2022 Spring WRRC Seminar Series

Natural Source Zone Depletion of Petroleum Hydrocarbons at the Water Table

Dr. Barbara Bekins

0:07 **[Keri Kodama (host):]**
All righty. Hi, everyone, and welcome to the next session in the WRRC spring seminar series. And today we have Dr. Barbara Bekins. She'll be

0:18 talking about natural source zone depletion of petroleum hydrocarbons at the water table.

0:24 Just to introduce our speaker, Dr. Barbara Bekins is a research hydrologist with the US Geological Survey, Water Mission Area located in Menlo Park, California. She has studied the

0:35 fate and transport of crude oil contaminants in groundwater for over 25 years. Barbara serves as

0:40 research coordinator for the USGS crude oil spill study site near Bemidji, Minnesota.

0:46 She has been elected a Fellow of the Geological Society of America and the American Geophysical Union, and is a member of the National Academy of Engineering. So, Barbara, please go ahead.

0:57 **[Barbara Bekins (speaker):]**
Hey, thanks so much for inviting me to this seminar series. I spoke in this series in 2018, in June.

1:09 And the material I'm going to be presenting today is newer since that talk, so this talk is

1:18 pretty much different from that one. But, I will give you an introduction to the site, which,

1:23 as Keri said, I've been studying for over 25 years, and the USGS has been studying it

1:30 for over—almost 40 years. So I would like, you know, I hope that this talk will provide

1:42 some reassurance to you—to you there that some of what will be happening to the fuel are

1:51 things that we understand, and that we—and that the knowledge that I give to you today

1:58 will help you understand some tools that we can use, and some ways to think about the fuel.

2:06 And also, some things that we don't know, but are within reach. And

2:13 our technology is giving us lots of opportunities to get a better understanding of these problems.

2:25 So, the talk will start with some background material about the spill that occurred in

2:31 Minnesota and the response to it, and what the USGS study motivation is. And then I will

2:38 move on to the crude oil source. And I'll try to connect it to the source that is the spilled fuel

2:48 at Red Hill, and how it changes with time. And then the third part will be about the

2:54 contaminant plume that's in the groundwater that—and I'll cover the nature of the organic

3:02 carbon that's in the plume, and also some biological test results we've been doing.

3:12 So, this is an aerial photo of the Bemidji site. It's located in northern Minnesota—

3:22 at the time of the spill, there was a pipeline break—there's a pipeline

3:28 running through the site that carries oil from Alberta, Canada over to the Great Lakes. This spill, the

3:36 pipeline was under pressure when it burst. And so the oil sprayed out—over this area called

3:42 the spray zone, and then it kind of ran down along the topography to this wetland here. And then they—

3:52 in the emergency response, they trenched in order to recover some of the oil. So here's

3:57 a scale bar to give you a sign of how big this is. This is a full size tanker trailer here.

4:10 So throughout the talk, I've got a few slides comparing Red Hill to Bemidji. So Red Hill is of course a layered basalt aquifer.

4:20 Bemidji is a glacial outwash. So here's a cross section, kind of a big sandbox. This distance from

4:27 the source to the water table at Red Hill is 80 to 100 feet. In Bemidji, it's about 20 feet. The

4:35 recharge is quite high, at least in the mountains at Red Hill compared to Bemidji. The groundwater

4:43 velocity is 1 to 10 feet per day. It's quite a bit slower at Bemidji, just 0.2 feet per day. And,

4:53 and the way to say you're welcome in Minnesotan is "you betcha" and here it's "‘a‘ole pilikia."

5:04 So, here is what it looked like when they did the emergency response.

5:14 There the pipe—the pipelines here, the pipeline break was here and this is a trenching that

5:19 I showed you in the previous picture. So the emergency response included pumping up the oil,

5:28 excavation and land farming, and burning or evaporation of oil-coated vegetation.

5:35 And here we see some of the pumping of the oil. Interestingly, in 1979 this guy's personal

5:43 protective equipment was basically a doo-rag. It's kind of a different world than compared to today.

5:55 The oil penetrated, migrated into the subsurface quite rapidly.

6:02 So of the 75% that didn't get cleaned up, about 25% soaked into these sandy sediments and you can see it here seeping out the side.

6:18 So here's an overview map of the site today, and important features that I'll be covering. So

6:24 here's where the pipeline break was. Today, there are six oil pipelines running through the site.

6:32 This is the area that was sprayed with oil. The groundwater flow is in this direction to the northeast, and

6:44 the oil as it flowed along the surface, these are the surface flow lines, infiltrated the aquifer in

6:51 three locations. And the most studied location is this area, it's called the North Oil Pool.

6:58 And wells that—the monitoring wells are shown here in green. There are hundreds of wells at the site,

7:06 to provide a research picture. The flow velocity is 5 to 50 centimeters per day. Now the important

7:15 thing about this site, and it was very successful in the early 1990s in demonstrating that benzene

7:24 biodegrades naturally. There was no need to add anything to accelerate the biodegradation and

7:31 so the 10 microgram per liter contour of benzene in 1996 was here. And in 2010, this well still

7:42 measured 3.3 micrograms per liter of benzene. So this aquifer is very efficient bioreactor

7:49 for benzene. And that is a success story that has been used to create protocols

8:00 for monitoring biodegradation of petroleum hydrocarbons in aquifers. So I'm not going

8:06 to talk much about the benzene, I'm just going to go on to the newer work that we've been doing.

