARET TIVEY: Oh, we'll get there. You're about you're about to see more graphs than you ever wanted to see. Basically, each of these processes either adds or removes material. If you mixed seawater and you mixed freshwater and you didn't do any of these things, then you'd see a perfect straight line like this, but we don't always.

And for some elements, we do, and I'm going to go through those, and for some of them, we clearly don't. And so you have to explain why you're seeing the removal or the addition. And a key reason why you need to know that is because if you just take the iron value that's in rivers and say that all of that iron makes it all the way out into the ocean, you're wrong because a lot of it is left in the estuaries, and you have to try and figure out and try to quantify how much of that iron flocculates and settles within the estuary. So right now, we're going to show you a bunch of plots.

AUDIENCE: That line, it doesn't-- I mean, that, to me, looks like you have something that's not in freshwater, and then you increase it as you go into saltwater. Whereas--

MARGARET TIVEY: Right, sorry.

AUDIENCE: Well, no--

MARGARET TIVEY: I'm thinking-- you're right. This could be-- if it's high-- you're right, most of them are higher in freshwater and drop that way.

AUDIENCE: It could go either way.

MARGARET TIVEY: But it can go either way. But let me just-- it's easier to look at real data. The old confusing them by trying to be simple.

AUDIENCE: But if it's conservative, wouldn't it just be a horizontal?

MARGARET TIVEY: Well, let's just show you. I'll show you the first one.

AUDIENCE: Then the concentration would be the same in the river--

MARGARET TIVEY: Boron. OK, most of these things-- in order to look at mixing, first of all, you have to figure out what to plot it against, and you have to be plotting it against something that you're pretty confident is conservative. And in general, the salinity is relatively conservative.

You are not dumping large amounts of halite or large amounts of any sea salt into estuaries, and we know that, therefore, you can say either chloride or salinity tends to be conservative. And so an element that is conservative should plot on a straight line relative to that property.

AUDIENCE: [INAUDIBLE] on the axes?

MARGARET TIVEY: The axes, again, this is one of these-- this is-- I believe it's micro-- it's a concentration. It doesn't matter what it is. It's a concentration. Concentration unit. And this is salinity.

And if you take a look at this, you can see that, within error, this boron is falling pretty much along a straight line. And so unless-- whether or not there's something actually going on here or actually going on here, you'd have to put the error bars on your analyzes and really try and figure that out, and we're going to get to issues with that in a little bit.

But this is one where you clearly have conservative processes. You obviously can't be dumping a whole bunch of boron out unless you're dumping it with the salt, but we know that you're not dumping salt out.

In contrast, here's iron. And again, it's simply concentration versus salinity. And so as you'll see, as Kristen pointed out, it can be either direction. Here, there's more boron in seawater than there is in freshwater; and here, there's more iron in the rivers than there is in the saltwater.

AUDIENCE: That straight line is what it would be without--

MARGARET TIVEY: Right. And the straight line is what it would be if there wasn't-- and these little dots, which are much, much smaller than the big, fat pen line, are the actual measurements. And one of the things that they've noted is, in general, iron and humic substances tend to follow this type of curve pretty well, and that's dominantly from flocculation of material and dumping in estuaries and precipitation in estuaries.

That's in contrast to some other things which I'll show you, which are much more complicated. Here, you have barium. And again, all of these are real profiles. Instead of trying to show you these idealistic profiles, these have all been taken directly out of the literature, and it's real data, which is why they're not all beautiful profiles.

This is for barium, and there's a fair amount of barium in both the freshwater and in the saltwater, but they're subtly different. But then you see this very, very large increase in barium, and that is likely from desorption.

And then they show some really nice fun ones where you have copper. And again, this is the kind of thing where you go out, and a lot of this work was being done in the '70s. And they were really trying to figure out-- both Ed Boyle and Ed [? Shakovets ?] in our program did a lot of this work trying to make sense of the data they were collecting and trying to quantify what's going on in the estuaries so we can better quantify river fluxes into the oceans.

And here, you can see that copper, it looks like it's being added at very low salinity, but then as the salinity increases some, it looks like some is being removed, and then at higher salinities, it looks like some is being added again. So copper is one that is more complicated.

And you'll find that a lot of these that are more complicated are ones that have multiple different valence states. And so there's a lot of redox processes that are going on at the same time that affect what's going on.

And then manganese is another-- and here, you show, there's a large removal-- in this profile, there's a large removal at low salinity and a large addition at higher salinity.

AUDIENCE: On the Iron plot-- sorry.

MARGARET TIVEY: Is there a question up there?

AUDIENCE: It might be the same one, I'm not sure. Can you just describe again why the barium has the shape that it does?

MARGARET TIVEY: Oh. The barium has the shape that it does-- well, I'd have to go back to the paper to be sure why it is, but my suspicion is it's from desorption, so that you have barium on various particles that are coming into the estuaries, and then when it mixes with the salt, the barium is being-- there's exchange going on, and some other ion is replacing the barium and the barium is being released. Sort of like calcium and sodium exchange.

AUDIENCE: Could you explain what was happening in the iron profile [INAUDIBLE]?

MARGARET TIVEY: In the iron profile-- oh.

AUDIENCE: On these plots, are you seeing just the free ion concentration or are you seeing also that in solution, but bound to some particle?

