

## MITOCW | 7.014-2005-L20

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This lecture is going to be very dependent upon the PowerPoint slides, because if I take the time to draw the cycles on the board, we'd be here forever. So I would say sit back and relax because you have the slides. They're on the Web.

And try to focus on what the take-home message is.

OK, but before we go on to biogeochemical cycles, I want to just briefly review some of the things that we learned in the second lecture. I got feedback from many of you, actually, on the things that were difficult to understand from that lecture, and those are important for understanding these cycles.

And the one thing that some people were confused by was this anaerobic respiration. Remember, I drew this on the board, and it showed a lot of reduction reactions.

And I think that was confusing for some people, so let's just go over that very quickly. You've learned in Graham's lectures, and in my lectures, that anaerobic respiration, respiration of organisms where there is oxygen, that oxygen is the terminal electron receptor here in that electron transport chain and it's reduced to water. So in aerobic environments, when organisms respire oxygen it's reduced to water.

If there's no oxygen around, the organisms, and in this case it's always bacteria, look for the next thermodynamically favorable electron acceptor. And so, whatever is dominant in that environment and is most thermodynamically favorable, they'll use. So, the sulfate reducing organisms use sulfate and reduce it to  $\text{H}_2\text{S}$ . Denitrifying organisms use nitrate and reduce it to these forms of reduced nitrate or reduce nitrogen. And we talked about iron bacteria [epi?] plus three, and reduce it to epi plus two.

Some can use manganese, etc. Whatever's there, and it's thermodynamically favorable, they'll use. OK, so that clarifies that. Some of the people said, you kept talking about symmetry. You kept talking about symmetry.

I didn't see any symmetry, and in hindsight I can understand why, because it just threw that out and I didn't really point it out.

So what I was talking about was as we went through these processes, you see here, these elements, sulfate and nitrogen, nitrate, are being reduced. There are other processes, particularly chemosynthesis in which these reduced compounds, here's  $\text{H}_2\text{S}$  and ammonia or be oxidized. So that's the symmetry that I was talking about. And if you didn't have that, if all the organisms were reducing things, the whole system would run down. You have to have organisms that are also oxidizing things.

And that's a key component of all of these, or not all of the biogeochemical cycles, but particularly the cycles of nitrogen and sulfur, which have this [redox?

chemistry. So that's a symmetry that I was talking about.

OK, now so let's talk about how we think about biogeochemical cycles.

Did you see the slide in the back? Try to turn the lights off? That was a double question. Can you see the slide in the back?

Yes? OK. So this is a generic map of the components of biogeochemical cycles. And we can think of the earth as a giant chemical factory in the sense that has what we call compartments, or reservoirs, or pools of a particular element. Or it might be water that we are analyzing, and then there are fluxes between these pools.

So here's a flux, an arrow. So typically these are diagrammed with boxes and arrows connecting them. And you don't have to use all of these boxes. It could be we are just looking at land, atmosphere, and ocean. I mean, you can construct whatever model you want cities. And these are just some useful conversion factors for the amount of things that we're going to have flowing between these compartments. And here, again, this is something we defined earlier when we were talking about productivity. The main residence time of, say, an element, say, carbon in the terrestrial biomass, is the pool size, the amount of carbon that they're divided by the mean flux in or out of the pool, OK? It's exactly the same concept we talked about for carbon. And then the fractional turnover, one over the mean residence time is simply the fraction.

If we're talking about carbon again in trees, it's the fraction that's removed per unit time. OK, so you can see that when we talk about mean residence time of an element in one of these reservoirs, if the whole system is in a steady state, in other words, if the amount in a reservoir is changing, the flux in is going to be the same as the flux out, right? You know that. Just like a bathtub, if you have water flowing in, water flowing out, the level will stay the same if the flow rate in is the same as the flow rate out. But often in nature, you don't have that exactly. And if you don't, the size of these reservoirs is either increasing or decreasing. So when you're analyzing these systems, your most of the time trying to get the very rough estimate of mean residence time.

