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DIEDRE TOOLE: Today, this is going to basically be an introduction to--

AUDIENCE: Introduce yourself.

DIEDRE TOOLE: What? Oh. I'm Diedre Toole. I'm in the marine chemistry and geochemistry department. And today, I'm going to be talking about atmosphere-ocean interactions. And just kind of as a caveat, when we start all this, this is going to very much be an introduction of terms and concepts that you're likely to hear over the next couple of years. There's going to be a lot of overview-ish feeling to this.

So what I'm going to talk to at first is a little bit of overview of what you did. I think it was lecture 4. It was lecture 4 when we talked about atmospheres and the composition. And then we're going to talk about aerosols and greenhouse gases and their different roles in the radiation budget. We're going to talk a little bit about UV radiation and ozone. And I'm going to show you an example of the polar ozone hole over Antarctica.

And then we're going to do some examples that specifically affect on the ocean. We're going to look at sulfur cycling and dust and how that translates to iron delivery, a little bit on acid rain, and then just a little bit on halogen chemistry and sea salt particles. Just so you are aware that they exist.

So I know this is an overview because you had it in lecture 4, but I just wanted to touch on it because I'm going to be using these terms a lot today and make sure we're on the same page.

So this is the temperature structure of the atmosphere. This is the surface of the Earth. This is the height in kilometers. And pretty much today I'm going to be focusing primarily on the troposphere and the stratosphere because probably 50% of the mass in the atmosphere is below maybe five kilometers. And then a good 90% is below maybe 30 kilometers. So in terms of the gases and aerosols that we're interested in, they're pretty much in those layers.

So what your atmospheric structure consists of is you have a boundary layer. It's about a kilometer thick. And on top of that is this region known as the troposphere. And it's about 10 kilometers thick. And it's heated from the bottom by IR radiation being emitted by the Earth. So it has an inverted temperature structure. So it's a region of really strong vertical mixing.

And so if you're a particular particle in that layer, you can traverse the entire layer probably on the order of a couple days. Or if you're in the middle of a huge tropical storm, you could do it in an hour. Also, on top of that, we have the stratosphere. It's very thermally stable because of warming at the top, and that's primarily due to ozone absorbing, the photons coming from the sun, and a little bit of oxygen photolysis. But because of this structure it's very stable. So it's very weak in terms of vertical mixing. There isn't a lot of mixing going on.

The tropopause is the break, this artificial boundary, between the two levels. And it actually is really important for us because there's a huge gradient there in terms of concentrations for the size or the chemical nature or the sources of the aerosols. And they are pretty well defined from one another in terms of transport. There is some transport across the tropopause. Like I said, you can have those massive clouds, massive thunderstorms in the tropics, and you can inject things up into the stratosphere.

You also have some large-scale transport that ascents in the tropics because that's where the tropopause is the coldest. So you have air going up in the tropics and sort of in a large scale coming down in the poles. There's also a couple other, such as tropopause folding. It's a lot like how an eddy forms in the Gulf stream. It'll inject a little bit of air from the stratosphere into the troposphere, and that eventually gets entrained because of all the mixing there.

But for the most part, it's a very slow leak from one level to the other. So it's really important to understand the chemistries and the two different areas because they really are just--

AUDIENCE: Hello? [INAUDIBLE]? Are you going to post this PowerPoint? Or should we be trying to scribble everything down?

DIEDRE TOOLE: Oh, no. I'm going to post the PowerPoint--

AUDIENCE: OK, thanks.

DIEDRE TOOLE: --right after class. So these are kind of the-- what?

AUDIENCE: Never mind.

DIEDRE TOOLE: [LAUGHS] This is kind of the atmosphere ocean interactions in a nutshell, the way I see it. Down here, we have what most of us focus on in one way or another, marine chemists, marine biologists, just ecology. Well, there's deep stuff too, but-- well, we'll talk about surface for now because ecology.

And through a lot of these biological processes, we have formation or uptake of these climatically-relevant gases, so your carbon dioxide, your oxygen, sulfur gases, such as dimethyl sulfide, nitrous oxide. And eventually those are ventilated to the atmosphere through gas exchange processes, which I believe you talked about on Tuesday.

Once they get up into the atmosphere, they can do a variety of things. They can affect the temperature through greenhouse-gas effects, which we'll talk about. They can affect ozone concentrations through a lot of chemistry-- I'm blocking your view there-- ozone concentrations through a lot of chemical reactions, which I'll touch on later. And they can also directly affect the radiation budget, which we'll also talk about.

And then these leads lead to other secondary things happening in the atmosphere, like change in cloud microphysics, which I won't really talk about today. The temperatures can affect the chemical reaction rates. And so different pathways will happen in different proportions. It's also the oxidizing capacity of the atmosphere and the hydrological cycle.

And so then what you have is you have all these reactions happening in the atmosphere and all these different things being formed and either forming with droplets and clouds. I'm going to talk about all the specifics later. And then there's a lot of deposition back onto the oceanic surface.

So we have sulfur returning to the surface. We have nitrogen. We have iron, all being deposited in the oceanic surface. And those are going to feed back into the ecology through primary production. But there's also going to be a lot of physical processes to that effect. For example, if we warm the environment, we're going to warm the water. And if we warm that upper layer of water, that's going to change the mixing, which will affect nutrient delivery.

And there's also a host of photochemical reactions that occur. And that's going to be a function of how much light reaches the oceanic surface. So the end point of this is that sunlight is a very powerful structuring agent. And this is the summary of what we're going to be talking about today.

So I think you guys have already seen this. This is in general in parts per million by volume, the components of the atmosphere. And so pretty much the standard, what most people know is that the atmosphere is 78% nitrogen-- hello? is that-- 78% nitrogen and 21% oxygen.

All the rest of these components are known as trace species, and they all contribute less than 1% of the total mass in the atmosphere. But they're pretty much the species that have the largest impact on the radiation budget and then the chemical input to the ocean.

So water vapor is by far the most variable trace component, and that varies seasonally and regionally. And argon is probably the most abundant, but it's an inert gas, so I'm not really going to talk about it much today. Some of the other ones that I'm sure you've heard about in terms of greenhouse-gas warming, carbon dioxide, hydrogen, nitrous oxide, sulfur dioxide.

And they vary very much in terms of their mixing ratios. As you can see, sulfur dioxide versus nitrogen, you've got about 10 order of magnitude difference. But in terms of climate effects, we're much more interested in sulfur than the nitrogen in the atmosphere.