8:14 The motivation for the study is that there are over half a million leaking underground storage

8:21 tank releases nationwide, and those are managed with risk-based corrective action. So if the

8:31 if there's no water at risk, and the plume is stable or shrinking,

8:37 then the site can be approved for no further action. And many sites are approved even though

8:44 they still have contaminant remaining in the ground. So, there are lots of sites around

8:50 the country where fuel is still in the ground, and the groundwater is monitored. And so this is

9:01 public policy today, and it is working well for fuel sites across the country. But we have—

9:13 continued to study the Bemidji site for several reasons. And we've been funded by

9:20 the USGS Toxic Substances Hydrology Program. And we're studying the fate, transport, and natural

9:27 accumulation of crude oil. And we are tasked with providing the results to industry consultants,

9:34 and regulatory, educational, research institutions like your own. And the reason why we've been—

9:41 continued to fund this problem, even though benzene—we have this success story about benzene

9:47 is that the oil is still in the ground and these processes of—there are many,

9:53 many processes that affect how the oil biodegrades and changes over time, including biodegradation,

10:03 dissolution into the groundwater, and then there's a dissolved contaminant plume and transport

10:09 of that contaminant plume. And then there are vapors that come also up towards the surface.

10:17 So, because the timeframe is very long for natural biodegradation,

10:24 and because there are so many spills where the source has been left in place for various reasons,

10:33 we have successfully argued to management that this study should be ongoing.

10:42 So, just a little tutorial here about biodegradation.

10:47 Reduced carbon which includes spilled fuel and oil can be oxidized by bacteria in redox reactions to

10:57 obtain energy, and create oxidized carbon. In some cases, that's CO_2—carbon dioxide. In other cases,

11:07 it's a more oxidized form than the parent carbon, and there's still energy available.

11:15 So, the most energetic reactions are coupled to oxygen as is our redox reaction of burning food.

11:24 In the absence of oxygen, and that occurs quite rapidly in the subsurface because oxygen is not very soluble in water. There are a series of electronic acceptors utilized

11:35 by bacteria and these are grouped together as anaerobic processes.

11:41 At the Bemidji site, the most important is iron, and then carbon dioxide and methanogenesis.

11:51 But at Red Hill, the story is a little different. So here is the—here's some chemistry from Red Hill Monitoring

12:00 Well 02 of the important electron acceptors. The blue is the data from the well that has,

12:10 typically shows some petroleum hydrocarbons in it. And the red is from a clean background

12:19 well unaffected by the plume. So you can see dissolved oxygen is up here close to solubility,

12:26 but at Red—but at Monitoring Well 02 it's depleted, and that's indicating that there is biodegradation

12:32 going on. Similarly, nitrate is depleted. Iron is— behaves the opposite. Iron is actually produced

12:40 as bacteria consume iron oxide on the rocks. And then they put iron II into the aquifer. So you

12:48 expect to see iron increased, in the middle of the plume. Sulfate is very high, because

12:56 you're close to the ocean and salt—sulfate salts of the ocean, and it's depleted here.

13:03 Methane is produced. So we know if methane is produced, then in some parts of the spill,

13:11 all of these other electron acceptors are quite low in concentration because methane

13:18 is inhibited by nitrate and oxygen, and competes with sulfate. This is total organic carbon (TOC).

13:28 In the clean aquifer, it's below one milligram per liter. And in the aquifer where—that's impacted,

13:35 it's higher. And that I'll be talking a lot about total organic carbon in this talk.

13:46 So now that you've had a tutorial on biodegradation, I'll just give you an overview of

13:53 the Bemidji site and many decades of results from that site. So the oil is here, present

14:00 from land surface down to the water table. Within the oil itself, the most degradable

14:07 compounds are the normal alkanes, and they degrade under methanogenic conditions to CO_2 and methane.

14:15 The methane outgases and moves towards the surface and it is biodegraded partway to the surface

14:24 into CO_2 and water. So there's no methane reaching the surface, but there's a lot of CO_2 reaching the

14:31 surface. And in fact, if you look at how much is biodegrading, we can show from that methane,

14:39 that CO_2 efflux that 86% of the biodegraded carbon is leaving as CO_2 at the land surface.

14:48 So only 14% of the carbon actually enters the groundwater contaminant plume.

14:56 And that's reflected here as the BTEX so the total petroleum hydrocarbon in the gasoline range.

15:04 And then there's this dissolved organic carbon (DOC) that isn't—and we call it non-volatile in order to distinguish it from BTEX, which is volatile.

15:16 And that degrades close in under methanogenic conditions. And then out here at the advancing edge of the plume, there are iron oxides on the aquifer

15:26 that the bacteria use in this redox reaction to oxidize the reduced carbon in the plume.

15:39 So, here's another comparison of Red Hill to Bemidji.

15:46 So the spilled hydrocarbons at Bemidji were a crude oil—a light, low sulfur crude oil from Alberta.

15:57 In 1979, an estimated 450,000 gallons were spilled. Within the North Pool, which is what

16:05 my talk will cover, they're about 37,000 gallons. Here's a chromatogram of that. And the—this is

16:14 retention time and response. The longer carbons are retained longer. So these are 25-carbon

16:24 n-alkanes and this is 15. And so I've aligned these, this is a chromatogram of JP-5 with the

16:33 estimated volume is 19,000 gallons released in November. So, this is retention time again.

