

2022 Spring WRRRC Seminar Series

HOW CLEAN IS CLEAN ENOUGH?

Methods to Assess Environmental Risks Posed by Releases of Petroleum

Dr. Roger Brewer

0:11 **[Keri Kodama (host):]**

All right. Hi, everyone. Welcome to another one of our WRRRC spring seminar sessions. This is another presentation in our Red Hill theme.

0:27 This week is Roger Brewer, and he will be talking about total petroleum hydrocarbons and the assessment of petroleum risks this week.

0:36 And so let's introduce our speaker. Dr. Roger Brewer is a senior environmental scientist

0:42 with the Hawai'i Department of Health. His environmental experience includes regulatory compliance audits;

0:48 characterization of contaminated soil, water, and air; contaminant fate and transport;

0:53 vapor intrusion and human health; and ecological risks—risk assessment. Roger's areas of focus

0:59 include the chemistry and toxicity of petroleum fuels and improved methods for the collection of representative environmental samples. So without further ado, Roger, please go ahead.

1:13 **[Roger Brewer (speaker):]**

Hey, thanks a lot. And thanks for having me. This is a really interesting topic, something I've been working on personally, since I

1:19 got started in the environmental business almost 30 years ago now. There's still a lot to learn.

1:27 So first, I want to go over some terminology. And you're going to hear me discuss as we go

1:33 through this presentation. First is BTEX, a lot of acronyms in this business. So BTEX is benzene,

1:39 toluene, ethylbenzene, xylenes, +/-, you might see an m— naphthalene or methylnaphthalenes. PAH

1:48 is polyaromatic hydrocarbons. Mostly we look at naphthalene things like benzo(a)pyrene. TPH,

1:54 here we talk—hear us talk about quite a bit. It means— stands for total petroleum hydrocarbon. This is

2:00 everything else that's in a petroleum mixture. So, petroleum is a mixture of hundreds of compounds. We have a few individual ones we look at, the rest we refer to collectively as TPH.

2:11 In—for now, under Hawai'i's guidance, this includes hydrocarbon related degradation compounds.

2:17 In our upcoming guidance, we're probably going to adopt some of my colleagues in California EPA where I used to work, to start using, instead of TPH, they refer to HOPs or

2:27 hydrocarbon oxidation products. These are usually biological related metabolites of hydrocarbons.

2:34 That's a big issue for contaminated groundwater especially. Then you hear me talk about action levels, these are concentrations of contaminant in the media that are below which no adverse health

2:44 or other environmental impacts are anticipated. Above an action level, it's a concentration in

2:49 the media courses, it doesn't necessarily mean you have a problem just means you need to look at it more detail, we also refer to these screening levels, then risk driver stuff,

2:58 especially when I think about today we're talking about what's driving risks, TPH compounds or BTEX, the risk driver is a compound or compounds in the mixture that poses the greatest risk to human