MARGARET TIVEY: What you are measuring here when you do this-- and we'll get to it when we do the in-laboratory ones, is you're taking the fluid and you're taking the filtered portion, the less than 0.45 micron portion of the fluid, you're analyzing that and coming up with the total iron. So this is looking at total iron in the 0.45-micron and less fraction, I believe. Yeah, that's what they usually do.

You'd have to read each paper carefully to find out exactly what they're doing, but in general, that's what they do. So no, you're not looking at the iron that's on the large particles that are left on the 0.45-micron filter paper, but anything that can pass through that filter is included in this.

AUDIENCE: So that would be truly dissolved free ions. It would be things that are complex in solution.

MARGARET TIVEY: So it includes--

AUDIENCE: And colloids.

MARGARET TIVEY: Right. So if we go back to this figure where we were looking at what was in the river water, once you get down below this 0.45 micron, it would include some of these clays as well. [? Katelyn, ?] did you have another question?

AUDIENCE: Well, I was just wondering, it looks like in the iron profile, that it dips below the conservative--

MARGARET TIVEY: OK.

AUDIENCE: --and rejoins it?

MARGARET TIVEY: Perfect. Perfect question. Now one of the things is, is it one simple process going on? And these are all assuming that you only have two endmembers. You either you have a seawater endmember and you have a freshwater endmember and you don't have any other endmembers.

And they're trying to simplify these things and come up with fairly straightforward processes that they can extrapolate globally so they can come up with a good idea of what global fluxes are.

However, because of the type of thing you just talked about, [? Katelyn, ?] there's also concern about whether or not there might be a third component. And so there are some examples-- and this shows one here. This was work done by Ed Boyle. He went and looked back at-- this is a dissolved silica profile.

And what could be-- it could be interpreted-- a lot of people would just interpret that as simple from either colloids or desorption-- no, not desorption, adsorption or something else, but what he attributed it to instead was a third component, a third mixing-- I mean a third endmember.

And the reason for that is silica tends to be conservative when you mix, and it was very-- it was somewhat confusing why you would see this decrease-- because what would be the removal mechanism? Nobody had a removal mechanism. So his hypothesis is that there's a third source here of fluid that has a lower silica composition, and that you actually have conservative mixing between this source and the seawater source, and between this source and the river source.

AUDIENCE: Can you point out what in the iron that you're talking about?

MARGARET TIVEY: Oh. We're going to get there. We're going to get to-- that's messy data. Again, none of these have error bars on them. You also-- all you have to do is have one aggregate get into your bottle or have one colloid stick to the side of your container-- I mean, there's a lot-- there are a lot of things that can create noise in these data sets.

But the key thing of this is for you to understand how to look at a profile and determine whether there's been removal or addition, and have some idea of what is likely causing that removal or the addition. And again, here, what confused-- the reason Ed Boyle went back to look at this was in general, he was finding in other profiles that silica was conservative, so an alternative interpretation of this is that you have a third source, fluid source.

AUDIENCE: So, an example of that would be like two different ocean currents--

MARGARET TIVEY: Well--

AUDIENCE: --mixing with a river?

MARGARET TIVEY: Or having--

AUDIENCE: --rivers and the coastal water or something like that?

MARGARET TIVEY: Right. Either two rivers and a coastal water, or in this case, it was actually a shelf source. And we're going to get into groundwater flow as well, you can end up with groundwater flow source.

Yes, he ended up with a-- for this one in particular, he had a river source, an open ocean source, and then an intermediate shelf source. I'm not sure what the source of the shelf source was, but it didn't go into that. But there was basically, you could go out-- so you then go out and sample that body of water, do some CTD casts and see if you can actually find that fluid out there. All right.

Now, because of these complexities and some of the questions that [? Katelyn ?] was raising, you do have a concern and a problem when you have messy data. I talked about some of the issues. And here is a profile that shows copper and a mixing line. And the real question is, is this actually conservative mixing, or do you have some addition going on here and a little bit of addition going on there? What's really going on, and the data are very, very noisy.

So Ed [? Shakovets ?] was one of the key people who helped develop this. You can also do your own mixing diagrams, this is all field data. So you can just take-- one option is to go out to the open ocean-- so go to this station, collect a bunch of this water, go to the river source, collect a bunch of that water, the fresh source, and then do the mixing in the lab after you've-- and you can either do this mixing depending on if you want to look at particle processes or colloid processes, you either filter or do it unfiltered.

This is an example of an unfiltered river water. It was-- says unfiltered river water's 0.4 micron filters, which implies that it's filtered seawater, but anyway, you have to know what-- you would report in the paper exactly what you did with those fluids. But when they did that mixing experiment, this was the data they got from the mixing experiment, and it really--

AUDIENCE: I'm so confused as to the definition of conservative mixing versus non-conservative mixing because-- I mean, is it lab mixing or is it field mixing? Because some of the processes that we went over wouldn't happen in a lab.

MARGARET TIVEY: Right.

AUDIENCE: They're not happening in a lab, but they're happening in the field, what you call it, and--

MARGARET TIVEY: You call it non-conservative mixing no matter what's going on, but you have to identify the process that's going on. So you're right, this type of mixing experiment is only going to look at desorption-- chemical processes between those two bodies of water. It's not going to be considering any of this resuspension of sediment.

AUDIENCE: Or biota--

MARGARET TIVEY: Or biota, right, unless there's-- well, except for microbial activity that's actually taking place in the water column-- in the two fluid samples that you've taken, but it's certainly not going to-- but for this, this is what they were looking at. They were trying to figure out, is copper being desorbed? Is there additional or is there a removal or is it being adsorbed?