And also they vary a lot in terms of their lifetimes or just their residence times is a way to think about it in the environment. Nitrogen can go for can survive for 10 to the 7th to 10 to the 9th years. So once it's up there, it's up there and in a chemically-inert form for a really long time.

And then ozone, which I'll talk about in detail later, it only lasts for a couple days at the high latitudes. So understanding their lifetimes and their distributions can tell us a lot about the chemical processes that form them and where they come from.

So one really special class of substances in the atmosphere is what's known as aerosols. Excuse me. These are the most important to us in this sort of environment because they have a direct effect on the radiation budget. And so really the way you define an aerosol is it's a suspension of particles in a gas. And if it's liquid particles, it's generally things we think of like clouds or mist, that type of mixture. And if it's a suspension of solid particles, we generally think of it as dust or smoke or soot, that type of particles.

And we're interested in aerosols for two basic reasons, for two basic radiative reasons, the direct and indirect effect on the incoming solar flux. So the way it works is-- I'm just going to define these really quickly-- is that the direct effect, it relates to changes in the net radiative flux, so the total amount of photons coming in from the sun in the atmosphere.

These aerosols modulate the absorbing and scattering properties of the atmosphere. So chemically, depending on what form they're in, they'll absorb at different wavebands. And depending on their size, they're going to scatter in different directions. And so eventually what that means is that you're changing the aerosol concentrations in the optical properties.

Something we won't talk about as much today is what's known as the indirect effect. And what this has to do is that aerosols themselves can change cloud properties because it's very hard for a cloud to form. You have to have something for water to condense on. There are occasions where water molecules will condense together, which is how you start. But it's much easier for water to condense onto something in the atmosphere.

And so aerosols form a perfect surface for this reaction. So they're a little particle floating around. The water can condense on them. And so you can change the number of clouds and the number of droplets. And that's going to affect your radiation budget.

AUDIENCE: Can I just--

DIEDRE TOOLE: Yeah, please.

AUDIENCE: Is it possible to get the picture-in-picture out of the screen there?

AUDIENCE: Oh, yeah.

AUDIENCE: Yeah.

DIEDRE TOOLE: What's happening?

AUDIENCE: With the-- this is then-- if you're blocking it, we can read it off of it.

DIEDRE TOOLE: Oh, I'm sorry.

AUDIENCE: [INAUDIBLE]

DIEDRE TOOLE: I need to be like-- I wish I had a remote for the--

AUDIENCE: It's fine.

DIEDRE TOOLE: It is how it is. OK. No problem.

So just to understand, this is more just to tell you that there's a lot of different ways in the environment that we can form aerosols. The details of this aren't as important. What's really important is that you understand that you can have this homogeneous, homomolecular reaction where-- just losing pieces of this-- where single gas components, they can condense together to form a suspended particle. And this is basically water molecules coming together and condensing at the right temperature. And they can start making the clouds. But that's fairly rare.

You also have this homogeneous, heteromolecular-type reactions. And that's the reaction of two or more gases to form a new particle. And this is just an example of ammonia plus nitric acid gives you ammonium nitrate.

And so once you have these solids, it's an exponential process. You have a new surface for something to condense on. And that's what this third reaction type is. It's a heterogeneous, heteromolecular. This is also known as aerosol scavenging. And this is one of the most common types of reactions in the atmosphere. And that's where gases react with a pre-existing particle.

And so in this case, what we have is we have sodium chloride, which is basically sea salt, something we'll talk about later. And that provides this really reactive surface, where gases can condense. And in this case, it's nitric acid. And you end up with HCl and sodium nitrate.

And what these solid particles do is they change the partitioning of some of the key species that we need to understand, to understand some of the atmospheric chemistry. And then the fourth type of reaction, fourth type of aerosol reaction you can have is chemical reaction within the aerosol itself.

And this is really important in terms of turning sulfur dioxide into sulfur ions and some of the nitric-acid reactions. Basically, this is really important for the acid rain-type reactions. And that changes the composition of the particles themselves.

So just to say in a nutshell, really why we care about the aerosols in the environment is because of their absorption and scattering abilities because ultimately, as oceanographers, what we're concerned about is the amount of light that hits the surface of the ocean. And it's all the absorbers and all the scatterers in the environment that is going to affect the amount of light.

And so different gases and aerosols are going to absorb at different wavelengths, and that's a function of what chemical they are. For example-- something we'll talk about later. It's really important-- is the direct absorption of UV by ozone. And so that can affect the heat balance in the atmosphere. But it also affects the penetration of wavelengths less than 290 nanometers.

Also, we have scattering. And scattering is really important to understand in terms of the light reaching the surface of the ocean because if we didn't have any scattering in the environment, the sun would just be one beam coming straight down. It would be very much a direct beam.

But we know that's not the case. There's a lot of diffuse light. If you look outside, I mean, you don't just see a single collimated beam. You see there's a lot of diffuse light coming from a lot of different areas of the sky. And that is pretty much from scattering in the atmosphere.

And there's two types of scattering. I won't really go into these very much today, but there's what's known as Rayleigh scattering. And that's when particles are generally the really, really small particles. And that's gases, gases that have just started their homogeneous reactions and are really small still.

The much more common type of scattering is what we can call Mie scattering. And that's when particles are either equal to or much greater than the wavelength of light, for example, the aerosols and cloud droplets I've been talking about. And those are much more forward scattering, but they also diffuse the light.

And so for example, even the smallest aerosols that we were concerned about, the cloud-condensation nuclei, which as I mentioned were when the water droplets condense together and you have that little particle to start forming clouds on, those are already on the order of 0.1 micron, which is much bigger than most of the solar radiation that's going to be coming directly from the sun.

OK. So in terms of the Earth energies figure before-- yeah.

AUDIENCE: It's in the notes?

DIEDRE TOOLE: Yeah. I think this is the notes. There's a lot of partitioning, I mean, in terms of you have your solar constant at the top of the atmosphere, and then you can partition that into an average solar flux based on some geometrical concerns and the surface cross-section of the Earth and the surface, the area of the Earth. And you come in with this average incoming solar radiation flux of 342 watts per meter squared. And this is coming from the sun, straight from the sun.

So obviously it doesn't penetrate straight to the surface of the Earth because the aerosols that we just talked about. You have a fair amount of 20% maybe that's reflected by the clouds and aerosols in the atmosphere. So it's important for us to understand the amount of aerosols and the amount of clouds because that's going to affect how much solar radiation directly reaches and can reach the ocean surface.

You also have some direct absorption by the atmosphere, and that's primarily in the-- well, I'll show you a second. That depends on the chemicals that are in the environment. But for a large part, a large chunk of it makes it all the way through to either be absorbed by the surface or reflected by the surface radiation.