So if the flow in and the flow out isn't the same, you can either average them and use that as your flux, or you could define your residence time with respect to the flow in or the flow out. So, these are just gross approximations. What we want to understand is the residence time thousands of years, millions of years, days, rough approximation. And the other thing I want to say before we go on, is that all of these cycles, we're going to talk about them element by element: phosphorus, carbon, whatever. But they're all tightly coupled in the system. And we'll bring that up again later. Before we go on, let's just look at the solar energy budget, which is driving this whole system, mostly, there is some geothermal energy, energy for the Earth's, the magma that is also driving biogeochemical cycles. But the solar energy is the primary driver.

And if you say that the total energy from the sun is 100%, it's that energy that is used in evaporation, and winds, and photosynthesis that is the important component driving the cycles. And you'll see that photosynthesis is a tiny fraction.

The energy that plants harvest is a tiny fraction of the total energy that is driving the Earth's system. And yet, this photosynthesis, which is the basis of the biosphere, has an enormous effect on the conditions on Earth. That's an interesting nonlinearity of the system. OK, so let's start with the geological cycle, which is the slowest moving, people don't even think of it as a cycle because while we are on Earth we don't see rocks flying through, well, sometimes you see rocks in a landslide or whatever, but for the most part you don't think of rocks as cycling. But they do. And if they didn't, the system would run down much faster than it is.

And we've all heard about plate tectonics, that the surface of the Earth is made up of these plates that are slowly shifting.

And when they shift you have earthquakes, like we've had recently a lot of. And also, you have volcanic eruptions that bring material from the inside of the Earth up to the surface and it overflows. And that's part of this geological cycle. So, here's a really oversimplified, when the geology professor in our department so that ever showing this he had a heart attack by how simplified it is.

But it's just so you get the idea. When he started editing it, there are so many arrows you can never cope with that.

But just get the idea. There's geothermal energy coming in from the inner core of the Earth where you have magma.

Think volcanic eruption, lava, which ultimately becomes surface rocks. And they're eroded by weathering by rain, and then elements from that go into the soils.

Soils eventually become sedimentary rocks. We're talking over really, really long time periods, which become metamorphic rocks.

Some of those are uplifted, and some of them are melted and become magma. But it is a cycle, a very, very slow cycle. In fact, somewhere I read 70%, you do not need to know this. This is not geology class.

But just so you have an idea, 75% of the rocks now on the surface of the earth have been uplifted. So it's almost as if the Earth is, on average, maybe halfway through a cycle. So, this erosion here, and weathering, as we talked about last time is critical for making nutrients available to the biosphere. And the force of this weathering is incredibly powerful. One number that I found in one textbook that I never knew before is that Niagara Falls is

eroding at 3 feet per year. The cusp of the falls from the water is moving back 3 feet per year. That's fast. Another little factoid when I gave this lecture one year, students asked what is going to burn out first on the Earth, the sun or the geothermal energy?

And of course I have no idea. We over someday.

The Earth is going to be history because without the sun and without the geothermal energy there's no source of energy.

So I went to my colleagues in this department, Earth Atmosphere and Planetary Sciences, and said, which is going to burn out first? And they said, roughly the same time. And we have about 2 billion years, so not to worry yet.

But it is, we are only here for a period of time.

So, that's the geologic cycle. Now, let's move onto the water cycle, and then we're going to go through the element cycles of nitrogen, phosphorus, and carbon. But the water cycle is obviously important in carrying those elements through their cycles.

And the cycle is actually fairly well understood.

As a fairly because not all of these things, when you're talking about global averages of things it's very difficult.

But the weather service is very interested in the global water cycle.

So there's been a lot of study done. So in terms of reservoirs, these numbers of black at the amount of water in a reservoir.

And the numbers and blue are the number of fluxes annually of the amounts of water moving from one to another.

So, there is a lot of water and groundwater. There's a lot of water and ice, and there's a lot of water in the oceans.

And there's very little water in the atmosphere.

These are the annual fluxes. So you can see, if I animated this right, so 111, these are in terms of square kilometers of water, that's a lot of water.

So, 111 minus 71 gives you 40. So that's the rainfall.

This is the evapotranspiration, and the net result is 40,000 that is flowing into the oceans. And in the oceans, here's the evaporation and here's the rainfall going in with just a net of 40 that's transported from the oceans to

land. So you have 40,000 going into the oceans, and 40,000 coming back, fairly nicely balanced. That's good. And so, let's just use this as an example to say, what's the residence time of water.