16:45 Actually, this is a carbon number here. So these are 10 carbons, 11, up to 15 carbons.

16:54 So we don't have compounds that have up to 30 carbons like we have in crude oil in Bemidji.

17:03 So that's one big difference in the two sites.

17:22 So, the first part of the talk is going to be on how the source changes over time. So in 2010,

17:33 oil was collected from 13 wells that had oil floating at the water table. And then they

17:40 were also sampled in a series, multiple times. The oil was analyzed for volatile constituents.

17:53 So the samples were collected from these wells shown in red.

18:01 And then this is a cross-section in the lower figure and the well screens are—the position

18:08 of the well screens are also shown in red. So the contour plot is oil saturation. So what

18:18 that means is how much of the pore is filled with oil. So in this case, 50% of the pore

18:25 is filled with oil, and then it drops towards the edge to less than 10%. So the wells intersect

18:34 areas with varying degrees of oil saturation, and that is going to affect how things change.

18:44 So in the next figure, I'm going to show you two contrasting wells with different saturations,

18:51 one whose saturation is close to 0.5 and another whose saturation is closer to 0.3.

18:59 So here are three compounds and on the horizontal axis, it's time since the spill,

19:06 and the vertical axis is fraction of that compound that still remaining in the oil.

19:12 So these are analyses of the oil. So we started out at the beginning with 100% of the benzene is

19:18 still in the oil. And then over time, it's dropped faster in this well shown in blue, where the

19:27 surrounding pore space saturation is 37% compared to this well shown in peach, where the surrounding

19:35 oil saturation is almost 50%. And that's because the water contacts it more readily in areas

19:44 where the oil saturation is lower. So in this case, even though it's contaminating the water,

19:50 the water is also serving to move the benzene into the bioreactor of the aquifer.

19:58 So m-xylene, up here is the effective solubility, so this is how many moles of benzene are dissolved

20:07 in oil in equilibrium with water, per mole of water. So this is the effective solubility.

20:16 m-xylene has an order magnitude lower solubility, and that's reflected in the fact that a lot less of that has been leached out of the oil over time.

20:28 But interestingly, o-xylene, even though it has a very similar solubility to m-xylene, has dropped

20:35 a lot in the oil, just as much as benzene. And so I'm going to explain why there's a difference.

20:46 So on this, I just brought up circles of benzene, o-xylene, and m-xylene that were

20:56 used for the illustration. On the bottom axis is effective solubility, and on this vertical axis

21:04 is fraction remaining. And the dots are all of the volatile compounds that were analyzed in 2010. And

21:16 so the first thing to notice is that more soluble compounds are more depleted in the oil,

21:23 and less soluble compounds are still largely retained in the oil, but are still somewhat

21:30 depleted compared to the starting composition. And then there's this interesting difference between

21:38 o-xylene and m-xylene. They have the same solubility, but o-xylene is a lot more depleted.

21:44 These are compounds that have been shown to biodegrade under methanogenic conditions.

21:50 So those compounds have—are more depleted because the bacteria living right next to the oil

21:57 are munching on them and as they deplete them, more dissolves from the oil. So

22:02 there's this enhanced dissolution that occurs because of the biodegradation.

22:09 And these compounds are also highly degradable. These are the n-alkanes, of 6, 7 through 12

22:17 carbons. And they are quite depleted, even though they're very insoluble. And we have concluded that

22:25 the bacteria can degrade these without necessarily dissolving them into the water because the

22:33 solubility doesn't seem to affect their losses. So, the take home message from this slide is that

22:41 compounds are lost from the source at different rates that depend on the properties of the compound.

22:50 So, one might reasonably ask, you know, well, I don't want to know about individual compounds,

22:57 I just want to know how much of the fuel is still there. So, it's difficult to say how much of the

23:06 fuel is still there because there are hundreds of compounds in the case of crude oil. So you cannot

23:16 measure hundreds of compounds. So—but there's a way to finesse the problem

23:23 by measuring a single conservative compound that you know isn't lost. So this

23:31 cartoon here is to illustrate how you would use a conservative compound. So

23:37 at the time the oil spills, you have this conservative compound with a

23:44 mass per mass concentration of 30%. So 30% of it is present initially. But then over time, this much,

23:56 30% of the mass is lost, and if you go back, but none of the conservative compound is lost.

24:02 So then if you go back and measure the conservative compound, its concentration is now

24:07 50%. And so you can take the ratio of the original concentration, which was 1/3 and divide it by 50—

24:22 by one half, and you're going to get overall 2/3, and so that's going to tell you that

24:29 2/3 of the mass is remaining compared to 100% that you started with, or you can do one minus

24:37 that and say a third of it has biodegraded. So the compound we use is a triaromatic sterane.

24:47 And by the way, each slide that has a reference, the reference is listed at the bottom.

24:55 So for the Bemidji site, here are the results. Here are years since the spill.

25:01 Here are the 13 samples collected in 2010, and we sampled them again in 2019 and 2020. And what you

25:11 see is that about, so here's 40%, about 50% of the mass that's been lost since the spill.

25:22 This sample, we're not sure—I had this analyzed twice. I don't know what's going on with it.

25:28 So I'll just say that if you ask me about it later.