And this amount of reflection is very-- it's very spatially variable. And if you think about it, if sunlight hits an ice cap, there's a lot of reflection. It's white. Whereas if the sunlight hits the ocean, it's a really dark target. So you're going to get less than 5% reflection. A lot of it's going to be absorbed. So these numbers are dynamic depending on what's in the atmosphere, the size of ice caps, land cover, that sort of thing. So these are just a current estimate of these numbers.

What we haven't talked about yet, which is also really important in the Earth's energy budget and the radiation budget, is the concept of greenhouse gases over here.

AUDIENCE: We did go over that.

DIEDRE TOOLE: Oh, did you go over it?

AUDIENCE: Yeah.

DIEDRE TOOLE: OK. OK. Well, we're going to skip through some of this really quick. OK. You guys have already had the Stefan-Boltzmann. OK. Well, we'll just skip through that really quick.

So in terms of what I'm going to be talking about today-- you already know the distribution, the wavelengths, the radiation is a function of their temperature, based on the blackbody emitter. But in terms of what we're interested in terms of gases and aerosols in the atmosphere.

They each have specific infrared absorption bands. And they add up within the atmosphere. They individually have absorption bands, and they add up within the atmosphere to form the total absorption spectra of the atmosphere. And so that means--

AUDIENCE: Can you tell us about the axis on the figures?

DIEDRE TOOLE: Oh, yeah. This is wavelength here. And it starts down-- in terms of what we're familiar with, this is the solar. This is the visible region in here. It's about 400 to 700 in here. And then this is the infrared region through here.

And so on these scales, ignoring the first one, it's absorptivity. So it's percentage. Is it? Yeah, in terms of percentage. So what you can see, again, is that depending on which gases actually are in the atmosphere, it's going to depend on which wavelengths get absorbed and where.

And for the most part, it's generally clear in terms of absorption by the atmosphere here, the wavelengths, the peak wavelengths of the sun. But you notice the greenhouse gases here, methane, water, oxygen, ozone, carbon dioxide, and water, they have huge absorption peaks in the infrared range. So they're going to trap a lot of those gases. We're going to have warming.

Can I go through this quickly? One thing that I just wanted to point out is that in terms of-- if you individually look at the components of each gas currently and add them up, it doesn't come out exactly the same. For example, how do I explain this?

Carbon dioxide, for example. Right now, they estimate that it absorbs about 12% of the radiation coming in. But that's because there are other constituents in the atmosphere that are able to absorb that infrared radiation. If you were to take everything out, besides carbon dioxide, that absorbs that infrared radiation, the carbon dioxide could actually end up absorbing a lot more, factor of three or four more.

So it's important to think about these changes in terms of climate-change scenarios, where if the different levels of the different gases change, that it might actually change our net effect of absorbing of the infrared.

I'm not sure how familiar you guys are with this, but I wanted to show you an example of what the solar spectrum looks like when it actually reaches the surface of the ocean because we have that idealized black-body curve coming from the sun. But clearly, as we have absorbing and scattering the atmosphere, the spectral composition is going to change as it reaches the ocean surface.

And so what we have in this figure again, is we have wavelength on the x-axis and then the spectral irradiance in terms of watts per meter squared per square micron. And the blue line, this is the solar irradiance outside the atmosphere. So that's before there's been any processing by the gases or the aerosols. This is just what reaches the planet. And then the yellow line is the direct solar irradiance at sea level.

So a couple of things are really important to notice. You can see these big dips. And those are from the absorption bands of the gases in the atmosphere. There's also a significant reduction in magnitude because a lot of that energy has been absorbed or scattered.

And also another thing really interesting to notice, that we'll talk about in a second, is that these lower wavelengths are gone. The ozone is a really important exception in terms of its abilities, and it basically makes life as we know it able to happen because the sun is blasting us with these really highly-energetic short photons in this UVC range. I mean, they have photons anywhere shorter than 280 nanometers.

So if one of those photons were to make it to Earth, it's extremely destructive in terms of life. It damages nucleic acid. It damages proteins. You really can't have that. And ozone effectively blocks all of that. And you can see that in the difference between the two spectra there.

So just to preface our talk to make sure-- there's a lot of terms people use when they talk about the different wavelengths of light. I mean, there's a little bit of play in these. But for the most part, UVCs are the really short, really energetic UV wavelengths.

UVB wavelengths are generally in the 280 to 320-nanometer range. And those are often-- they inhibit a lot biological processes, bacterial production, primary production. But they're also involved in a lot of photolysis and photochemical-type reactions.

UVA is a much longer UV wavelength. That's the 320 to 400-nanometer range. And those actually, in some cases can be good for some of the ecology going on. You can have a lot of repair processes that happen. If you're bacteria or phytoplankton in the upper water column and you're getting hit with UVA and not UVB, you can do a lot of your cellular functions that allow for repair.

The visible wavelengths are generally considered 400 to 700 nanometers. And it's not a coincidence that that's the maximum of the solar output of the blackbody curve from the sun. And then infrared wavelengths go from about 700 nanometers up to 1 millimeter, where they start running into radio waves.

But just to show you an example, this partitioning of light that hits the surface. It's a very dynamic thing. It's dependent on what's in the atmosphere. And as the concentrations of the chemicals and gases in the atmosphere change, the amount of light that hits the surface is going to change, too.

And so this is just an example we took at Palmer Station in the year 2000, and this is also solar irradiance. But you can see that the red line corresponds to high ozone. And just so you guys know, this only goes from 290 to 350. So we're only halfway into the UVA. We're not all the way out to the visible or the IR.

But you can see that there's this difference between these two spectra, based on high ozone concentrations in the red and low ozone concentrations in the blue. So what--

AUDIENCE: Stratospheric ozone?

DIEDRE TOOLE: This is column-integrated ozone.

AUDIENCE: OK.

DIEDRE TOOLE: But yeah, generally down there it's stratospheric ozone what we're losing. And so effects on these aerosols up in the higher levels of the stratosphere can have direct effects on the biology in the upper layers of Antarctica, based on the difference, the different amounts of UVB. I mean, if you think about it, this is probably a 50% increase at some of these wavelengths that are really harmful to the biology, so can have a pretty dramatic effect.

And so I just wanted to stress the importance of UV radiation in the ocean. And I mean, overall, it's a very small percentage of the total solar flux, if you remember, from the shape of the blackbody curve and even what was hitting the surface of the Earth. But it has huge impacts for the biological systems and the chemical systems that we look at in the upper water column.