And then this was-- some other examples are in your notes. This is a much messier one. Take a look at that nice nickel profile. And I'm sure that scatter, in large part, has to do with errors on the analyzes. And then when they did it in the lab, they got a much cleaner data set.

And similarly-- and then for calcium-- I mean for cadmium, the data were, again, ambiguous. For instance, is there actually a third source sitting here or is this simple desorption? And when they did the mixing calculation-- or the mixing experiments in the lab, they saw that you get this non-uniform-- or you get more desorption occurring at low salinity than at high salinity, but the entire profile can be explained by desorption.

And again, all of these details-- I mean, there isn't-- you cannot just look at a data set and identify exactly what's going on. It's simply an interpretation of field data. And as shown by Ed Boyle, going back and reinterpreting one, the interpretations that are out there for all of these profiles are not necessarily 100% true. I mean, this is their hypothesis as to what's going on right now.

Now there's a-- again in your notes, there's a generalization. This table gives you an idea of, in general, what happens with various ions, and in general, silica-- can you actually see that? Probably not. But silica, uranium, nickel, selenium, arsenic, a lot of these things in most rivers and estuaries are conservative except for manganese, actually, it can differ. It can be any.

So this basically talks about whether or not there's input, namely addition, whether there's removal, or whether there tends to be conservative mixing, and it generalizes. And you'll see that copper, manganese, and a couple of other elements can have any one of the three going on depending on what estuary they're in. OK.

AUDIENCE: What's that sign? The sign for the universal behavior that got cut off at the bottom? Is that underlined or a circle around the crop?

MARGARET TIVEY: I believe it's the underlined-- you're right, that's-- sorry. That's universal behavior. And so you'll see that barium is almost always-- so barium, radium, cadmium are almost always added, whereas iron and beryllium and aluminum are almost-- and rare earth elements are almost always removed. And humics.

AUDIENCE: Is that what the AG is?

MARGARET TIVEY: The humic acids. OK. But you'll notice that it's not very many of these that have this universal.

Today, we're going to finish up talking about some of the inputs from rivers and hydrothermal vents. So what we're going to talk about today, we discussed the generation of vent fluid and the generation of rivers. So today, we're going to talk about what happens when these enter the oceans. So when rivers enter the oceans. And this is in terms of estuaries. So I'm going to spend the first third of the class on that.

Then I'm going to talk some about groundwater and how groundwater input can also affect estimates of fluxes from the continents into the oceans. And then finally, we're going to look at vent fluid entering the oceans. And this includes both the formation of deposits, as well as of plumes.

And while the deposits are left on the ocean floor and are a near-source issue, the plumes actually can rise 200 to 300 meters above the sea floor. And you're at about 2,500 meters' depth in the oceans, and you actually create a lot of mixing in a part of the ocean where you wouldn't normally suppose that you were going to have a large driver of mixing.

So it has a lot of implications for physical oceanography and for chemical processes that are at a depth that we didn't really consider that important 30 years ago. OK. All right.

So before I start-- or the first thing I want to talk about is that when rivers enter oceans and when vent fluid enters oceans, you have contrasts. And you're going to have different contrasts for different ones of the fluids. For rivers, your dominant contrast versus the oceans is the change in salinity. So that's the key one for rivers.

And the key one for vent fluids-- or there's two, really, it's temperature, which actually creates a large buoyancy, and I'll get to that. So it's temperature and pH are your key differences.

So going back, I want to remind you of what the rivers were like or how rivers were generated. We started with rainwater. And rock. You have weathering. You have congruent dissolution, discongruent dissolution. And the key thing is you create a fluid that's carrying both dissolved ions, but also, you have particles.

And on those particles, you have adsorbed metals. And you also have clays, iron oxyhydroxides, and humic matter. Put that up there. And those all have negative charges, and so those have ions associated with them as well, and we'll get into that.

And we went briefly through, at the very end of the lecture, we went briefly through trace metal release when you have pH changes. So you can have subtle changes-- the pH of river water is going to vary from about 5 to about 7. Is that right? Probably? Maybe a little more.

And depending on what its pH is, that can have some effect, but those aren't the dominant ones, it really is this change in salinity. And then the last thing for the rivers was on top of all of this, you have the cyclic salt-- the cyclic salts. OK. So that's just sort of a review. Do I need to show that? OK.

Hopefully you have your notes today. If not, you'll have to remember them because it's much easier to show these pictures as we go through the different types of estuaries. So essentially what you're doing is a river's coming down to the oceans, and it's going to enter. And any of you who've been near a river mouth, there's multiple different types of estuaries.

And the key things that are going to affect the type of mixing in that estuary have to do with the discharge rate. If you've got a very high rate of discharge, you're going to have one style of mixing. And it also has to do with the depth that the estuary's at. And so we're going to discuss four different types of estuaries briefly.

And in these figures-- and my apologies for the quality, they were Xeroxed initially I think about 15 years ago and have been written on and Xeroxed again. So the first type is type A, and here, you have-- and it's where you have a shallow estuary with a small river. So you have a small discharge coming into a small estuary. You have a lot of these around here.

And on this figure, what we have-- you have four stations, 1, 2, 3, and 4. And then this just shows the mixing. So you have a station-- I mean the surface. What is that? I don't even know what that's supposed-- this is station 1, 2, 3, 4. But this is the surface, this is the bottom of the estuary, and this is simply showing the type of mixing that's going on.