25:33 So the Red Hill spill was JP-5. And what we'd like to know is could we, could we do this with JP-5,

25:43 is there a conservative compound? And yes, so these highly branched alkanes listed here,

25:51 and are listed in this memo that's on the web, can be used to estimate losses because they aren't

26:00 lost very quickly. So these are results, recent results that are in this memo dated March 7,

26:11 of samples collected from the sump and the Red Hill shaft water gallery, the drain line.

26:19 And so what you see is that they're not very different from each other. So that tells you two things. One is that they all represent the known spilled fuel.

26:30 But there is one big difference right here, this sample from the water gallery

26:35 has lost a lot compared to the others. And it's lost nC-10, which it's lost to volatilization.

26:45 So these conservative compounds can not only tell you how much mass is lost,

26:50 but they can also tell you something about the processes that were responsible for the losses.

26:58 So the second part of the talk is going to be about the contaminant plume.

27:03 So this is just a cartoon that we published in a fact sheet: the source zone, the pipeline break,

27:13 the plume is anaerobic, and then there's oxygen seems to slowly diffuse into the plume,

27:20 with distance downgradient.

27:27 So I'm going to be talking a lot about dissolved organic carbon. And I'll explain

27:34 to you why—how that compares to total petroleum hydrocarbons in a minute.

27:41 So in the—this is distance along the x-axis concentration, and again, NVDOC is nonvolatile

27:50 to distinguish it from the BTEX and the petroleum volatiles. So coming in the—in the clean water is

28:01 about 1.4 milligrams per liter, and over 12,000 individual molecular formulas. So

28:10 natural organic matter is incredibly complicated. And it really complicates our task of figuring

28:17 out what is added in the source zone. So as the clean groundwater enters the source zone,

28:25 concentrations increase to 30 milligrams per liter, and about 2000 additional

28:33 formulas are added. So the plume has over 14,000 molecular formulas. So if you just try to compare

28:42 molecular formulas, you're going to see a lot of similarity between downgradient and upgradient.

28:49 So we have to be more sophisticated in our techniques for saying how is this organic carbon

28:56 different from what came in? The good news is that this organic carbon that enters in the source zone

29:03 does biodegrade quite rapidly in the aquifer. And so by about 200 meters downgradient,

29:11 it's only about a milligram per liter over the background concentration. And then it pops back

29:21 up here probably because this well is maybe more in line—the main part of the plume.

29:32 So it doesn't degrade completely. So there are some compounds left here that are—

29:43 that sort of keeps me up at night and I'd like to know what is not finishing biodegrading. But

29:49 one thing that's clear is that the added carbon reflects ancient carbon. So we know that it came from the oil because it's carbon-14 dead. So we'd like to know what

30:01 are these compounds? And do they have biological effects?

30:06 So I promised you I would relate this to total petroleum hydrocarbons. So here's non-volatile DOC

30:14 versus distance. The orange is total petroleum hydrocarbons in the diesel range, the green

30:20 is TPH in the gasoline range, and the gray is total petroleum hydrocarbons in the diesel range

30:28 with silica gel cleanup. So Roger talked a lot about this last week. Silica gel cleanup

30:35 isolates the true hydrocarbons. So what we're seeing is that the TPH is mostly these polar

30:44 metabolites or biodegradation products. And here's the background DOC, just for reference.

30:52 So the plume is about 22% TPH in the gasoline range.

31:00 But it's dominated by this NVDOC that's added in the source zone.

31:07 So why are the analyses different? Well, non-volatile organic carbon is analyzed with

31:15 high temperature combustion methods, so the samples are filtered in the field, that's why it's called dissolved organic carbon. Later, I'll be showing you total organic carbon,

31:24 and the only difference is that the samples aren't filtered. Then the sample is acidified

31:31 and purged with nitrogen to remove the inorganic carbon. And the volatile organics are removed.

31:38 So that's why we know this is a non-volatile DOC. So then the remaining DOC is combusted

31:45 and the outgassed CO_2 is measured. So that's why you want to remove the inorganic CO_2 first.

31:54 So that essentially gets you all of the DOC except the volatile DOC.

32:02 To measure petroleum hydrocarbons, the first thing that's done so the samples are preserved in the field. And then the organics are extracted with methylene chloride or hexane.

32:14 There's a GC analysis, and all the chromatographic response between 10-carbons and 28-carbons are

32:22 added up, and compared to a diesel standard. So the things that TPHd doesn't measure

32:29 are that partially oxidized compounds do not extract well with methylene chloride,

32:35 and also some of the extracted compounds elute outside of this 10-carbon to 28-carbon window.

32:45 But probably—but certainly the extraction problem is the most serious one. So,

32:51 this is a bar chart comparing four different extraction methods.

32:57 Dichloromethane is what's used to do a total petroleum hydrocarbon analysis. And the total

33:06 carbon that's extracted with dichloromethane in the Bemidji plume is shown here in black.

33:12 The total carbon that's extracted with these other solid phase methods that are newer,

33:17 and well, they're also—it's not just that they're newer, they're designed for extracting partially

33:24 oxidized carbon, because that's what works in the environment. So—this method is what's

33:32 used by people who study natural organic matter and its fate in the environment.

33:38 So the rest of the talk will concentrate on the difference of what you see with

33:45 carbon extracted with this Oasis HLB solid phase extraction method,

33:51 which gets pretty close to 100%, not 100, between 80 and 100%, with three replicates.