Let's just calculate this. We can just approximate.

So the mean residence time is equal to the pool size divided by the flux, right? So what's the pool size? Well, how much water there in the ocean? Thank you. [35?

times 10<sup>9</sup>. And, what's the flux?

Well, we have 425,000 evaporating and we have 40 going here. So, I would add this and that so it's balanced. So, I would use 425.

4.25 times 10<sup>5</sup> equals just roughly how many years? 3,000 years roughly. So we would say the residence time, the average molecule, the average water molecules floating through this system would spend on average thousands of years in the oceans before it would evaporate and get back into the system.

So you should now think about what the average residence time is, for example, in the atmosphere. And you can see when the pool is very small relative to the fluxes, the residence time is going to be very short, right? That's something to remember.

When the pool is huge relative to the fluxes, the residence time is going to be very long. So, you should think about that as you go through your notes. But, in oceans, the residence time is thousands of years in groundwater. The residence time, again, can be very long, which is why we don't want to contaminate our groundwater because it's going to take a really long time to flush that through. Lakes: the residence time is on the order of decades, streams on the order of weeks, and atmosphere I'll let you calculate it and figure it out.

OK, let's move on now to an element cycle, the global phosphorous cycle.

First of all, there's no [redox? chemistry in the cycle. That's important. OK, that's the first thing to remember.

And it's called a sedimentary cycle because there is no atmospheric component. There is essentially no phosphorus in the atmosphere.

Everything in this field, there's always an exception.

There is something called phosphine that comes out of bogs that is really interesting. But it's not a huge amount, so it doesn't really matter in this analysis. And, let's look at it here. We have a fair amount of phosphorus in land plants. And there's internal cycling here.

We have the mining of phosphorus from rocks.

This is a fertilizer. No, that's not a mine; that's a house. Sorry. The mine is invisible.

Here's the mine. So, the phosphorus is being mined.

It's put on crops as fertilizer. The crops are eaten by the people in the house, and the phosphorus ends up in sewage.

Even if it's treated, it ends up in the rivers, and it ends up flowing into the oceans.

And there's a little bit in dust transport here, but if you look at this whole system, it's basically the phosphorous cycle is a one-way flow to the oceans. The only return of the cycle is via the sedimentary cycle where you go from sediments.

Those are sedimentary rocks until you go to mineable rock and through uplifting. And this is on geological timescales.

So, on the earth today, the global phosphorous cycle is really not a cycle. It's a one-way flow to the oceans.

Well, it's a cycle, but it's an extremely unbalanced cycle because eventually this one will come back. It cycles very rapidly in the biota, internal cycling in the ocean. So, it comes of the river, it's taken up by phytoplankton, there you can buy zooplankton, and then the phosphorus is excreted or bacteria [UNINTELLIGIBLE] on dead organisms take up the phosphorous. It's excreted as organic phosphorous, and it cycles rapidly through this system. OK.

So the other important feature of this one way flow, and also humans have altered.

In other words, humans are responsible for this, basically, one-way flow by mining the phosphorus and putting it into the agricultural system. OK, yeah, and there's the return flux. OK, moving on to the nitrogen cycle, which is much more complicated because it is [redox?

chemistry, OK? And, humans have also had a major, major, major effect on the global nitrogen cycle.

So, let's first look at the global nitrogen transformation.

So this isn't a pools and fluxes diagram. This is a summary for you of things you already know. You already know this. It just looks different than what you learned in the second lecture.

So let's just go through it very quickly. If we think of the compounds of nitrogen as being either reduced or oxidized and we think of the environment where they might be found as either being aerobic or oxic, having

oxygen, or anaerobic and oxic, not having oxygen. We can draw a schematic of these processes that hopefully makes good sense. If we start with organic nitrogen, but say it's a dead whale that you saw is organic nitrogen, bacteria work on it, and through this process which you haven't really learned about explicitly at, can convert that to free ammonia.