So when you have low discharge into a small estuary, you have a well-mixed-- well-vertically-mixed processes going on. So you're basically bringing freshwater out. And then you're going to have some tidal sloshing back and forth, but you end up-- what you want to do is take a look at-- if you look at what the salinity profile is at each of these stations, you go over to the next side of your figure, and pretty much the salinity is not stratified at all.

So these estuaries are-- they're dominated by tidal mixing, they're vertically well-mixed. And this is all in your notes. Probably not as bulleted as this, but they're vertically well-mixed, there's a net outward flow at all depths, and there's a seaward increase in salinity that's similar at all depths.

Now you can also have the same thing going on, but you can end up with-- also in a shallow estuary, but you can end up with a two-layer system. And for this two-layer system, we have the same thing going on. First, let's look at what's happening with the flow.

The low-salinity river water is flowing out on the upper part. Seawater is flowing in on the lower part. And this is dominantly density-driven, but then you still have fairly-- you do have some mixing, some vertical mixing. And you end up, if you take a look at the profiles across each of these stations, you end up with a slightly stratified salinity gradient.

AUDIENCE: And what happens if an estuary is type A or type B? What would cause the inflow of seawater?

MARGARET TIVEY: I think it has to do with the discharge-- a lot of it has to do with the discharge rate. If you have a-- correct me if I'm wrong, if anybody-- I mean, if you have a high enough discharge, it's simply a mass-- you're pushing flow out, you're going to draw fluid back in. It's more of a-- you'd have to look at the physics of the system.

AUDIENCE: Also, if you have a really shallow estuary, it gives you more turbulent mixing--

MARGARET TIVEY: Right.

AUDIENCE: --better vertical mixing, too.

MARGARET TIVEY: Right, but these were both for small-- for shallow. Both of these have fairly good vertical mixing, but you do have the-- but you can also-- and this is the other thing, you can also have the same estuary have the different types at different times of the year.

In fact-- so now I'm going to jump to the-- there's a type D, which I really think should be type C because it's one-- it's a variation on type B. And this is when you have a large river entering a shallow estuary. So again, this has to do with discharge rate. And here, you end up with a salt wedge.

And as in the case before the surface waters have low salinity, seawater intrudes underneath as a wedge. And again, here's what the flow looks like. You have a higher rate of discharge, so the flow is coming out here, and this draws in, seawater is coming in here. And it's a mass balance of what's going to happen as the fluid flows.

But here, instead of having a very well-stratified-- one of the key differences is, you end up with this wedge. So out at station 4, the salinity increases at a much shallower depth, whereas at station 1, it's fairly fresh down towards the bottom. And there's an example in your notes about the Chesapeake Bay where at times of high discharge, you have a salt wedge, and at times of lower discharge, you have a stratified, a vertically stratified--

Now you also have the situation where you have a very deep estuary. And the example we're using here is that of a fjord, and you have a sill located here. And again, this shows the flow. The freshwater is flowing out at the upper levels. You have return of seawater at lower levels, but not at the deepest levels because you have the sill blocking those deep levels.

But then what happens is, you end up with higher-salinity fluid basically pooling underneath behind the sill, and it's not mixing up as often. And so you end up with a very highly stratified salinity gradient.

And the reason we're talking about these salinity gradients is it's that-- is that the major change, the key property that is affecting whether or not you have non-conservative processes is this change of salinity, so it's important to know where the major change in salinity is occurring within the estuary.

And so, again, this just shows a picture of the different types. And you'll have a lot of mixing, but you're mixing up in the shallower region because you have a sill which is preventing entrainment down here. All right.

So now we get into what are the processes that are going to occur, the non-conservative processes that occur in estuaries? And we went over this last week. I'm going to show you a lot of diagrams. And most of these are going to be salinity diagrams where you have the seawater salinity here and freshwater salinity here.

And if it's-- and you have some element here. And so if this is seawater salinity and this is freshwater salinity, if it's conservative mixing, you're simply going to have a straight line.

And of course if you have removal, you're going to be coming on this side of the straight line. So that's removal here, and this is addition here. OK. So you have a number of different things going on. A key one you have going on-- we talked about what's in the water. And one of the main things that's going on is you have particles in the water. So you have river colloids. And again, these are dominantly iron and humic substances.

And what happens is the sea salt-- well, for all of these, we talked about them having a negative charge on the outside, and this is described well in your notes.

Basically, the colloids are electrically charged submicron particles. There's going to be the clays, the organic material, and some of the humic-- and some of the iron oxyhydroxides. So they're too small, they're very, very small, they're not going to undergo gravitational settling. And this negative charge on the outside, there are these electrostatic interactions which keep them in solution and help to keep them in solution.

What happens is, when you bring in a higher-salinity fluid and you bring in salts, this neutralizes the electrostatic charges, the electric charges. So when the electric charges are neutralized, the colloids clump together, they aggregate, and then they're large enough to gravitate to settle by gravity. So basically, you are neutralizing salts. If I could write today. Salts neutralize the electric charges, which allows aggregation, and then settling.

AUDIENCE: You'll sometimes hear it described as flocculate.

MARGARET TIVEY: Right. Which actually drives me crazy because flocculation, to me, is all fluffy and it stays in the water, and it does for a little while, but then it gradually settles. So I'll put that as flocculation. There's two C's, right? As opposed to flagellate. Flocculation. OK. OK. And then the second one.