34:02 So coming back to Red Hill, we do have total organic carbon data for

34:09 Red Hill. And these are data from Monitoring Well 02, collected between December of 21 and

34:19 March of 22. And on the horizontal axis is total petroleum hydrocarbons in the diesel range,

34:26 the vertical axis is total organic carbon. So what you can see is that

34:38 first of all, the most important thing is that organic carbon is lower than for the

34:43 crude oil site. So at our site we had up to 30 milligrams per liter and you have more like 10. So what that tells us

34:51 is that these biodegradation products are present in lower concentration

34:57 at this site and I think that's good news because as Roger said last week,

35:04 the dose makes the poison. And so to the extent that we,

35:10 we need to know more about these partial transformation products, we have fewer of them

35:18 at Red Hill. They—the TOC is not quite double the TPH, so there are things in the TOC that

35:28 aren't captured by the TPH. There are a couple of approaches that I'd like to

35:36 pursue. One is to see if the total organic carbon drops with distance. And the other is

35:41 to look at the carbon-14 signature of the TOC. Because that way we can distinguish if it's TOC

35:48 that came from the fuel or if it's natural.

35:54 So what is this NVDOC? So partial transformation adds oxygen to the hydrocarbons in the oil, which

36:03 creates polar bonds, which increases solubility. So here's naphthalene. It's a polyaromatic

36:10 hydrocarbon (PAH) with two rings. It can react by—bacteria can catalyze a reaction with CO_2

36:19 using this enzyme naphthalene carboxylase, and form this naphthalene carboxylic acid.

36:28 So that's just one example. And this is more soluble than the parent compound naphthalene.

36:39 And in general, PAHs can be mobilized from the oil by

36:46 these carboxylase reactions or other reactions that add oxygen functional groups. And we find

36:55 oxy-PAHs in the Bemidji plume. I don't have time to cover it, but it is published.

37:04 So, overall, at Bemidji, the overall average formula, so hydrocarbons we just have carbon and

37:11 hydrogen, but we have these oxygens added. In the bond types, Roger mentioned this last week that,

37:21 the GC work done by Dawn Zemo has classified compounds by bond types. And this was

37:29 also done in 1998 for the Bemidji plume, where the bond—the compounds were classified by

37:37 bond type, and this is percentage estimates of the different types.

37:43 So, we'd like to know more about what happens as this pool of carbon biodegrades.

37:51 And we've applied three different advanced techniques. I'm only going to

37:56 explain one of them in the interest of time, but the results of all three are published.

38:03 So this one I'm going to talk about because I know that University of Hawai‘i has this capability,

38:08 this EEMS capability. And I think it would be really great to brainstorm about what

38:16 EEMS could be used for in in the Red Hill case. So it's Excitation Emission Matrix Spectroscopy

38:25 (EEMS). And what happens is the sample is put in an instrument where there's an excitation spectra—

38:33 a range of excitation spectra applied, a series of a single frequencies are applied to the sample,

38:41 and then the emission of the sample is measured for each applied frequency. And then the degree—the amplitude of the emission—

38:49 of the emission is plotted here as a color contour plot, in this two dimensional space. And then each

38:57 of the samples is measured so there's a two dimensional plot for each of the samples in the plume.

39:05 And then, PARAFAC, the parallel factor analysis, What that involves is that, you take all the samples, and you find a way to breakdown

39:17 the data into a simple number of factors. And so each factor is a section of the chromatogram

39:27 that can be used to recreate the spectra or most of the spectra for all the samples. So this is

39:35 the six factors that resulted from the parallel factor analysis at the Bemidji site.

39:48 And now we're gonna look at all the samples that were collected in the plume, so each

39:56 black dot is a sample, and on the horizontal axis is travel time or distance from this spill—so

40:02 travel time in years. So each plot is telling you the percent contribution of that part of

40:11 the spectra to the sample, to each sample. So we start here with samples that are near the source.

40:20 And there is a large contribution of C1, which is associated with reduced petroleum hydrocarbons.

40:29 And that drops with distance, as does C5. So these two are associated with properties near the spill.

40:38 And in each plot, the range of background values is shown in gray. And so as we move down,

40:49 what we see is this part of the spectra, C3, there isn't much near the source and C4, there isn't much

40:57 contribution near the source. But as the pool of carbon migrates downward, we see an increase in

41:05 C3 and C6. So, these are more oxidized compounds compared to more reduced compounds near the oil.

41:14 So, the reason for using a technique like this is because, remember, we're talking about 14,000

41:22 individual compounds at least. So, it's really astonishing that with just 2000 compounds added in

41:32 the source, and then biodegrading with distance, we see this huge difference in the character of

41:39 the pool of the DOC as it migrates downgradient. And that is telling us that the bacteria are

41:45 effectively oxidizing this pool of DOC so it looks less like it looked near the oil, and more like

41:53 natural organic matter as you get downgradient, but not completely like natural organic matter.

42:02 So the last part of the talk is to cover the biological effects of the different

42:08 fractions in the plume. And there were 6 wells that were part of this study.

42:14 It's published—it was published in 2020. And I just compared the fractions that were

42:21 extracted with the best organic carbon extraction, the fraction extracted with

42:26 dichloromethane, so the TPH method, and then dichloromethane with silica gel cleanup.