Like I mentioned before, it's primarily responsible for protein and nucleic-acid damage. It can inhibit really basic processes, like photosynthesis and bacterial production. But it can also help in a lot of photo-enzymatic repair processes, depending on the spectral composition, where you are in the water column.

It also does a lot of things photochemically, which I'm not going to talk about very much today. But one of the things that it's really involved in is inorganic nitrate and nitrite photolysis. And basically, there are certain areas of the planet that always have high concentrations of nitrate, nitrite. And when the UV hits them, they form really reactive radicals that can start a chain of photochemical reactions.

And something that I'll mention later is some of these UV wavelengths. They're also responsible for the reduction of iron-3 to iron-2. So they make it more bioavailable. So that's important in terms of limiting micronutrients.

It also has-- on the organic level, there's a lot of organic photochemical reactions, in terms of breaking down dissolved organic matter, bleaching color-dissolved organic matter and just generally altering its structure. So the bottom line is that UV is really important in structuring our ecosystems, and its flux is dominated by ozone.

So even though this is something that's happening in the environment, and it's kind of removed from what we think about in a daily basis, we really need to understand what regulates ozone concentrations to understand some of the functioning of our ecosystems.

And so these are atmospheric profiles of ozone. And in the first one we have ozone number density as a function of pressure. And this first dashed line is the tropopause. And the dashed line is the top of the stratosphere, just for reference.

And as you can see, there's actually quite a bit of ozone in the troposphere, but it reaches a maximum in the stratosphere. But when you look at it in terms of mixing ratio, which is parts per million by volume-- it happens to be the unit that used in this case-- there's much less in the troposphere, and it still reaches the maximum stratosphere.

Basically, the way this works is that in the troposphere there's just a lot more particles. So the mixing ratio of ozone is much smaller. So it basically makes up a smaller percentage of the total particle and gas load as compared to the stratosphere, where it's actually a really large component.

And as you can see, most of the ozone is actually compressed into a fairly small region, as they call it, the ozone layer. And it's on the order of about 30 kilometers into the atmosphere is where it peaks.

And so I'm not going to go a lot in today into any of the atmospheric chemistry. I just wanted to show you in terms of the stratosphere and the troposphere, like the most basic reactions that are ones that-- again, it's not even so much that the details are important.

You just need to understand that, for example, like the stratosphere, it's dominated by oxygen atoms and ozone-related reactions. That's what determines its temperature structure, which determines its stability, which determines the abilities of aerosols to be transported.

So for example, in this case, you have oxygen. When it's hit by photons of light from the sun, it breaks down to excited-state molecular oxygen. And then this excited-state molecular oxygen can combine with another oxygen to produce ozone. And this is actually one of the most important reactions in terms of our planet and life surviving is this production of ozone.

The thing, though, is that these reactions are slow. It would take on the order of maybe 20 years with these photochemical reactions to actually replace the amount of ozone we have in the atmosphere right now.

They also do, as I mentioned before, something important. M is just a generic term that you use for the-- it's the third body-collision partner. It's either oxygen gas or nitrogen gas. And it's the way that the heat is dissipated. So you have these photons, these high-energy, short-wavelength photons being absorbed, and then their heat is dissipated through this third-body collision partner to the surrounding area.

And so again, that's why we see that temperature profile in the stratosphere. At the top of the stratosphere, where there's more photons available to be absorbed, you're seeing more of this reaction. So more heat is dissipated. And that's why you have that temperature structure.

You also then have the ability of ozone itself to absorb light, breaking it down into molecular state, excited oxygen again and then oxygen gas. And then these can combine-- the excited-state oxygen can combine with ozone to form oxygen gas again. And so what you can see from these is it's a very cyclical thing. You're not having oxygen destroyed. You're not having oxygen produced.

The net of these reactions is that ozone is generally left to its own devices. It's in stable, steady-state concentration. The problem, what starts happening, though, is that ozone can be destroyed by a number of free radical catalysts that are found in the atmosphere, and these can be the hydroxyl radical, the nitric-oxide radical, chlorine or bromine.

And while OH and the nitric oxide, they're predominantly natural, chlorine and bromine have anthropogenic origins in the CFCs. And that's really what motivated a lot of this research, was people started to notice the Antarctic ice hole. They started to understand the connection between CFCs. And so that's why a lot of this research was carried out.

But the important thing to know about these types of cycling in the atmosphere is that there's two types of cycling. There's catalytic cycling, where you form a free radical of some and that starts off as a catalytic chain of destroying ozone or destroying odd oxygen, which is the molecularly-excited oxygen and ozone.

Or there's a null cycle, which happens a lot, which basically means the chemicals in the environment are just cycling between the different pools without net loss to the odd oxygen pool. And so just depending on their interactions, they're cycling through. But we're not really losing ozone.

I just wanted to talk about the Antarctic ozone hole for a little bit and what forms it and-- what?

AUDIENCE: [INAUDIBLE]

DIEDRE TOOLE: Yeah. It's important. So I'm just going to spend a couple slides talking about the polar ozone hole and what this means in terms of productivity and what forms it.

Really, this forms because the polar region has really unique meteorology. As the polar winter, their winter, comes along, it's dark. It's completely dark. So you're not having photons hit the upper stratosphere. So you start to have a cooling in those upper stratospheric layers. And so you actually get this descending of this really cold, upper stratospheric air ascending down through the stratosphere.

And so you have this very low temperature air. It's often less than negative 80 degrees C that's sort of descending down through the stratosphere. And what that allows for is for the formation of these what's known as polar stratospheric clouds. And that's really unusual. You don't expect to see particle clouds in stratosphere in this area.

And there's two kinds. You can either have a water-based, which is essentially ice crystals, or nitric acid-based clouds. And so you also have a vortex of air forming as it descends in winter. And you can have this vortex form, and it can get to be extremely fast. It can get to be on the order of maybe 100 meters per second in the upper atmosphere, some of the winds.

So effectively you end up with a strong westerly circulation. And that's going to isolate this region from the lower latitudes. So in terms of chemistry and in terms of circulation, you have a very isolated air mass. And it's dark. So no photochemical reactions are really happening inside.

But what's really interesting is that these polar stratospheric clouds, which form from the autumn until early winter, they provide a really unique surface for chemical reactions. And these surfaces usually don't exist in the stratosphere. And so what happens is that--

We have these species, the chlorine nitrate and HCl. They're known as reservoir species. They're there. They're there in fairly high concentrations. Generally, they're fairly soluble. So they'll be rained out. But they're not usually involved in a lot of the reactions. They don't usually involve destruction of ozone reactions.