That ammonia can be used in chemosynthesis, which you learned about. OK, the specific type of chemosynthesis is called nitrification, where this ammonia is converted to nitrite. Is that an oxidation or a reduction? Shout it out. Yes, yes. It's an oxidation.

This was obvious because you can actually see the oxygen.

So, in that, nitrite also in chemosynthesis can be further oxidized to nitrate. And chemosynthesis, so this is an energy releasing process for these bacteria. Now, so here we now have nitrogen in an oxidized form, and we are in an anoxic environment, and that should immediately tell you, oh, that's an electron acceptor for the anaerobic bacteria which are going to dump their electrons on this and convert it to NO or N<sub>2</sub>O.

These are gases, and nitrogen gas.

This is denitrification or anaerobic respiration, which we already talked about. And it also can be converted through nitrogen fixation, N<sub>2</sub> gas can be converted to ammonia.

We already talked about this, too.

Remember, bacteria and cyanobacteria are the only organisms that can take nitrogen gas from the atmosphere and converted to ammonia for the use of other organisms. OK, and then there's one other thing here which is called assimilatory nitrate reduction.

And that is when organisms just take up nitrate, and inside them, and they reduce it so that they can, they have to reduce it to ammonia in order to reduce it for protein synthesis. So that's another route for nitrate to become organic nitrogen in an oxidized environment.

So these are the important biological transformations in the cycle. So, here's the cycle in all of its complexity.

And redox is important. That's a feature. I'm going to list these things, and then we'll look at them on the diagram, has a gaseous phase, in other words, is an important atmosphere component, N<sub>2</sub>, NO, N<sub>2</sub>O, and by the way, this is a very powerful greenhouse gas.

So, the balance or imbalance in the nitrogen cycle that results in more or less N<sub>2</sub>O is very important for global climate regulation.

Nitrogen fixation by microbes and humans: very important.

And denitrification by microbes is the only way to return nitrogen to the atmosphere. If you didn't have denitrification, this process that you learned in my second lecture that you thought was just some weird way things get through life, is incredibly important in maintaining the global nitrogen cycle.

So, let's look at this, the details here. So, in terms of nitrogen fixation, that's taking  $N_2$  gas and converting it to ammonia. Biological fixation by plants, or it's really not by plants. It's by the symbiotic microbes in their roots is 140 times  $10^{12}$  of grams per year. The industrial electrician fixation, that is, what's done by humans, there's a process called the Haber process that's incredibly energy intensive. It takes a lot of fossil fuel to break that nitrogen triple bond. In other words, to take nitrogen gas and convert it to ammonia, you have to break this triple bond which is very energy intensive. But they figured that out during World War II basically, or was it World War I? Anyway, one of the wars, how to break that bond, and that was the beginning of the nitrogen fertilizer industry. So, this is human nitrogen fixation that is used to fertilize crops. So this is a huge fraction of the natural fixation. I mean, this adds a huge amount of nitrogen flux to the system. OK, in this flux here, this is cultivated legume. So, this would be agricultural bean plants that naturally have nitrogen fixers in them, and that also import nitrogen into the system.

So, we consider that part of the human flux. OK, to balance this, we have denitrification, which as I said is done by microbes on land and in the ocean.

So, looking at this, is it balanced? Is nitrogen fixation on a global scale and denitrification balanced? Did I hear a no?

Which is greater? Denitrification, yeah.

If you add this, this, and this, you get 260. Is that right? Yeah, and then you add this, this, and this you get 310.

So, there's more nitrogen going into the atmosphere than we're taking out. And people don't understand this.

They think the denitrification has been disproportionately stimulated by this huge flux of nitrogen into the system. But this is an important imbalance that a lot of people are studying very hard. OK, yeah. That's the major feature that you want to look at in the system. And then, if we compare, this figure is from your textbook comparing the biological nitrogen fixation. Plus, lightning fixes it a little bit.

Compared to the human, you can see that humans are now responsible for an equal amount of nitrogen flux on a global scale as the natural system.



This is a dramatic perturbation, and that's only in the last 50 years or so, dramatic perturbation to the system.

This amount that we are doing is, 140 gigatons is equivalent to 10 million trucks of dry nitrogen fertilizer that we are putting into the system with completely unknown effects. OK, the next series of slides are just to illustrate in one ecosystem the importance of the biota and maintaining nitrogen in the ecosystem.