42:35 The method uses human liver cells. So if anybody read "The Immortal Life of Henrietta Lacks,"

42:44 so these are—in her case it was cervical cells, but these are human liver cells that are used as a

42:54 model of liver metabolism. So the way the method works is that the cells are transfected with

43:07 dummy DNA that is activated and duplicated when a transcription factor is activated in response to

43:18 an environmental contaminant. So this method tests for many transcription factors simultaneously.

43:28 And the activities are reported as a ratio of induction values to control cells. So here's—

43:34 that's hard—that's a lot in one slide. Here's an example of how things are reported. So in this

43:42 case, 52 transcription factors were tested at once, and only two of the transcription factors

43:51 had big activation from this Bemidji sample very close to the source, with DOC at 16 milligrams

43:59 per liter and TPH at 3.5 milligrams per liter. They were the pregnane X receptor (PXR), which

44:06 is known to be activated by xenobiotics, and the Aryl hydrocarbon receptor (AhR), which is known to be

44:14 activated in response to planar hydrocarbons, particularly PAHs. So the good—so the good news

44:25 is, I guess that this plume is activating those things that we expect it to activate.

44:36 So now I said that I would compare the different fractions. So on the

44:41 horizontal axis is DOC concentration and on the vertical axis is how much the PXR

44:49 transcription factor was upregulated compared to the control. So one means there's no activation

44:57 compared to the solvent control. And here's the background well with not much activity.

45:06 But then we—the green dots are the true hydrocarbon fraction isolated with silica

45:14 gel cleanup. And we saw that that's very small at the site. So the true hydrocarbon

45:21 fraction is not really responsible for what these liver cells are doing.

45:27 This is DOC extracted with dichloromethane so that would be the TPH fraction is in orange. And then

45:36 this is DOC extracted with HLB. So what you see is that there is some activity that's not reflected

45:46 in the TPH, in this case not that much. But silica gel cleanup is, is not really capturing

45:58 that—if we need to worry about these, they're not captured in the silica gel cleanup fraction.

46:06 So here's another way of doing the same test, is this chemically activated luciferase expression,

46:14 and in this case, we only tested the Aryl hydrocarbon receptor and we tested it

46:21 again, in human liver cells. So on this plot is the concentration of NVDOC for reference,

46:34 so distance downgradient from the center of the oil, and the concentration of TPHd downgradient for your reference. And then on the right-hand axis

46:47 and shown in red, is the response of these cells that are human liver cells that were—that glow it—

46:57 proportionally to how much the Aryl hydrocarbon receptor is activated. So the—and then this

47:05 is normalized to beta-Naphthoflavone, which is a known activator of the Aryl hydrocarbon receptor.

47:16 So you can see that the NVDOC, kind of aligns with the response of the cells, telling us that you

47:27 know, they are—they're responding quantitatively, to what is quantitatively present in the water.

47:38 So this is a very complicated slide, but I just wanted to remind you that the concentrations

47:49 at Red Hill are down—so this, somehow this slide has changed. So I'm going to back up,

47:59 the concentrations at Red Hill are 10^1, about 10. So Red Hill concentrations are down here,

48:08 where these things are just starting to register. And concentrations dropped with distance,

48:18 so if we look at, you know, sort of what's near the source, that's this orange. And

48:28 what's interesting is that as concentrations dropped with distance,

48:34 the response of the cells dropped with distance, as we saw here, so there's less biological activity with distance.

48:46 Down here, the most downgradient well, it still has a big response, but that's only if you concentrate the carbon. If you actually look at the response down

48:58 at that well, at its in situ concentration, it's down here. So as these things biodegrade

49:06 and their concentrations drop with distance, their biological response drops with distance.

49:15 So in summary, the oil source—86% of the carbon exits as CO_2 surface efflux.

49:26 And we see a lot of CO_2 efflux at Red Hill. Losses differ by compounds. So you

49:31 can't really think of all of the oil going at once, it goes in fractions.

49:40 And we see that at Red Hill too. Overall loss is 50% in 40 years, and that's of oil, which

49:48 has a lot more refractory material in it than jet fuel. In the groundwater contaminant plume,

49:57 most of the non-volatile dissolved organic carbon is comprised of compounds not quantified by TPHd.

50:05 And that appears to be true at Red Hill, although TPHd is a higher fraction of what's there.

50:14 The good news is that these, these partial transformation products do biodegrade quite

50:21 effectively, and they drop from 30 down to 3 milligrams per liter. They do have biological effects.

50:28 So there are more studies ongoing to determine if that—if there are human health implications,

50:38 because this is just a liver cell assay. It doesn't, you know, the liver is processing that

50:44 stuff and it doesn't tell us if the whole organism would be affected. So that's all I have. I'm gonna

50:52 leave up my acknowledgement slide of all the people that have worked on the Bemidji site on the

50:59 studies that went into this talk. And I'm happy to stay around for questions. I'll stop here. Thanks.

Q&A Begins

51:11 **[Keri Kodama:]**
All right. Thank you so much for taking the time to join us in our seminar series. A lot of great information in that talk. So I think we'll open the floor to questions now. So earlier

51:23 in the chat, I had three questions from Paul Eyre. So I'm gonna go ahead and read those off

51:29 one by one. Do you want to answer them one at a time? Or do you want me to read them all at once?