But what happens is that as the season progresses and you have these polar stratospheric clouds with these surface for chemical reactions, things start changing. Things start happening really fast. And one thing you notice is that this region, it's very deficient in oxides of nitrogen. So you can't form--

Once you start breaking down these compounds, they cannot go back to their null cycles, where they're just cycling through and not affecting ozone or odd oxygen. Once you have these reactions and they start to progress, you lose your nitrogen compounds, and you lose your water compounds. So they're stuck in this free radical form, which is often chlorine gas.

And you can't go back on the reaction because-- and also, you have these clouds where these surface reactions are really, really enhancing this. And so what happens is you have these clouds, and you have now a lot of chlorine gas floating around, and as soon as the spring starts and you get that start of the input of the solar photons, chlorine gas disassociates into chlorine.

And chlorine can react with ozone to form chlorine oxide, which is another highly-reactive radical, which can react with ozone and oxygen. And then you have chlorine oxide reacting with oxygen, again, to form chlorine gas and oxygen. And what you can see from this is your chlorine through these two steps. It's regenerated. So you started with it. It had its reactions.

And then at the end, it's still available to react. It hasn't been bound to anything. So it's still available to go through these reactions. And you also see that there's this destruction of odd oxygen. You started with your ozone and your molecularly-excited atomic oxygen, and you ended up with two oxygens. So you have this destruction of the single molecule of ozone, but your chlorine is still there.

And so it can go off, and it can react with ozone again. And so this is a catalyzed reaction, where the chlorine can just keep cranking through the ozone molecules until something happens to get the chlorine out of this gas phase. And generally what happens is that in the late spring, the vortex breaks up. The sun comes out. It gets warmer. You start to melt your cloud particles.

So a lot of the water and the nitrogen that were frozen now are available to react with the chlorine to form soluble gases. You can get back to your reservoir compounds essentially in the late winter, early spring. They get back into the melting clouds, and they're rained out.

And so just to convince you that this actually happens, these are images from an Antarctic cruise that I was on. There from TOMS. That's a satellite. It's the total ozone mapping spectrometer. And it basically looks at column-integrated ozone. And it presents results in terms of Dobson units, loss of scale. That's interesting.

And basically, what Dobson unit is, is if you take the entire column of ozone through the troposphere, through the stratosphere, and you compress it down to standard temperature and pressure, one Dobson unit would mean that it's about 10 microns thick. So pretty much a standard Dobson unit concentration for Antarctica when there's not an ozone hole is maybe 300, 350.

And under the ozone hole, which is represented by the-- can I play it again? by the more blue purple colors here, you can start to see the formation of the polar vortex, and the air being cordoned off from the surrounding air. But you can also see, as it turns more and more purple, that you're having lower and lower ozone concentrations because of that catalytic destruction of chlorine.

Does anybody have any questions? Ready to move on? Yeah.

AUDIENCE: Could you go over again, just briefly, how you initially get the chlorine gas in the state where it then can react with [INAUDIBLE]? I misunderstood because I think I first thought that it was initialized by like--

DIEDRE TOOLE: Oh, OK. What happens is these two reservoir species actually interact, collide with one of the polar stratospheric clouds. And what you lose out-- for example, for this first one, you lose out a nitric acid that would essentially react and become the solid on the cloud. And you'd have liberation of chlorine gas.

AUDIENCE: OK. Thank you.

DIEDRE TOOLE: And that doesn't need to involve light in any way. It's as soon as-- and once you-- and so you're going to have a buildup. And you can see that of these chlorine gas in time until you get enough light. Anyone else? OK. I'm going to get moving here. Wait. How do I get past this with them? OK.

Oh, just to go over this really quickly, I just wanted to let you know that in the troposphere, there's predominantly two types of photochemical reactions that happen. The first part is-- it's a daytime-nighttime split is essentially how most of the tropospheric reactions work. And the oxidation reactions during the day are generally initiated by the highly-reactive hydroxyl radical. It has a lifetime on the order of a couple seconds. So as soon as it's formed, it's going to react.

And basically the way that we get that in the troposphere is from the reaction of ozone within the troposphere itself. Plus, light leads again to oxygen and the molecular state-excited oxygen. And then this reacts with a normal greenhouse gases that we're used to, like water, methane, and you produce these hydroxyl radicals.

There's a host of thousands of different types of chain reactions and things that go on. But the most important thing to know is just during the day it's the OH radical that's determining the chemistry and what's going on.

And at night-- obviously we can't have this reaction happening at night because there's no light. And so at night, it's nitrate radicals that are formed from the nitrogen dioxide combining with ozone. And that produces these nitrate radicals. And that initiates most of the chemical reactions that happen at night. And these two radical species govern the fates of almost all the trace gases in the troposphere.

Does this show you a summary of what we've talked about so far in terms of radiative forcing at the Earth's surface? What this is, is it's IPCC estimates of the mean radiative forcing of the climate system for the year 2000 relative to 1750. So it's, how much has this changed over the course of this 250 years?

The x-axis really is just our level of scientific certainty. And they range from high to low to very, very low. They should be more specific. And in terms of the y-axis, it's radiative forcing, which is watts per square meter. So if your radiative forcing is positive, that means you're warming. That means more of the photons are actually reaching the surface of the Earth, whereas--

AUDIENCE: It's not coming-- most of them are come-- from the greenhouse gases.

DIEDRE TOOLE: Well, most of them are. Yeah. But it depends on which one specifically you're talking about. Well, OK, we'll just say in general. If you're radiative forcing is considered positive, it's warming because Scott's right. These are photons being emitted from the Earth and trapped by the greenhouse gases, whereas if your radiative forcing, it's cooling, is negative. Excuse me. That's cooling.

And so for example, in terms of stratospheric ozone, that's more the incoming solar photons that we're concerned about. So we can see in the last 250 years, because of the ozone hole that we just talked about, we've lost some of the stratospheric ozone. So more of the cooling is happening because we're not getting that absorption by the ozone of those photons and warming the stratosphere, whereas the opposite is the case for tropospheric ozone.

And the one thing that I just wanted to show about this is that our uncertainty in a lot of these processes, we understand the physics of them, that they're happening. But in terms of quantifying them and coming up with a magnitude for their exact effect on the radiation budget, it's pretty uncertain.

I mean, you can see for the aerosol indirect effect, which is the clouds, so about the formation of the clouds and reflecting back to space, we don't even have a mean estimate. We just have an error bar.

So there's lots of other effects on here too, that I haven't talked about today, and I won't talk about today, that can affect the radiation budget. And some of that is airplanes flying in the stratosphere, volatile organic carbon species. I'm just going to try to stick to a few of these to talk about.