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3:09 health in the environment. In other words, if all the other compounds, say BTEX such, were below target
risk levels or below action levels, this other compound, maybe TPH, or
3:19 something could still be above action level, still pose a risk. We refer to it as the risk driver.
3:28 A few misconceptions—talk about—see. The first is that TPH is only useful as a screening tool.
3:39 It's a qualitative screening tool. That's not quite true. So TPH
3:44 and hydrocarbon related degradation compounds often dominate contamination. And we'll see
3:50 this later on in the presentation. They have to be quantitatively evaluated as part of the environmental
hazard evaluation, or what also referred to as a risk assessment.
4:01 So we might agree on that, but some people would say well the methods aren't available to qualitatively
assess risk posed by TPH compounds, this other mixture that's—that was actually something
4:10 we're working on when I first got started in 1990s. So you can evaluate TPH as a mixture,
4:16 quantitatively in the same manner as we do individual compounds like BTEX and PAHs.
4:22 Another misconception: TPH only needs to be considered if benzene and other individually targeted
compounds are not detected. That's not true and again something else we'll talk about
4:31 is that the TPH component of petroleum can still pose a risk, even when the concentration of BTEX and
PAHs or other individual compounds meet the target risk, or action, or screening levels.
4:43 And last, something we have discussions about: Do we really need action levels? Can we make
everything site specific—come up with site specific detailed chemistry of petroleum and such. But that
may be—
4:53 work for a few sites, but there are hundreds of 1000s of petroleum release sites in the US and definitely
not that many of us regulators, so we really need conservative but reasonable
5:04 rational screening levels to screen out low risk sites. So we can focus on the high risk sites.
5:13 Some references to look at. The first said, the document risk based screening levels, sorry, I can't see my
slides.
5:28 Risk-based TPH action levels, their screening levels, you know, whose document you're looking at. It's
very similar California Environmental screening
5:34 levels. Just something that I worked on when I worked for California EPA. Our last edition published in
2017. These are actual levels for air, soil, and water. And
5:45 as that also we published in 2018, a series of TPH risk case studies. It was, it's—it's referenced in
5:54 the ITRC's document on how to assess TPH risk. We did it independently, and published this through
6:00 our office. And then a few papers on reports we did on chemistry and toxicity of petroleum vapors
6:06 are mentioned later on. In 2012, we did a detailed field study of chemistry and toxicity of
6:12 TPH and petroleum paper, some sites around Hawai'i. And we published a paper on that in 2014.
6:25 Some other references, I'm not going to get through all these, several— several entities that published
summaries of the toxicity of TPH.
6:35 You can see these in the slides later on when you get a copy. Down at the bottom, ITRC in 2018,
published
6:41 a document. Some of us were part of that team on how to assess TPH risk petroleum contamination.

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6:50 That's kind of the background. Here's an outline. I want to go over a lot of topics today, but it's gonna give us few details on each topic.

6:58 First, we want to go over this basic seven environmental hazard evaluation, what can be referred to as environmental risk assessment. I really don't like the term risk assessment because when

7:07 we discussed that some people focus entirely on the toxicity or toxicologists who may not know the other issues we look at. Then we will look at what is petroleum made of,

7:16 and what is TPH and how are toxicity and risk evaluated and associate with TPH.

7:22 Also how to individual TPH components partition when released to the environment. Then what drives

7:29 risk—a topic we're especially focusing on base—TPH or these HOPs degradation compounds or BTEX,

7:36 when you're dealing with petroleum contamination, especially in something like groundwater, or it could be in soil or air also. So then how are TPH and HOPs tested for, and we'll end with that.

7:49 See a quick schematic of potential environmental concerns posed by contaminated soil and groundwater really for anything, including for TPH. So for contaminated soil,

7:58 we might look at a direct exposure say if kids playing in contaminated dirt or adults, or ecotoxicity. At

8:07 another big issue is leaching of contaminants and contamination of deeper groundwater, also

8:13 vapor intrusion into indoor air. For contaminated groundwater we're often concerned about impacts to

8:20 drinking water wells, drinking water supplies, but also especially here in Hawai'i and coastal areas where there is no rivers and lakes, is discharged into aquatic habitats. May not be a source of

8:29 drinking water, but could severely impact aquatic habitats. And then the last one, number seven,

8:35 gross contamination, which can be free product machines in such on motor or vapors.

8:41 Or I've got another slide I'll show you in a minute on other examples of gross contamination.

8:47 So we know all these different environmental hazards, things we want to screen for up front that most of the contaminated sites we address. And to develop action levels or screening levels,

8:59 or assess risk, then there's a few basic things we need first. We need toxicity factors for the compounds of interest. We need physiochemical constants like solubility sorption and its volatility

9:10 and such in exposure assumptions. How long with kids or adults being exposed to the dirt? How many years, days per year, and such. How much dirt are they eating? How much air are they breathing? Or

9:18 water they're drinking? It's a basic soil and groundwater properties. And then we can plug that into

9:24 separate models and approaches for assessment of risk or for development of screen—action levels.

9:30 It would be separate models for direct exposure, vapor intrusion, leaching, gross contamination.

9:37 This is just an example of some action levels and our guidance for benzene in particular. So you see the four media: soil, soil gas, indoor air, and groundwater. And using

9:47 these different models and these toxicity factors and physiochemical constants and such, we can derive

9:53 screening levels. These are intended to be safe levels of benzene in all these different media.