And I'll also just show you the importance of experiments in ecology.

And this is the Hubbard Brook Experimental Forest, which is up in New Hampshire. Some of you might have even visited there. This was my first job as a graduate student was actually working in the forest. I was measuring phosphorous concentrations in the streams. And what they do there, just like that experimental lake study I showed you, here, they have permits from the forest service to clear cut entire watersheds. A watershed is just an area that collects the rainfall and directs it into a single stream.

You can collect the rain and measure what's in it, and you can collect the water coming out and measure what's in it.

And the difference is what the ecosystem is actually doing.

So, what they did was they had these two watersheds that were the same, and they clear cut one of them. And they asked with the influence of this clear cutting was on the quality of the water coming out of the system. And to make a long story very short, it's a really fascinating study that's been going on for four years that I want to tell you because then you'll know how old I am.

But, here's the control watershed, and here's the water coming out of the devegetated one, showing massive [reflux?

of nitrate from the system as well as other cations.

And your textbook does a terrible job of not explaining this.

And I don't have time to go into the details. But, the major reason this is lost, the vegetation is really important in that, but it's important in also maintaining the microbial community in the soil. And when it's cut down, the microbial community changes.

And that is very important and resulting in the loss.

It's a beautiful study, which unfortunately we don't have time to go into. But if you're interested, I can point you in the right direction. OK, now, let's go into the really important, well, they're all important because they're all

coupled.

But this is the one that's getting a lot of attention, the global carbon cycle. And it's getting a lot of attention because we have had an incredibly significant impact on it, and we are worried about that causing major global warming.

And as an aside, I'll just tell you that I actually think the global nitrogen cycle is a sleeping giant, and that the public doesn't know much about that right now.

But in the scientific community, we know the perturbation we've had on that cycle could end up being equally, if not more, traumatic for the Earth's climate as this. But that's an aside.

So let's focus on this now. So, here's the global not carbon cycle, which you've seen now several times in my lectures.

So here's gross primary productivity, and respiration by land plants, respiration by the soils. These are RA and RH that we talked about before. And in this, we have their balance, roughly balanced, and then you have uptake by the oceans, and loss of CO<sub>2</sub> by the oceans. Your textbook says this is all a physical and chemical process that's absolutely wrong.

The biota are central to that, and that's another lecture. But you already know that, that the phytoplankton are sucking a lot of CO<sub>2</sub> in through photosynthesis. So let's look at the budget here.

And, this is the introduction of CO<sub>2</sub> into the atmosphere by burning fossil fuel, and the introduction of CO<sub>2</sub> into the atmosphere by destruction of vegetation. So, we have 7.

gigatons going into the atmosphere due to human perturbation.

The annual increase of CO<sub>2</sub> in the atmosphere is 3.

gigatons. So, 3. gigatons annual increase, and, let's see. If we look at the difference here between respiration and photosynthesis we see that there's 2 gigatons going into the vegetation, actually net into the vegetation.

And if we look at this, we see that there's two going into the ocean. So, if we ask, of all of this anthropogenic CO<sub>2</sub> where's it going? 3.5 is going to increase in the atmosphere. Two is going to vegetation, and two is going to the ocean. And it's this that we are very concerned about because it's causing a dramatic increase in the CO<sub>2</sub> in the atmosphere. Even though these are tiny fluxes relative to the global biological fluxes, these tiny fluxes lead to a significant increase because the pool is so small of CO<sub>2</sub> in the atmosphere. So, this is a trace of CO<sub>2</sub> since 1960. Here's a question for you to think about. I'm not going to answer it. Its summer and winter are out of phase in the

Northern and Southern Hemisphere, why isn't this just smooth?

This cycle that we see here is an annual cycle of the Earth breathing.

Remember I showed you that the first lecture showing photosynthesis greater than respiration during the summer, and the reverse during the winter. Think about why it isn't just smooth and canceled out by the two hemispheres. OK, and if we look at that same graph, this is atmospheric CO<sub>2</sub> from ice core data as a function of time. This is today, and this is time before present going backwards. This is 450,000 years ago. We can see that CO<sub>2</sub> in the atmosphere, and this is measured in, you take a deep ice core in Greenland, or something, and you measure the CO<sub>2</sub> concentration at different slices of the core.