So now I want to show you some examples of compounds that originate in the ocean, or compounds that are being injected into the ocean, and how that's affecting these feedback loops. And the first thing I'm going to talk about is something very near and dear to my heart. It's the biogenic sulfur cycle.

So basically the way this works is you have a gas, a sulfur gas. It's dimethyl sulfide. It's a reduced sulfur gas produced through a host biological interactions, phytoplankton reactions, bacteria, zooplankton. But the end result is that you have a ventilation to the atmosphere. So you have DMS gas free in the atmosphere. And this is still within that boundary layer, that first kilometer we talked about.

But what happens once it gets into the boundary layer is it goes through a lot of photochemical oxidation reactions. I'm not going to give you the exact specifics on those here today. It goes to sulfur dioxide, which can eventually be processed to sulfate aerosols. So like we talked about originally, sulfate aerosols in the atmosphere, they can have a direct effect. They'll directly scatter some of the sunlight back to space, based on their scattering geometry, the size of the particle.

They also provide a surface for the clouds to condense on. So as soon as you have sulfate aerosols, you're going to have the water droplets starting to condense on them. And they're going to effectively act as cloud condensation nuclei. And so once you get more CCNs, that increases your number concentration of droplets and your cloud albedo. There's a whole host of cloud microphysics that go into that.

But ultimately, what happens is that you increase the cloud albedo, which makes the Earth's surface more reflective. And if you think about it, this is a gas that's emitted from the ocean. And as I said earlier, the oceans are really dark target. I mean, it's nearly 95%, 98% absorption. So if you take a bright white cloud and stick it on top of that, you can have a pretty dramatic effect on the radiation budget.

And this is especially so in large areas of the southern hemisphere, where you really are far away from any of anthropogenic sulfur inputs. Aerosols are primarily from these marine sources.

So what we need to understand and what we're trying to understand is, once we have this change in clouds, in the cloud albedo, we're going to have less of the solar radiation, less of the photons from the sun actually reaching the surface of the Earth. But we don't really necessarily know is how that affects the surface temperature of the Earth.

You have less photons reaching the surface of the Earth because the clouds are reflecting them back. That's going to decrease the temperature of the Earth. That's also going to decrease, obviously, the irradiance.

And so what this cycle tells us that, though, where the understanding isn't there yet, is how that feeds back in to affect the marine ecology and how that affects the phytoplankton abundances or the speciation, which eventually then is going to feed back into how much DMS gas is there to be injected back to space.

A couple of things in terms of sulfur budgets to notice is that these sulfate aerosols, they affect the atmospheric acidity, which I'll talk about in a couple slides. So they contribute to acid rain.

They also kind of are the main reason that people started studying them is that they affect the sulfur transport to continents to land. It's a way, essentially for sulfur to get out of the ocean into the atmosphere and then through wet deposition of these aerosols, which is essentially being rained out to contribute them to land. They're also involved in an autocatalytic destruction of ozone cycle.

But in terms of assessing the importance of this cycle on biology and upper ocean chemistry, one thing we always need to consider, and we really have to keep in mind, especially these days, is fluxes in terms of natural biological fluxes versus anthropogenic fluxes and how they feed back onto one another.

So we do know that this oceanic source of sulfur gas, it's ubiquitous. It represents over greater than 50% of the oceanic sulfur flux to the atmosphere and greater than 50% of the biogenic flux. But we need to understand how that relates to anthropogenic flux, to put it in context. And we know that the estimated anthropogenic flux of sulfur, it's probably about three times larger than the biogenic sources of sulfur.

But what we do know is that the lifetimes are much shorter. Because when DMS comes out of the ocean, it's a highly reduced form. And so it has to go through a lot of oxidation steps before it can reach a form that can form an aerosol and can condense into a cloud and be rained out.

In contrast to this, a lot of the anthropogenic sources such as the oil refining, coal and oil combustion, sulfur is emitted immediately as sulfur dioxide. And so really what happens is it goes up as sulfur dioxide. And it's a very regional effect. A lot of it can be rained out fairly locally to the point source.

Other sources of sulfur for the troposphere are the decay of vegetation. It's a little bit less, but very similar in magnitude to that of oceanic sources, and also sea spray, which I'll talk a little bit about later.

Volcanoes are a really interesting source because they're one of the ways that sulfur can actually get injected into the stratosphere. They can inject sulfur dioxide directly to the stratosphere because really, the issue with a lot of sulfur compounds is that most of them are too soluble or too reactive to make it that high up in the atmosphere. There's one exception, which I'll talk about in a second.

But in terms of us and radiation forcing and understanding that feedback system, the important thing to know is that when you look at the upper troposphere, the upper tropospheric levels, less than 20% of the sulfate aerosols in the sulfur dioxide at those altitudes are derived from anthropogenic sources. More than 80% is derived from biogenic sources, which I said the decay of terrestrial organic matter, the DMS.

I just wanted to, again, reiterate that DMS does impact the atmospheric chemistry pretty substantially. There's a lot of cyclical reactions and a lot of complex reactions, but I just wanted to say the main take home message is that DMS reacts in the troposphere with the OH radical during the day and the nitrate radical at night, which is fairly typical of most chemical reactions in the troposphere. And it's formed the sulfur dioxide.

But there's also another interesting species. There's a way you can get through this way, is carbonyl sulfide. And this can be formed from DMS. And this is the only species of sulfur that can actually make it up to the stratosphere. And that's because it has a really long lifetime.

And one way that we know that is that-- you can assess the lifetimes of things in the atmosphere based on their distribution. If you look at a chemical, and it's very well mixed, and its distribution looks pretty uniform, especially relative to very non-uniform point sources, you can say that it has a really long lifetime. And that's the case with COS. If you look in the upper stratosphere, it's completely well mixed.

And it's found pretty much throughout the globe. I mean, it has a very low gas phase reactivity, too. So it's pretty much considered that-- it's the background atmospheric levels of methane, sulfonic acid, sulfur dioxide, and non-sea-salt sulfate in the stratosphere. And basically what that's telling us is that's the way that sulfur forms aerosols in the stratosphere, is through this compound, this compound.

And also, just kind of as a side, an interesting note, is that in the North Sea region, these biological fluxes of sulfur, they can account for up to 25% of the tropospheric sulfate aerosols over Europe. So still, their anthropogenic sources are having a big impact.

AUDIENCE: What's the relative contribution? I mean, carbonyl sulfide is also formed within the water column.

DIEDRE TOOLE: Yes.