So that's the first key. The second one that's very important is desorption. And this is what I talked about-- we talked some about this going on within rivers with the pH changes, because when the pH gets lower, you can desorb some of that-- when it gets higher, some of the trace metals desorb from particle surfaces.

But the desorption in the river, you sometimes-- and Scott talked about this on an earlier lecture, and I talked about it as well, you can have calcium released from clay surfaces and replaced by sodium. You can also have radium. Can do the same thing.

The third one-- the first two are the key ones that are going on right in the water. If you just took a batch of seawater and took a [INAUDIBLE] or desorption going on in terms of nonconservative processes. But there's a third one. When you can't explain it by these two, the other thing you can have happening is our interactions with estuarine sediments.

So basically, you have-- there's pore water gradients, and so you can-- if you actually stir up sediment on the bottom, you release pore fluids that are in the sediment. You also bring up sediments that have ions adsorbed on the outside, so you can release those. So really, the process is one of resuspension, an interaction with the resuspended material, and the other one is release of pore waters. And it's not just release, it can be release and exchange. Put them all on one page.

AUDIENCE: What do you guys think of pore waters in an estuary? Have you guys been to any of the little estuaries around here, the salt marshes? There's lots of what in a estuary? Lots of organic matter. So if you dig down into the mud-- it's a good field trip for you guys this weekend. Go to an estuary and dig down in the mud, you very quickly get to anoxic mud.

MARGARET TIVEY: And you'll be able to tell because it'll start to smell really, really bad.

AUDIENCE: And so that's one of the things in pore waters from estuaries, is you're now releasing anoxic waters, which are going to have very different metal composition. So in some ways, there is some analogy between the pH and--

MARGARET TIVEY: Right.

AUDIENCE: --pH changes that we're going to talk about at the end.

MARGARET TIVEY: Yeah. Yeah, and in fact, at the very end, when I'm talking about the vents, I'm going to talk about the microbial activity, but I'm not going to talk about it for the estuaries.

AUDIENCE: We will talk about microbes more when you guys-- after the midterm.

MARGARET TIVEY: Oh, is that right? OK.

AUDIENCE: --or some bugs.

MARGARET TIVEY: OK. All right. And then, speaking of bugs, this is the last one, which is you can have uptake. Did you read the notes this morning so that you could interject that properly when I needed it? Uptake by estuary--

AUDIENCE: This one's burned into my brain. I think I have this class burned into my brain.

MARGARET TIVEY: You have uptake by estuary and biota. And they can remove elements. Or this can remove elements. Presumably it can also release elements, but I think it's more the-- or not uptake, but the regurgitation-- no, the--

AUDIENCE: I guess I'm kind of confused as to what the definition of conservative mixing is.

MARGARET TIVEY: Oh, we'll get there. You're about you're about to see more graphs than you ever wanted to see. Basically, each of these processes either adds or removes material. If you mixed seawater and you mixed freshwater and you didn't do any of these things, then you'd see a perfect straight line like this, but we don't always. And for some elements we do, and I'm going to go through those, and for some of them we clearly don't. And so you have to explain why you're seeing the removal or the addition.

And a key reason why you need to know that is because if you just take the iron value that's in rivers and say that all of that iron makes it all the way out into the ocean, you're wrong because a lot of it is left in the estuaries, and you have to try and figure out and try to quantify how much of that iron flocculates and it settles within the estuary. So right now, we're going to show you a bunch of plots--

AUDIENCE: That line, it doesn't-- I mean, that, to me, looks like you have something that's not in freshwater, and then you increase it as you go into saltwater. Whereas if it was--

MARGARET TIVEY: Right, sorry. Oh--

AUDIENCE: Well, no--

MARGARET TIVEY: I'm thinking-- you're right, this could be-- if it's high in-- you're right, most of them are higher in freshwater and drop that way.

AUDIENCE: It could go either way.

MARGARET TIVEY: But It can go either way. But let me just-- it's easier to look at real data. The old confusing them by trying to be simple.

AUDIENCE: But if it's conservative, wouldn't it just be a horizontal?

MARGARET TIVEY: Well, let's just show you. I'll show you the first one.

AUDIENCE: Then the concentration would be the same in the river--

MARGARET TIVEY: Boron. OK, most of these things-- in order to look at mixing, first of all, you have to figure out what to plot it against, and you have to be plotting it against something that you're pretty confident is conservative. And in general, the salinity is relatively conservative. You are not dumping large amounts of halite or large amounts of any sea salt into estuaries.

And we know that, therefore, you can say either chloride or salinity tends to be conservative. And so an element that is conservative should plot on a straight line relative to that property.

AUDIENCE: [INAUDIBLE] on the axes?

MARGARET TIVEY: The axes, again, this is one of these-- this is-- I believe it's micro-- it's a concentration. It doesn't matter what it is. It's a concentration. Concentration unit. And this is salinity.

And if you take a look at this, you can see that within error, this boron is falling pretty much along a straight line. And so unless-- whether or not there's something actually going on here or actually going on here, you'd have to put the error bars on your analyzes and really try and figure that out, and we're going to get to issues with that in a little bit.

But this is one where you clearly have conservative processes. You obviously can't be dumping a whole bunch of boron out unless you're dumping it with the salt, but we know that you're not dumping salt out.