51:35 **[Barbara Bekins:]**
So I haven't been reading the chat. What percentage is related to the degrading petroleum hydrocarbons?

51:44 Based on carbon-14 data, yeah. What is the source of the remaining organic

51:49 carbon or bacteria in the water included in the end NVDOC data?

51:55 **[Keri Kodama:]**
Oh, Dr. Bekins, sorry. There was a direct message question from Paul Eyre to me. So if I could read those to you first.

52:05 **[Barbara Bekins:]**
Oh, I misunderstood. Okay. Yeah.

52:09 **[Keri Kodama:]**
Okay, so the first one is, "Could the contamination

52:14 below the Red Hill fuel tanks be remediated by flushing the aquifer from above with a remedial

52:20 solution through the perforated shallow angle borings that penetrate beneath each fuel tank?"

52:28 **[Barbara Bekins:]**
That's a very interesting question.

52:35 I have to say that I don't have good knowledge of the literature. In practice, there is a very large

52:46 industry flushing LNAPL, and DNAPL from aquifers. The trick is to target the flushing solution

52:58 adequately. So you need to make sure that it contacts the LNAPL. So the first step would be to

53:09 find it. And then the other issue is that the flushed water has to be collected

53:16 as it arrives at the water table. That and as we know from the GAC system,

53:24 we are still in the process of evaluating where the water—how that collection system

53:34 captures flow lines under Red Hill. Interesting comment.

53:41 **[Keri Kodama:]**
Okay, the second question is, "Do you have a sketch of the degree and extent

53:46 of contamination beneath the tanks drawn to scale with data from the history of monitor well data?"

53:52 **[Barbara Bekins:]**
No, I don't. I wish I did. That would help.

54:06 **[Keri Kodama:]**
One last question from Paul Eyre and then can go on to the public chat. So the last one is, "Why isn't TPH used to determine the mass loss rather than the trimethyls?"

54:23 **[Barbara Bekins:]**
The TAS, the triaromatic sterane. So the reason why TPH isn't used is because TPH doesn't capture everything and

54:39 you have to take—collect the TPH sample in the same location every time. So we, let's see

54:47 how to say this, so we have—the saturation is so different. It varies from 10% to 50%.

54:57 So if you just collect the soil sample you're not gonna get the same

55:05 TPH extracted from the soil as you would have gotten 10 years ago, 20 years ago, 40 years ago.

55:18 **[Keri Kodama:]**
Okay, before I move on, actually, Paul Eyre followed up with, "If you don't know about the shallow angle borings beneath the field tanks,

55:27 he asked if Tom or Don Thomas or maybe Robert Whittier could maybe jump in."

55:33 **[Barbara Bekins:]**
I do—I do know about the shallow angle borings. I was responding to the feasibility. I do know about the shallow angle borings.

55:43 **[Keri Kodama:]**
Okay. Yeah, that was that was his follow up. So, move on to Roger Brewer's question. If you want it to read them yourself. That's—

55:54 **[Barbara Bekins:]**
Yeah, so I read Roger's, and everybody can read it for themselves. So the organic carbon that's added in

56:05 the C-14 data show that virtually—that all of the added organic carbon in the source zone is

56:12 ancient organic carbon. The bacteria are not included in DOC because they are filtered out.

56:21 Roger, you and I should talk offline about, you know, I know there's a hypothesis advanced

56:29 by Kirk O'Reilly, that the DOC is biosynthesis products of the bacteria. And we have a new USGS

56:39 report that looks at the difference in the DOC compared to biosynthesis

56:47 products. Particularly the nitrogen compounds—nitrogen containing compounds.

56:55 So Roger, you and I, this is of course a very complicated question. But basically,

57:01 everything that's added in the source zone is from the petroleum hydrocarbons.

57:13 [overlapping dialog]
[Keri Kodama:]
Okay, the next one—

[Barbara Bekins:]
The next question is Marek [Kirs]. "Was there any attempt made to stimulate or augment

57:20 bacterial populations involved in biodegradation? If not, why not?" So no, no attempt was made to

57:27 stimulate the bacteria. The reason—so there's several reasons why. One is that the USGS

57:38 management doesn't—our instructions were to do basic research on the environmental

57:45 processes and not engineering research. And that turned out to be a good bet by management because

57:54 the natural processes have been adapted across the country. And it turns out that

58:02 bacteria that can degrade petroleum hydrocarbons are ubiquitous in the environment.

58:09 And even those that can degrade petroleum hydrocarbons anaerobically. And so the bioreactor

58:16 was quite quick to—the natural bioreactor grew and was established within a few years.

58:26 Having said that, there is an interesting effect where nutrients that are carried naturally from the surface, say there's a lot of nitrogen deposition in Minnesota,

58:38 ammonia deposition, because it's farm country and that is carried rapidly into the subsurface

58:47 at one end of—in a topographically low area and oil has degraded a lot faster at that

58:54 end because of this natural process of nitrogen deposition, atmospheric nitrogen deposition.

59:06 Next question, Tao Yan. "Given the geological, mineralogical differences between Red Hill and Bemidji,

59:13 can we and how do we extrapolate the observed biodegradation rate from Bemidji to Red Hill?"

59:21 Well, let's see. There are several good things that Red Hill has going for it, one is that you have

59:36 a lot of sulfate. So that's going to make biodegradation somewhat better.