And it tells you what the Earth was like back then.

And, this just dramatically shows you what we are doing just that the last hundred years. We have increased CO<sub>2</sub> in the atmosphere dramatically by burning fossil fuels. And CO<sub>2</sub> is a greenhouse gas, and so we are very concerned about that. OK, this is just read showing that slide from last time of upwelling to remind you that the biogeochemical cycles of these elements are tightly coupled. Remember, we talked about nutrients, nitrogen, phosphorus, being upwelled from the deep water, phytoplankton taking them up, drawing down CO<sub>2</sub> and then we had oxygen and CO<sub>2</sub> going back and forth in the water. So, the oxygen cycle, which we haven't even talked about is tightly coupled also to the CO<sub>2</sub> cycle. I'm not going to show this there. OK, moving on, and I know this is quick, but this is in your readings.

There is a newspaper article about the Biosphere 2 experiment which now is pretty dated. To make a long story short, many years ago a very rich person built the system out in the middle of the Arizona desert. And it had seven ecosystems in it.

It was sealed. It was closed. And, he put people at, which were called biospherians, and the idea was to see whether humans could create a closed biosphere that would sustain human life. And, it was a miserable failure, which is sad because it costs a lot of money, and has since been taken over by Columbia University to use it as an experimental facility.

But the one thing that they learned, here's what happened. They put the people in. And it turned out that there was not enough photosynthesis to supply enough oxygen for the people to breathe.

Oxygen levels steadily went down. And the reason for that, they learned later, was that they had put way too much rich soil in the system. So, the bacteria in the soil were sucking the oxygen out of the atmosphere. And there were subsidizing the system with rich soil so that people would have enough food. But there was a puzzle, because if

this was the case, because the cycles are coupled, you should expect to see the same amount of, if this oxygen is coming from photosynthesis, you should see the same amount of CO<sub>2</sub> coming into the system.

And you should see an increase in CO<sub>2</sub> in the atmosphere.

And they didn't. In other words, they saw oxygen going down, but they didn't see surplus CO<sub>2</sub> in the atmosphere. And it took a bright graduate student from Columbia University to go in there and figure out what was going on. And it turned out that, so why didn't CO<sub>2</sub> increase? It turned out that this CO<sub>2</sub>, which was coming out of the system from respiration in the soil was actually binding to the calcium hydroxide in the cement and making calcium carbonate. So, the cement, another human invention, was playing an important role here.

The point is that none of this, this is only understandable in hindsight, because it didn't work. You can go in and figure out, what the heck, where did these imbalances come from? So, it was a very interesting study, and we learned that it's not easy to mimic natural biosphere on a very small scale.

OK, I'm going to skip that one, and come to this real quickly, because this was just on the news this morning as I was driving into work. I thought, perfect for this lecture.

The UN just announced this millennium ecosystem assessment.

It's on the web. And 2,000 scientists have been working on this for over ten years trying to assess the state of the global ecosystems and their capability to support future generations, i. . you guys. And they say the next 50 years, and those are the 50 years that you guys are in charge, are absolutely critical for whether or not these systems will sustain, be able to sustain human populations. So you can go to the web if you're interested in that. OK, quickly to our civil and environmental engineering major, I'm just going to say that our new motto is nature, tools, and toys, that nature is ecology. There is a two series ecology course.

Tools are mechanics: basics, fundamentals for analyzing systems.

And toys is design. The part of the curriculum is going to be designing instrumentation for studying environmental systems.

And there are these brochures here and in the back.

So I encourage you to pick those up if you're at all interested in that major. Now, let me show you this cool clip. Don't leave yet.

This is worth it. It's only two minutes, and its nature at its best.

So, all I need to do here is hit play. And this is the soccer player's look like this. Oh, why didn't that work.

[Miophon?] our little bugs in the sand.

That's my favorite part.

Life is a geological agent.

See, that would have been a great kick off for spring break, but welcome back from spring break. All right, I'll see you in a few weeks.