In contrast, here's iron. And again, it's simply concentration versus salinity. And so as you'll see, as [? Kristen ?] pointed out, it can be either direction. Here, there's more boron in seawater than there is in freshwater; and here, there's more iron in the rivers than there is in the saltwater.

AUDIENCE: That straight line is what it would be without--

MARGARET TIVEY: Right. And the straight line is what it would be if there wasn't-- and these little dots, which are much, much smaller than the big, fat pen line, are the actual measurements. And one of the things that they've noted is, in general, iron and humic substances tend to follow this type of curve pretty well, and that's dominantly from flocculation of material and dumping in estuaries and precipitation in estuaries.

That's in contrast to some other things which I'll show you, which are much more complicated. Here, you have barium. And again, all of these are real profiles. Instead of trying to show you these idealistic profiles, these have all been taken directly out of the literature, and it's real data, which is why they're not all beautiful profiles.

This is for barium, and there's a fair amount of barium in both the freshwater and in the saltwater, but they're subtly different, but then you see this very, very large increase in barium, and that is likely from desorption.

And then they show some really nice fun ones where you have copper. And again, this is the kind of thing where you go out, and a lot of this work was being done in the '70s, and they were really trying to figure out-- both Ed Boyle and Ed [? Shakovets ?] in our program did a lot of this work trying to make sense of the data they were collecting and trying to quantify what's going on in the estuaries so we can better quantify river fluxes into the oceans.

And here, you can see that copper, it looks like it's being added at very low salinity, but then as the salinity increases some, it looks like some is being removed, and then at higher salinities, it looks like some is being added again. So copper is one that is more complicated.

And you'll find that a lot of these that are more complicated are ones that have multiple different valence states, and so there's a lot of redox processes that are going on at the same time that affect what's going on. And then manganese is another. And here, you show-- there's a large removal-- in this profile, there's a large removal at low salinity and a large addition at higher salinity.

AUDIENCE: On the iron plot-- sorry.

MARGARET TIVEY: Is there a question up there?

AUDIENCE: It might be the same one, I'm not sure. Can you just describe again why the barium has the shape that it does?

MARGARET TIVEY: Oh, the barium has the shape that it does-- well, I'd have to go back to the paper to be sure why it is, but my suspicion is it's from desorption, so that you have barium on various particles that are coming into the estuaries, and then when it mixes with the salt, the barium is being-- there's exchange going on, and some other ion is replacing the barium and the barium is being released. Sort of like calcium and sodium exchange.

AUDIENCE: Could you explain what was happening in iron profile [INAUDIBLE]

MARGARET TIVEY: In the iron profile-- oh.

AUDIENCE: On these plots, are you seeing just the free ion concentration or are you seeing also that in solution, but bound to some particle?

MARGARET TIVEY: What you are measuring here when you do this-- and we'll get to it when we do the in-laboratory ones, is you're taking the fluid and you're taking the filtered portion, the less than 0.45 micron portion of the fluid, you're analyzing that and coming up with the total iron. So this is looking at total iron in the 0.45-micron-and-less fraction, I believe. Yeah, that's what they usually do.

You'd have to read each paper carefully to find out exactly what they're doing, but in general, that's what they do. So no, you're not looking at the ion that's on the large particles that are left on the 0.45-micron filter paper, but anything that can pass through that filter is included in this.

AUDIENCE: So that would be truly dissolved free ions. It would be things that are complex in solution.

MARGARET TIVEY: Right. So it includes--

AUDIENCE: And colloids.

MARGARET TIVEY: Right. So if we go back to this figure where we were looking at what was in the river water, once you get down below this 0.45 micron, it would include some of these clays as well. [? Katelyn, ?] did you have another question?

AUDIENCE: Well, I was just wondering, it looks like in the iron profile, that it dips below the conservative--

MARGARET TIVEY: OK.

AUDIENCE: --and rejoins it.

MARGARET TIVEY: Perfect. Perfect question. OK. Now one of the things is, is it one simple process going on? And these are all assuming that you only have two endmembers. You either you have a seawater endmember and you have a freshwater endmember and you don't have any other endmembers. And they're trying to simplify these things and come up with fairly straightforward processes that they can extrapolate globally so they can come up with a good idea of what global fluxes are.

However, because of the type of thing you just talked about, [? Katelyn, ?] there's also concern about whether or not there might be a third component. And so there are some examples-- and this shows one here. This was work done by Ed Boyle. He went and looked back at-- this is a dissolved silica profile. And what could be-- it could be interpreted-- a lot of people would just interpret that as simple-- from either colloids or desorption-- no, not desorption, adsorption or something else.

But what he attributed it to instead was a third component, a third mixing-- I mean a third endmember. And the reason for that is silica tends to be conservative when you mix, and it was very-- it was somewhat confusing why you would see this decrease-- because what would be the removal mechanism, nobody had a removal mechanism.

So his hypothesis is that there's a third source here of fluid that has a lower silica composition, and that you actually have conservative mixing between this source and the seawater source and between this source and the river source.

AUDIENCE: Can you point out what in the iron that you're talking about?

MARGARET TIVEY: Oh, we're going to get there. We're going to get to that's messy data. Again, none of these have error bars on them. You also-- all you have to do is have one aggregate get into your bottle or have one colloid stick to the side of your container-- I mean, there's a lot-- there are a lot of things that can create noise in these data sets.