AUDIENCE: What's the relative contribution of that pathway versus [INAUDIBLE]?

DIEDRE TOOLE: Most of it is synthesized within the atmosphere. The ventilation of it is very small, or is considered to be very small. I don't know if someone's measured it directly with flux measurements. I mean, there's other compounds, too, that come from deeper sources, and so on.

OK. Another really important type of aerosol that we see in the troposphere is what's known as a mineral aerosol. Kind of what motivated people to start looking at this work is that-- I think you guys are going to get to this later-- is that there's huge areas of the world, the world's oceans, like the equatorial Pacific, the subarctic Pacific, the Southern Ocean, where concentrations of the macronutrients, like nitrate and phosphate, they're high year round, but we really have a low standing stock of phytoplankton.

I'll just leave it at that. We're going to talk about it later. But these areas have been deemed these high nitrate, low chlorophyll HNLC regions. And so people, for a long time, we're trying to figure out, why isn't the phytoplankton growing there? They seemingly have the nutrients that they need. They should be happy. But primary production and standing stocks were still low.

And in 1988, they initiated this, put forth this hypothesis that maybe it was a micronutrient limitation in iron. And that spurred a lot of-- hmm?

AUDIENCE: Well, Riley said that in the '60s, too.

DIEDRE TOOLE: Well-- OK, this is who's generally given credit for-- [LAUGHS] I don't know if it's fair credit, but that's another discussion. So a lot of people started looking at ion, trying to figure out where ion came from. What are its sources? What are its sinks? How is it processed?

And there's been a lot of work on it, but one of the things that people have come upon is that the inputs of new iron to the surface waters, especially in open-ocean regions away from land, it's dominated by the atmospheric deposition of soluble ion in these aerosols through wet and dry deposition.

And so if you want to look at a budget-- this is recently published in*Science--* in terms of open ocean-dissolved iron, you have a lot of sources that just say they won't make it to the open ocean. I mean, a lot of the erosional processes from land, it's trapped on the continental shelf, and it doesn't make it to the open ocean.

So this particulate iron from fluvial systems, glacial sediments and coastal erosion, I don't think those are relevant for open-ocean systems. But some of the more relevant pathways are the fluvial-dissolved iron-- though that's very low-- is in this atmospheric contribution. These are deeper contributions, so deep ocean contribution.

And so you can see obviously-- I mean, the potential sources are very small, and it's pretty much atmospheric input. The one thing about iron is that, depending on its oxidation state, it depends on its bioavailability. I mean, primarily it's in these two forms, iron-3 versus iron-2. And when a particle from fluvial, from however it's transported to the ocean, iron is not really soluble under oxic conditions.

So what happens is it quickly changes state. It has a very short half life, if you want to think about it in terms of-- when a particle of iron hits the surface of the ocean, it's this very quick competition, whether it's going to be taken up really rapidly by biology, whether it's going to become particulate form adsorbed to a particle, or whether it's going to do some of complexation with organic material.

And so it's in this way that iron in the ocean has a very nutrient-like distribution. This is data compiled by Dave Carl. And this is just depth over the upper 4,000 meters, and then dissolved iron concentration ranging from 0 to about 1.5 picomoles. And so what you can see is that iron is-- hmm?

AUDIENCE: [INAUDIBLE]

DIEDRE TOOLE: Ion is a-- it exists at very low subnanomolar concentrations in the surface waters. It's usually about 0.2, 0.1 in the surface, and it becomes more soluble with depth as a function of temperature, but also as a function of those organic ligands, which can complex it.

But like I said, it's extremely insoluble in oceanic waters, so the bioavailability of ion is controlled by the presence of the organic ligands. And so if you're sitting out in the middle of one of the subtropical gyres, pretty much from the atmosphere is the only way you're going to get your iron.

And what I have here is a map of estimates of dust flux. And one thing that's really important to remember-- we'll talk about this in a second-- is that dust is not necessarily equate to iron. The iron comes from the dust, but there are different reactions in the atmosphere that will affect its solubility and affect its delivery to the ocean.

So as you can see from this, it's fairly obvious there are definite point sources for the dust. That's Northern Africa, Southern, Southern Africa, Australia, the hyperarid regions. And the amount of dust that can get entrained in the atmosphere is a function of a lot of geomorphological features, just the amount of dust there, the topography, how arid it is, how erosion capable it is, wind speed.

And then once these dust particles are entrained into the atmosphere, how long they stay in the atmosphere depends on a lot of processes, like precipitation. The bigger particles obviously fall out first, where smaller particles can be transported longer. Just transport processes-- amount of water vapor in the air also matters a lot.

So it's also interesting to note that it's very dependent not just spatially but seasonally, like I mentioned, the amount of rainfall, and where that rain is happening is going to determine how this iron is delivered to the ocean. And on longer scales, glacier, interglacial variability determines the amount of iron, in terms of the dryness of the planet, the amount of water that's tied up in the ice caps, the height of the sea surface. And it's very episodic, based on wind speeds.

So the one thing that we really need to consider, though, is once we have these dust particles blowing around anc landing on the ocean surface is how much that actually is iron, and how much of that is actually available to phytoplankton for primary productivity and for their other functions. Iron is involved in a lot of enzyme functions that are pretty critical to phytoplankton processes.

And generally, what a lot of people consider is that the Earth's crust, the soil particles are about 3.5% iron. And so that's a good average, of the particle 3.5% of it is iron. But there's a lot of reactions that happen in aerosols that can potentially increase the solubility of that iron. And some of that has to do with the acidity of the aerosol.

And so when they hit the surface of the ocean, they might have a much higher solubility ability than the 3.5% or even down as 1% some people use as estimates. But that's a very important way in which the atmosphere delivers a key micronutrient to areas of the ocean that would pretty much be starved of iron otherwise.

And these are just some examples of different ways you can estimate the amount of iron and get at things. One is a SeaWiFS true color image from February 28 of the year 2000. And you can see, this is the coast of northern Africa. This is Spain. And you can just see these vast plumes of dust particles being blown across the continent. And so they have satellite algorithms, looking at aerosol optical depth to estimate the amount of dust.

There's also what some people have done, which is just a much more direct way, is they've just taken rainwater from areas where they expect a lot of dust to be delivered and filtered it. And so this is one that we did in July of 2004. And it's kind of a hard picture to see. But you could see a lot of dust particles coming from the rain. And analysis showed that there's a lot of iron in those.