59:44 You probably have a lot of iron, it's not named Red Hill for nothing.

59:49 And so iron is an incredibly effective electron acceptor for biodegradation. The biggest

1:00:00 problem with extrapolating rates is not the geochemistry in my opinion. It's the

1:00:07 groundwater flow velocity, and the complexity of the aquifer, making it difficult to convince yourself

1:00:15 that you were looking at the same package of water as it moves downgradient. So one idea, you know,

1:00:25 one thing that people have done to get around that problem at other sites is to create kind of a

1:00:35 wall or a line of wells, so you capture a cross-section of the plume,

1:00:43 and then you sum up the concentration over a cross- section. So instead of being in the business of

1:00:49 saying this well flows to that well, you're in the business of saying this water flows—

1:00:55 this water from this plane flows to this water and this one downgradient.

1:01:03 [Chat question from Iris van der Zander] "Is the decrease of biological activity from the plume center a result of dilution of

1:01:08 polars or due to different proportions of alcohols, ketones, etc. downgradient?"

1:01:16 Yeah, so it's not due to dilution. The paper that shows the three methods

1:01:24 that show the difference in character of the DOC is one very important line of evidence

1:01:33 that it's biodegrading, the whole pool of DOC is getting more oxidized.

1:01:40 And hydrogen to carbon ratio is decreasing, the oxygen to carbon ratio is increasing.

1:01:48 The C-14 data's also very compelling. I did not show it. Those data were collected as part of an agreement with Chevron who's worked at the site.

1:02:00 And Chevron has not yet published those data. But to me, they present a very compelling

1:02:07 picture that what's actually happening is biodegradation, rather than dilution.

1:02:17 [Aly] El-Kadi says, "I know this is outside the scope, but I'll ask anyway, what's the objective of the

1:02:22 modeling effort?" Oh, yeah. A subject dear to my heart. So it was an overall mass balance effort.

1:02:35 The work was funded by the Strategic Environmental Research and Development Program.

1:02:46 And it was funded as part of a project to look at secondary impacts of bioremediation.

1:02:54 And so the, the goal was to look at the fate of iron, reduced iron, which—

1:03:02 which can be a co-contaminant, the fate of arsenic, the fate of CO_2, and methane.

1:03:10 And so, the whole mass balance effort was to cover not just the loss of the hydrocarbons

1:03:19 and the plume, in the groundwater—in the plume and the source zone, but also the fate of the

1:03:27 biodegradation reactants that are part of the process: the methane, the iron, being the main ones.

1:03:37 But there's a couple of papers— well you'll see, you saw the references. So I'm happy to talk to you about it more.

1:03:45 [Chat question from Aurora Kagawa-Viviani] "Do I have thoughts about the most important research gaps to be addressed on the Red Hill issue?"

1:03:53 Yes. Oh, I—Paul, I don't know why, where I got that incorrect number. Thank you for that correction.

1:04:09 I don't know where I got the incorrect number. I will check my slides.

1:04:14 [overlapping dialog]
[Keri Kodama:]
Okay. Could you specify what the incorrect, or the correction was? I think that might have been directly to you.

[Additional comment provided by Dr. Bekins:]
Paul's comment was about sulfate, which he said should be around 20–25 mg/L. I have since verified that my number, 96 mg/L, was measured in the vicinity of Red Hill. His number is more regional and reflects deeper groundwater. In my opinion shallow groundwater concentrations are appropriate because the fuel stays near the water table.

1:04:20 **[Barbara Bekins:]**
Yeah. Okay, so the

1:04:28 most important research gaps, so I tried to cover those. I would like to know

1:04:36 the nature of the total organic carbon. I mean, we have studied the heck out of crude oil,

1:04:42 but we have no examples of heavy fuel. We have studied a gas station plume and

1:04:49 DOC is slightly larger than TPH, but not by much and doesn't have biological effects.

1:04:56 So that's really good news about the many gas station sites around the country.

1:05:01 So we would like to have heavy fuel, you know, an intermediate fuel like jet fuel to look at these

1:05:09 partial transformation products and their health effects. There are also many, many opportunities,

1:05:17 I think, for developing new tools to deal with complex aquifers like this one. Geophysical tools.

1:05:30 I think those were, and then the CO_2 efflux, I think that the CO_2 efflux method has been used

1:05:39 at the site, but it's very expensive. If there was a research component to come up with cheaper CO_2

1:05:46 efflux methods, they could really turn into like a location tool for finding source zones.

1:05:56 So I'd like to see some of that done. I think that's—those are my main ones.

1:06:05 I guess if there's no others, I would say that, you know, the idea that there's a conservative

1:06:10 compound, I think is really important. You know, everybody's struggling with

1:06:17 how to assess whether the source zone of a spill has lost mass over time.

1:06:24 And this idea of archiving the original spilled product and using a conservative compound,

1:06:31 I think could be really productive way in the future. So if we had a better

1:06:37 idea of what compounds are conservative in JP-5 that could be a research goal too.

1:06:50 **[Keri Kodama:]**
Okay, great. If there are no other questions, then we can wrap up.

1:06:59 Alright, so just once again want to thank Dr. Bekins so much for joining us. And thank you

1:07:08 to the audience as well for taking the time to join us in our seminar. Glad to have you here.

1:07:14 Transcribed by https://otter.ai