But the key thing of this is for you to understand how to look at a profile and determine whether there's been removal or addition, and to have some idea of what is likely causing that removal or the addition. And again, here, what confused-- the reason Ed Boyle went back to look at this was in general, he was finding another profiles that silica was conservative, so an alternative interpretation of this is that you have a third source fluid source.

AUDIENCE: So an example of that would be like two different ocean currents--

MARGARET TIVEY: Well--

AUDIENCE: --mixing with a river?

MARGARET TIVEY: Or having--

AUDIENCE: --rivers and the coastal water or something like that?

MARGARET TIVEY: Right. Either two rivers and a coastal water, or in this case, it was actually a shelf source. And we're going to get into groundwater flow as well, you can end up with groundwater flow source. OK.

Yes. He ended up with a-- for this one in particular, he had a river source, an open ocean source, and then an intermediate shelf source. I'm not sure what the source of the shelf source was, but it didn't go into that. But there was basically, you could go out-- so you then go out and sample that body of water, do some CTD casts, and see if you can actually find that fluid out there. All right.

Now, because of these complexities and some of the questions that [? Katelyn ?] was raising, you do have a concern and a problem when you have messy data. I talked about some of the issues. And here is a profile that shows copper and a mixing line. And the real question is, is this actually conservative mixing or do you have some addition going on here and a little bit of addition going on there? What's really going on, and the data are very, very noisy.

So Ed [? Shakovets ?] was one of the key people who helped develop this. You can also do your own mixing diagrams. This is all field data. So you can just take-- one option is to go out to the open ocean-- so go to this station, collect a bunch of this water, go to the river source, collect a bunch of that water, the fresh source, and then do the mixing in the lab after you've-- and you can either do this mixing depending on if you want to look at particle processes or colloid processes, you either filter or do it unfiltered.

This is an example of an unfiltered river water. It says unfiltered river water's 0.4-micron filters, which implies that it's filtered seawater, but anyway, you have to know what-- you would report in the paper exactly what you did with those fluids. But when they did that mixing experiment, this was the data they got from the mixing experiment, and it really--

AUDIENCE: I'm so confused as to the definition of conservative mixing versus non-conservative mixing because-- I mean, is it lab mixing or is it field mixing? Because some of the processes that we went over wouldn't happen in a lab. They're not happening in the lab, but they're happening in the field, what you call it, and--

MARGARET TIVEY: You call it non-conservative mixing no matter what's going on, but you have to identify the process that's going on. So you're right, this type of mixing experiment is only going to look at desorption-- chemical processes between those two bodies of water. It's not going to be considering any of this resuspension of sediment.

AUDIENCE: Or biota--

MARGARET TIVEY: Or biota, right, unless there's-- well, except for microbial activity that's actually taking place in the water column-- in the two fluid samples that you've taken, but it's certainly not going to-- but for this, this is what they were looking at. They were trying to figure out, is copper being desorbed? Is there additional or is there a removal or is it being adsorbed?

And then this was-- some other examples are in your notes. This is a much messier one. Take a look at that nice nickel profile. And I'm sure that scatter in large part has to do with errors on the analyzes. And then when they did it in the lab, they got a much cleaner data set.

And similarly-- and then for calcium-- I mean for cadmium, the data were, again, ambiguous. For instance, is there actually a third source sitting here or is this simple desorption? And when they did the mixing calculation-- or the mixing experiments in the lab, they saw that you get this non-uniform-- you get more desorption occurring at low salinity than at high salinity, but the entire profile can be explained by desorption.

And again, all of these details-- I mean, there isn't-- you cannot just look at a data set and identify exactly what's going on. It's simply an interpretation of field data. And as shown by Ed Boyle, going back and reinterpreting one, the interpretations that are out there for all of these profiles are not necessarily 100% true. I mean, this is their hypothesis as to what's going on right now.

Now there's a-- again in your notes, there's a generalization. This table gives you an idea of, in general, what happens with various ions. And in general, silica-- can you actually see that? Probably not. But silica, uranium, nickel, selenium, arsenic, a lot of these things in most rivers and estuaries are conservative except for manganese. Actually, it can differ. It can be any.

So this basically talks about whether or not there's input, namely addition, whether there's removal, or whether there tends to be conservative mixing, and it generalizes. And you'll see that copper, manganese, and a couple of other elements can have any one of the three going on depending on what estuary they're in. OK.

AUDIENCE: What's the sign for the universal behavior that got cut off at the bottom? Is that underlined or is it a circle around the crop?

MARGARET TIVEY: I believe it's the underlined-- right, that's-- sorry. That's universal behavior. And so you'll see that barium is almost always-- so barium, radium, cadmium are almost always added, whereas iron and beryllium and aluminum are almost-- and rare earth elements are almost always removed.

AUDIENCE: And humics.

MARGARET TIVEY: And humics.

AUDIENCE: Is that what the AG is?

MARGARET TIVEY: The humic acids. OK. But you'll notice that it's not very many of these that have this universal behavior. I'm surprised silica is removed sometimes. OK.

You can also have some other interesting things happen. There's an example of uranium, a nice, nasty one. And this-- I'm sorry, this plot is truly hideous. It's best to read the notes and read the figure caption, but all this is really showing is that in some places, you tend to have conservative mixing of uranium; in others, you have a removal of uranium; and in others, you have addition.