Just to touch on another way in which the atmosphere and the ocean are directly coupled and which affects a lot of what we do, is nitrogen deposition in the form of acid rain on the surface of the ocean. And one of the biggest sources of nitrogen to the atmosphere is nitrous oxide from the ocean. And it contributes about--

Generally, this nitrous oxide is formed in nitrification processes, a little bit associated with denitrification. So you're going to find these produced at deeper depths. And so when these waters are upwelled or in deep convective areas, you're going to have spurts of nitrous oxide being injected into the atmosphere.

We also have lots of sources of the higher nitrogen oxides from anthropogenic sources. And when they talk about anthropogenic a lot, they talk about NOX, which is the sum of nitric oxide and nitrogen dioxide. And a lot of these sources of nitrogen comes from fossil fuels, biomass burning, and fertilizer. There's also some interesting natural processes. Like lightning, for example, can form a lot of these oxides.

And just considering the NOX chemistry in the stratosphere is, it's another way to destroy ozone. So you have nitric oxide plus your ozone leads to your nitrogen dioxide and oxygen. And then when you combine this with an OH radical, you yield nitric acid. So this is a way for anthropogenic and natural inputs to load up essentially the acidity of a lot of the water particles in these regions.

And this nitric acid is highly soluble in droplets. So whenever it has any encounter with condensed-phase water, it dissolves in there. So it's very subject to wet deposition. And just kind of an interesting side note, in terms of the ocean's effect, is that the photolysis of nitrogen dioxide is the only known way of producing ozone in the troposphere. There are injections of anthropogenically-produced ozone, but that's the only known way of chemically producing it in the troposphere.

And so what happens to this nitric acid once it forms? We've increased the acidity of the atmosphere. And you have all these wet deposition processes. Eventually, it rains out. Your particles get big enough, and they rain out of your clouds.

So what I've shown here is a map of estimated distributions of pH of rain particles globally. And one thing we should know from the beginning is that natural precipitation rain is slightly acidic because of CO2 and carbonic acid dissolving in it from the atmosphere. So the common definition is that a pH of less than 5.6 is considered acid rain.

And so we can see definite point sources, where the pH is as low as four, associated with anthropogenics. But you can also see large areas of the open ocean, where the pH is relatively low also. And this is generally associated with nitric acid. And I didn't go into the details of this. But this sulfuric acid from the sulfur cycle, they also will decrease the pH. And besides decreasing the pH, they also deliver nitrogen and sulfur to the surface ocean.

One just the last thing that I wanted to mention really briefly, just so you know it's there. I mean, if you remember talking about the ozone hole and the ozone loss, we talked a lot about chlorine. So halogen chemistry is actually very important in the environment in terms of catalytic-destruction processes.

But there's also a lot of organic biogenic sources. Specifically in the ocean, there's what's known as the methyl halides, which is chlorine, bromine, and iodine forms. And these have really long lifetimes, greater than-- about a year, with respect to the OH radical. So they can reach the stratosphere, and they can function and as a catalytic species in that ozone destruction. Exactly how the CFCs from anthropogenics can do it. These can get up in the stratosphere and do the same thing.

And another really important source of halogens that I just want you to be aware of, I didn't want to talk about too much today, is sea-salt particles. This is an inorganic halogen, but there's a way that these halogens can be activated. And essentially, the way this works is you take your sodium chloride, which is essentially your sea-salt particle, has been injected to the air and either dried or still in a condensed phase, and then you react it with one of your chlorine-reservoir species.

These are the same reservoir species that we talked about in terms of the ozone hole. And that liberates chlorine gas and then sodium nitrate. So what you have then is your chlorine gas, which can be photolyzed into chlorine atoms. And you can start the same exact catalytic-destruction cycle of ozone that happens in the polar ozone hole.

So sea-salt particles are also a very important removal pathway of nitrogen oxides and some of the acidity, some of the acid rain causing compounds we were just talking about. And the way they work is you take your nitric acid and that if it comes across a sea-salt particle can break down into sodium nitrate and HCl, and then that goes from there and has a bunch of reactions.

But essentially, these sea-salt particles produce a lot of surfaces where you can change the acidity of the atmosphere. And so they affect the NOX partitioning in the ozone chemistry overall. And there's actually-- in terms of overall mass, the flux of sea salt particles to the aerosol load is pretty enormous.

So just to summarize this tour we did today of the ocean and the atmosphere is that atmospheric gases and aerosols impact the global-radiation budget and the heat budget. The trace constituents really dominate these effects. The reaction pathways and the feedback mechanisms, they're often complex. They're interrelated and have these cyclical mechanisms, making climate-change estimates difficult.

But many of these biogeochemical cycles are really important to us, as oceanographers and marine chemists, because they deliver key substances to the ocean, like iron and nitrogen and sulfur and vice versa. The ocean can deliver them to the atmosphere. So that's it. Any questions?

AUDIENCE: Hi. When you're talking about the iron, so when they do, like, the iron experiments, what form of iron are they adding? Are they just-- I mean, they're clearly not just dropping them in, like, scrap metal.

[LAUGHTER]

DIEDRE TOOLE: Throw an anchor over. I mean, it really depends. I mean, the iron-- I don't know actually what the specific chemical that they put in--

AUDIENCE: Could just be an iron chloride.

DIEDRE TOOLE: I imagine so. I mean, they obviously try to put it in in a more soluble form and hope that it retains its solubility for as long as possible. Oftentimes, that's why they do a second edition and sometimes a third injection because it absorbs some particles and changes its oxidation state.

AUDIENCE: I can email you the answer to that question.

AUDIENCE: There was a story. I remember hearing about some guy who was trying to-- he was getting people to pay him to take, like, old pieces of scrap iron out and dump it in the ocean.

DIEDRE TOOLE: Really?

AUDIENCE: Yeah. He was saying it was going to fertilize the ocean and decrease increase CO2. [INAUDIBLE].

DIEDRE TOOLE: That's interesting. We could get someone to pay him to do it.

AUDIENCE: Yeah.

[LAUGHTER]

Oh, they can't hear us at all.

AUDIENCE: Those stock compounds that you were talking about, the chlorine and nitrogen compounds--

DIEDRE TOOLE: The reservoir compounds.

AUDIENCE: --where do those come from?

DIEDRE TOOLE: They're just-- they ultimately start out as-- well, where do the original compounds in the atmosphere-- they're very long-lived compounds. They're regenerated each year through these reactions.

I'm sure you can have formation of them if you have-- because you have a very slow mixing between the troposphere and stratosphere. You can get some of the halides mixed up. It's probably mostly started with the organic naturally occurring halides and sea salt, injecting the chlorine, and then those compounds forming. But they do regenerate themselves each year.