10:01 So in this case, if you look at benzene in soil, we talk about your driving risk in terms of

10:06 compound but also in terms of potential environmental concerns. So for benzene contaminated soil leaching into groundwater is the lowest action level, it's 0.3 milligrams

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10:17 per kilogram. And it's the lowest action level of all the other potential environmental concerns. So we can say, if you have benzene contaminated soil, your main concern could be leaching into

10:26 groundwater. Or, if you take care of cleanup to a site to address leaching the groundwater, you should be addressing all these other concerns as well. Something similar for contaminated groundwater.

10:38 See the different action levels for different environmental concerns. For drinking water, the action level is 5 micrograms per liter, that's the lowest action level

10:45 of all the ones listed. We say in this case, if it's a source of drinking water then drinking water toxicity poses the highest risk. If you clean up the groundwater to address the

10:56 drinking water toxicity, you address all these other concerns. One thing you can drink benzene—

11:02 the safe level for benzene and drinking water is 5 micrograms per liter, but you can't really start tasting it into 170 micrograms per liter. That has important

11:09 implications that you could be drinking benzene contaminated groundwater without knowing it.

11:20 So a lot of what we do comes down to toxicity factors for individual compounds. So one point I

11:26 always want to make is that everything is toxic at some, some dose, at some potential. So water

11:32 is toxic, you know a few gallons per day is a safe dose but one thing about for water, if you drink more

11:38 than a few gallons at one time, you could suffer from acute hyponatremia, which essentially will kill you.

11:43 Aspirin, more toxic than water. So if you look at mini--tabs in the grocery store or something, they're 81

11:49 milligrams per day, and that's considered a safe dose for aspirin. Anything above that on a

11:55 daily basis could pose potential gastrointestinal—sorry about misspelling their effects.

12:01 Barium is a little more toxic than aspirin, 3 milligrams per day is considered as the safe dose

12:06 for young children. It's equal to about two small grains of sand per day of pure barium, then

12:13 there's multiple non-cancer related health effects. Arsenic is more toxic than barium, 0.0045

12:20 milligrams per day and that's about one millimeter grain every two years, it's a tiny amount. This is

12:26 10,000 times below an acute toxicity level. That gives you an idea of how toxicity works.

12:33 And looking at an example, I can still—for how you take this to develop screening levels. Real simple one, silver the maximum daily dose for 15 kilogram child, on average six years—six years

12:43 old, 75 micrograms per day. We assume children drink 0.78 liters per day of water,

12:49 that's EPA got it. So 75 divided by microns per day divided by 0.78 liters

12:57 per day, comes out to 96 micrograms per liter, if I did that, right, of silver, its action level.

13:09 That's the key point I want to make here, then is dose makes the poison. You always hear toxicologists talk about this, a risk assessors.

13:15 So you can have something that has a very high toxicity, like in this case, benzene, it high toxicity, but a very low dose. And the risk posed by that would be fairly low,

13:25 where you could have something a lot less toxic, like barium but a high dose of barium, even though it's low toxicity, could pose a high risk. So we would say that is what is driving health risk.

13:38 That comes into play when looking at TPH versus BTEX as risk drivers, what's most concerned

13:44 in water. There's more information on environmental hazards, or environmental hazard evaluation, and

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13:50 series of training webinars we posted in 2017. The first five parts are on how to collect a good sample.

13:56 That's really the biggest problem environmental work, is getting a good sample to begin with. Something that is representative, the question being asked. And then Part 6, we talked about once

14:05 you get reliable data, and what do you do with it? Here's the webpage for our webinars.

14:12 Let's skip on to what's—what's petroleum made of. So you might be familiar with these. It's not this

14:18 typical. It's a gas chromatogram for analyzing petroleum—it's the chromatogram of gasoline. So,

14:27 you see a lot of spikes and such over on the left side as you're viewing this, of a gas chromatogram. Those are the more volatile compounds. And the C here stands for

14:34 the number of carbon molecules in each compound. So eight, benzene has six, then you see C8, C12

14:41 and such. Anything less than C12 is considered volatile, maybe some of the C12 are just compounds

14:46 up to 16 carbon molecules are considered semi- volatile. Then for gasoline, you see it's just an example

14:54 from California guidance; 23% in this particular guidance of gasoline fuel is made up of BTEX

15:01 and a tiny bit of naphthalene, 77% is made up of all this other stuff we lumped together as TPH.