And supposedly, on this diagram, you see addition of uranium, but I can't see it myself. And one of the hypotheses for what's going on is that the uranium is bound in the iron oxyhydroxides, these colloids-- and this is in your notes. These colloids flocculate, they settle on the bottom. Then these iron oxyhydroxide coatings dissolve, releasing the uranium back up into the water column, so with time, you end up with an addition of uranium in the estuary.

AUDIENCE: Well, the iron oxyhydroxides dissolve in anoxic sediments, right? Is that the key step?

MARGARET TIVEY: I would think because-- except you can also have exchange. I mean, uranium is-- we don't need to go into all the details. The point is, as I said before, I don't want you to memorize exactly what's happening to every element. I want you to understand the processes that can go on.

And another additional-- another process that can lead to addition is interaction-- is dissolution of material that has settled on the bottom as the conditions change. And if there's any dissolution or any ion exchange going on, things can get desorbed later. Things that take a longer time than they take-- so you just have to think, think about what processes could possibly be going on.

OK, now we're going to get into radium isotopes, which is going to segue us into groundwater, but in general, radium isotopes can help unravel some of these very complex processes that are going on. I have to make sure that-- I have to speed up, otherwise I won't get to my favorite part. The vents will get shafted again.

OK. So radium isotopes, Bill talked about radium isotopes. I'm not going to go into all the details, but you know that there are multiple different isotopes of radium. Radium behaves similarly to calcium and barium. And you can have radium adsorbed on exchange sites, such as negatively charged-- on the exchange sites of negatively charged clay particles in river water.

And then it is rapidly desorbed in estuaries by ion exchange. The ion exchange occurs as salinity increases. However, if the radium was only occurring because of this mixing, you would expect to see the exact same ratios. So you'd expect-- if you see the isotope ratios, you ask yourself the question, are isotope ratios the same on the particles, on the river particles, as they are in the estuary water?

And the answer is no. Basically, there's a lot more radium-224 than-- the radium-224 is too high in the estuary. And when they looked at that, they then took a look at what other processes might be happening, and that was when they account for this excess radium-224 by resuspension of sediments.

And that results in extra release of radium-224, which can grow into the sediments because it grows in rapidly, whereas radium-226 and radium-228 take a lot longer to grow in. So 224-radium grows into said particles more rapidly. And that allows you to use radium isotopes as tracers of processes.

And there are a couple graphs in your notes-- I'm not going to go through them because you can look at them, but they show excesses, they show addition of radium. And when you do these calculations-- well, I'll just show you one. Take a look at the radium-224, 226, and 228, and you see that there's much greater in growth of-- I mean, much greater abundances in addition of radium-224. Wonderful figures.

AUDIENCE: I just-- you can't see the symbol, so you don't really know which one's which.

MARGARET TIVEY: Well, you can in your notes.

AUDIENCE: You can? OK.

MARGARET TIVEY: Yeah. One of the things we're trying to do is figure out the time to redraft every single one of these figures, but we also have to go back and find exactly what paper they all came out of. OK. All right.

AUDIENCE: How not to obey the copyright law.

MARGARET TIVEY: Exactly. That's the next problem. OK. So-- well, for-- it's fine as long as you're lecturing.

AUDIENCE: No, I mean these, since we don't have the paper--

MARGARET TIVEY: Right. That's right, yeah. OK. All right. So, groundwater.

AUDIENCE: Question.

MARGARET TIVEY: Yeah.

AUDIENCE: I'm a little confused by this term that you said growth in, that radium-224 has a--

MARGARET TIVEY: Do you remember Bill Martin had a whole lecture on radium and thorium isotopes?

AUDIENCE: Are you saying that it's how fast it is derived from its parent isotopes? Is that what you mean by--

MARGARET TIVEY: Yes. So radium-224, you're basically producing much-- radium-224 is being produced much more rapidly than radium-226. It's growing in-- it's called growing in--

AUDIENCE: Another way of saying that is because radium-224 has a shorter half-life, when you have a perturbation, it will reach secular equilibrium with its parent more rapidly than a longer-lived radium isotope. And we went through that a little bit, how long something takes after perturbation to get back to secular equilibrium. And that depends upon the half-life of the daughter isotope.

MARGARET TIVEY: OK. And again, it's described fairly well in the lecture notes, but then you'd also want to go back to the lecture notes or actually do a problem where you're using radium isotopes so that you really understand how it works. It's tough to understand it the first time you go through a lecture.

AUDIENCE: How do you distinguish from a radioactive process versus a kinetic fractionation of different isotopes? Like, if you're--

AUDIENCE: But what's the mass difference between radium?

AUDIENCE: Well, sure, it's relatively small, but, I mean--

AUDIENCE: Very small.

AUDIENCE: But you could presumably measure very small.

AUDIENCE: Well-- well, OK, but the signals you're seeing are much larger.

AUDIENCE: OK.

MARGARET TIVEY: Right.

AUDIENCE: --can expect by mass fractionation--

MARGARET TIVEY: And I'm going to--

AUDIENCE: --in context of what you see?

MARGARET TIVEY: And I'm going to be talking about radioisotopes a little more in the groundwater, so let's answer those questions once we've gone through all of this--

AUDIENCE: And we'll talk about it more in my section.

MARGARET TIVEY: Oh, you will? OK, good, because otherwise I won't get to vent fluids. OK, groundwater. Groundwater is fairly-- well, it was overlooked for many years. Basically you have a continent, you have-- just as you-- you have the oceans here. You have a continental system. And you've got some kind of--