15:07 So that's the big question, what is—what's this other stuff? How do we assess the toxicity of it?

15:14 That's gasoline. Here's kerosene, is the example using JP-5 fuel. So here you see—

15:21 there's gasoline, everything's on the left. Kerosene, now it's a small hump, right in the middle. So it's kind of straddling this volatile—the middle of the volatile range here.

15:31 And in this case, now, for this particular sample—89% of the sample, this fuel was TPH, is

15:38 non-BTEX, non-PAH contaminants. Their total BTEX, I think, in this example, was 11%. This turns

15:46 out to be fairly old information for kerosene. Some of the more modern kerosene we've seen,

15:52 current, doesn't have any BTEX or very minimal levels in it. That's jet fuel. Mostly this other stuff, TPH, here's diesel, now we've,

16:02 we've really spread out the chromatogram, including a lot more chemicals, compounds in it.

16:07 And it goes all the way from volatile range, but not much of it. Most of it's up in the semi-volatile to non-volatile, very low volatility range. Now, 99% of what's in the fuel is

16:18 TPH. It's this other stuff that we have to think about, we can't just look at BTEX,

16:25 especially when you start looking at middle distillate fuels like this.

16:32 So here's a—so what is this other stuff, this TPH. Something I've been thinking about for way

16:37 too long. This is my last job as a consultant. It's in a large western state, which I won't name.

16:42 That red circle is me staring at this fireball coming out from this remote control backhoe. This is a gasoline station site that had been cleaned up, all the gasoline contaminated stuff they

16:51 thought was dug up 20 years ago, and they're putting an underground parking garage. I was— at that time, I'm a geologist but I also do risk assessment. I was reading the risk assessment

17:02 document in my office, it was a nothing site and the guy I worked with calls up and said the site's on fire.

17:07 Well, how can that be, it passed a risk assessment, was approved by the state regulators. But they

17:12 only looked at BTEX, and especially benzene and such, and there wasn't anything in the soil vapors where if they tested the soil vapors, which I didn't know at the time, for TPH,

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17:21 all these other compounds, they would realize they had flammable levels of gasoline vapors in this soil.
17:28 So it's a good example of how you can't just look at BTEX.
17:36 When laboratories report—report TPH and it's something we'll discuss later on also,
17:44 one issue is when they start looking at what is TPH, the laboratories have to run three different tests.
17:50 And they'll, depending on how volatile the compounds are, they're trying to analyze in the mixture. So they refer to this as gasoline range compounds, diesel range compounds,
18:00 and residual range compounds. Or you could call it TPH-gasoline, TPH-diesel, TPH-
18:06 oil. But this causes some problems when we're— we get data back from laboratory you're gonna get three numbers, but we have to do it because it's all one mixture, is add up all three of those
18:17 numbers and that gives us a total TPH. And you can subtract individual compounds, as needed.
18:26 Keep that in mind. So we know what's petroleum made up now in general, it's mostly
18:32 stuff that—there's TPH, HOPs, BTEX. And how do you look at BTEX and assess toxicity,
18:39 I mean TPH to assess the toxicity and in risk. And also, what happens to these TPH
18:44 components when released to the environment, look at that next.
18:51 This was as a group that got together in 1990s, just right when I was starting out, involved on the
18:56 side. And it's called the total—see the, Total Petroleum Hydrocarbon Criteria Working Group. They published
19:04 a series of documents on how to assess TPH, what is TPH made of, what's the toxicity? How do you
19:10 use this in a risk assessment? A lot of people were involved in this, a lot of experts from oil
19:16 companies. Also risk assessors and experts from the US Department of Defense in the Navy, Army,
19:23 Air Force, and such. Then several states, including our office at the time, Massachusetts was well ahead of everyone else. And also Washington and California eventually
19:35 published guidance and such on how to assess TPH and risk assessment.
19:42 The main thing they did is they, they took this mixture this—of TPH and divided it up into two separate groups of compounds. The aromatic compounds made up benzene rings,
19:51 and then everything else referred to as aliphatics. And they assigned toxicity factors to the group
19:58 of compounds within a narrow range. They have similar toxicity and similar physio- chemical constants and fate and transport constant—or factors. So you can see here like for aromatics,
20:08 they're divided into two separate groups from a—it's called equivalent carbon, eight carbons, a 10 carbons, then greater than 10 carbons between two carbons,
20:16 all the compounds that fall in those two ranges. Then for aliphatics, they're broken into four different ranges from
20:24 five to eight carbons, eight to 12, grade eight to 12, and then greater than 12 to 18.
20:30 You can subdivide into a lot more groups than this but in terms of toxicity, especially these main
20:35 six groupings, you can do a lot with for assessing TPH. And there's a lot of information on effective
20:43 carbon, how you—this whole approach in detail and the TPH Criteria Working Group documents.

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20:52 So that one had—they had each one of these different carbon ranges for aliphatics, aromatics, then the group went through an assigned representative molecular weights, vapor pressure,
21:03 solubilities, Henry's constants, sourcing coefficients. Now these physiochemical constants that you could use then to do modeling and assess risk, see the—for each one of these groups. Also
21:17 assign toxicity factors to each of the groups, some of the groups they put together, really
21:22 is four main groups. We follow Massachusetts guidance here: C5 to C8 aliphatics
21:29 compounds, just an example oral reference dose, inhalation reference concentration, and you see that two other
21:37 groupings for aliphatics. So that the lower the number, the more toxic it is, so the C8—C18
21:42 aliphatic is more toxic than these lighter range volatile things. That's why diesel tends to be
21:48 more toxic than gasoline when you're just looking at TPH, this has all these heavier aliphatic—aliphatics in it.
21:54 And then the really heavy stuff greater than 18 carbons, and higher, not that toxic.
22:01 Here you're getting into motor oil and waxes and such, it's not volatile. Then you have the C8 aromatics,
22:07 which fall in between the lighter range aliphatics and aromatics. So we have toxicity factors,
22:13 now, in addition to physiochemical constants, for each one of these carbon ranges.
22:18 Right away, just in terms of what happens to this stuff when petroleum genuinely—when it gets released in the environment. If you look at just the Henry's constant, especially
22:28 you notice the aliphatics, that if the number is above one, it means that the—this compound—
22:33 these compounds prefer to be in the air not in the water. Just the ratio of the concentration in gas,
22:38 or the concentration in water, so it's greater than one, most of its going to be in the air.
22:44 Aliphatic's prefer to be in the vapors. If you look at the Henry's constants for the aromatic compounds, including BTEX, then they're all less than one. So aromatics prefer to be in the water.
22:54 That gives us some hint then, initially what we're looking at. And you can look at it this way, here I've broken up—C released it a different type of fuel to the environment.
23:06 So if you collected vapor samples above gasoline, kerosene, diesel, whatever, then you'll find
23:13 mostly TPH in the vapor samples that you collect. And most of that stuff will be aliphatics.
23:19 This actually some—from some field work that we did several years ago. If you look in the groundwater, what's in the groundwater with—that's where all the aromatics are going to go, when they
23:27 get leached out of the fuel. When the fuel hits the groundwater, aromatics would dissolve and go into the groundwater. You'll see a lot of BTEX, especially associated with gasoline. With
23:37 kerosene, you may not—may or may not see BTEX. And same with diesel, but not in the fuel. If not,
23:43 then you'll see a lot of these other aromatics, you see eight and higher aromatics dissolved into
23:49 the water associated with kerosene and diesel. So we think about what happened to Red Hill, it
23:54 was jet fuel, which turns out not to have had much BTEX in it. Most of what was dissolved in the
24:00 groundwater there, just from this simple approach, we know were aromatics—probably nonspecific aromatics,

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24:06 no BTEX, and that's jet fuel we don't think. That tells us now a lot about risk.

24:14 So we can look at this in more detail and look at what the carbon range makeup of this TPH mixture is in vapors, in the fuel, and dissolved in water. So

24:24 we did a field study several years ago, I mentioned before, we collected vapor samples of—most of them age sites and some fresh samples of gasoline, kerosene, JP-8, and diesel.

24:36 And most of the vapors are made up of C5 to C8 aliphatics.

24:41 And there's some BTEX mixed in with that for gasoline, not so much, but it depends on the

24:46 fuel actually for kerosene and diesel. This is the TPH makeup of these fuels for—in vapors. In the fuels

24:54 that here I've just had the original hydrocarbon range makeup of the fuels. You see for gasoline, most of

25:01 gasoline in terms of TPH, excluding the BTEX now is C5, C8 aliphatics. Just a little bit

25:07 of higher range aliphatic C8, C18. And then a little bit of the other aromatics greater

25:13 than C8 aromatics. You see, when you get to kerosene, you're losing all this lighter range, more volatile stuff. They use JP-5 on aircraft carriers, you might know, they're,

25:25 they don't want it to be that volatile, but it has to be able to push a plane. So most of what JP-5 is made of is of these C5, C18 aliphatics and then greater in C8 aromatics. The pic chart I have here

25:37 is an older formulation that's in the current JP-5 fuels. It's probably no green, there's not

25:42 really much C5, C8 aliphatics anymore. Diesel fuel, least from what we've heard in literature,

25:47 doesn't have any C5, C8 aliphatics, which is odd because when we collect vapor samples about diesel fuel in the field, we see a lot of C5, C8 aliphatics. Something's missing there.

25:57 These are all measured and such, we want to do the same thing with water. What's the TPH makeup of

26:03 dissolved phase petroleum and water. We spent two years and quite a bit of your federal tax

26:08 dollars doing laboratory studies where we took a layer—we took different types of fuel, gasoline,

26:14 diesel, and JP-5, JP-8 and we put a layer of the fuel on top of water, let it sit for 20 days.

26:20 And then we tested the water to see what the BTEX, PAH content was. But also, we want to see what

26:26 the aliphatic, aromatic makeup was, what dissolved in the water. So we get very detailed breakdown of

26:32 that. And then we can assess the toxicity directly of the dissolved phase TPH compounds in mortar.

26:40 But that didn't work. We tried several times, labs couldn't reliably separate aliphatic and aromatic

26:45 carbons dissolved in the water. That's something we're still working on research-wise. We couldn't

26:51 do that, so we had to model it instead. So down at the bottom here, and actually some oil company—

26:58 some chemists told me modeling is probably more accurate anyway, trying to estimate what the TPH makeup is. So for gasoline, what you'd expect to be dissolved in the water when you have gasoline

27:06 floating on groundwater would be mostly C5, C8 aliphatics. Either highly volatile, but

27:12 they're also highly soluble, and they also make up a big portion of it, not a big surprise. Anything else dissolved in the water in terms of the TPH would be these other aromatics. It's aromatics

27:21 more, especially soluble. Things like kerosene and diesel, most of what dissolves in the water,

27:28 we can model this would be C8 and higher aromatic compounds. If there's any BTEX

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27:34 in the original fuel, you might see some of that or the thorough range. Sorry, not BTEX,
27:40 I mean C5, C8 aliphatics. You might see it dissolved in the water also. Now we know what the carbon
range makeup is, and the vapor is fuel
27:48 and dissolved in the water. So you think the next step is we could just develop action levels for each one
of these carbon ranges. And then just go out in the field and test those the same way
27:58 we do BTEX. That's not really practical, because of first is just the cost of doing
28:03 this in laboratories, and very few laboratories can actually run the carbon range analyses.
28:09 And then also, especially with respect to water, then you have degraded mixtures so that getting
28:16 the carbon range data wouldn't be very useful. Because all the degraded stuff would just come out TPH.
28:22 So an alternative—See, oops, sorry. An alternative, which I don't have the numbers in here, would be to
28:32 develop carbon range weighted TPH action levels for specific types of fuels. So sorry,
28:39 I meant to have the numbers here, I don't. But let's say an example for TPH-gasoline, we could because
28:45 we know the carbon range makeup of gasoline vapors we can calculate action levels for indoor air, and
then for soil gas. We know what the carbon range makeup is as fuel is, so we can calculate action levels
for
28:55 TPH for vapor intrusion and for direct exposure in soil. Actually vapor intrusion, we
29:01 probably use soil gas. And then for drinking water, we know what the carbon range makeup is of
dissolved phase
29:07 TPH in water. Then we can calculate risk-based action levels again for drinking water.
29:17 So the idea here is instead of calculating or coming up with action levels to individual carbon ranges, is
to calculate weighted toxicity of all these different carbon ranges
29:27 that make up the TPH. This is similar to calculating the calories in a cookie. So
29:34 you might know that individual calorie counts for individual ingredients of a cookie, whether it's flour,
eggs, or chocolate or something.
29:43 So you could test, if you had a cookie in front of you, could test individual—what's
29:48 the concentration of chocolate, the concentration of flour, and such. But an easy way to do it if
29:53 you know the general makeup of the cookie, then you can calculate a weighted toxicity just based
30:00 on the calories in each individual ingredient. There's no need to test for individual components.
30:06 You would just calculate a weighted calorie toxicity if you want to call it that, and the highest, you know
what the weighted toxicity is not going to be any higher than
30:14 the calories in the chocolate. If you assume there that have the highest calories, and it's not going to be
lower than the calories in the flour. So it's a very tight range in reality of toxicities for
30:24 mixtures based on the ingredients. We do the same thing for looking at fresh or degraded
30:30 petroleum or TPH. The toxicity of the mixture can't be any—any less than the least toxic
30:38 compounds in that mixture. And it can't be any greater than the highest toxicity compound in that
mixture. So in terms of TPH, can't be less than C5, C8 aliphatics
30:49 or the say the C8 or higher aliphatics, can't be greater than that.

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31:02 So I'm now going to skip through that quite fast but basically, you can calculate these weighted toxicity factors. We discussed the general approach

31:09 in our 2017 guidance and then our updated tap water approach. It's in the memo we published just a

31:15 few months—or in February. So it goes through how to calculate weighted toxicity factors for

31:21 TPH mixtures for different types of fuels, especially with respect to tap water.

31:30 And here's an example of calculated weighted toxicity factors based on the carbon range makeup.

31:35 So again, based on measurements in the field and other fuel, we can—we know that carbon range makeup of

31:40 TPH in vapors for gasoline, kerosene, diesel, and such. In general, you could do the site specific

31:46 and we have some default values. Once we have the toxicity factors, we can calculate risk-based

31:51 air screening levels or action levels for TPH associated with different types of fuels.

31:56 We do the same thing for dissolved in tap water. Where in water, if we know that the general carbon

32:03 range makeup, we can calculate a weighted toxicity factors and then we can calculate action levels

32:09 for each one of these different types of fuels for the TPH, in general. And we—

32:14 in the field, we just test the sample for TPH and compare that to an action level.

32:24 Oh, so here it is. Here's the example for TPH for middle distillates, the MD.

32:33 So these are carbon range weighted action levels for TPH diesel fuel. So you see all the pink is

32:40 for human health, green ecotoxicity easier for terrestrial at site specific, and in gray is gross

32:45 contamination. So now we can treat TPH in terms of middle distillate fuels just like we would

32:51 benzene and such. We go out and test samples in the field, we have action levels for those.

33:03 So that the last things I want to talk about then is, what drives risk? Is it TPH or HOPs. So just to recount

33:14 real quickly, we went over just in general what environmental hazard evaluation basics are, what do we look for in the field, different environmental concerns. It could

33:24 be more than just toxicity. What's petroleum made of, we know that fuels in general

33:33 are dominated by non-BTEX compounds, all this TPH stuff. And we looked at what is TPH made of, how are

33:33 toxicity and risk evaluated. So, we have six or more basic carbon range groupings of aliphatic

33:40 and aromatic compounds that can split TPH into. And we know they differ for different types of fuel.

33:47 And we can look at how these different carbon range compounds partitioning the environment

33:53 and then we can estimate weighted toxicities for this carbon range mixture in air, or vapors that

33:58 were fuel, or dissolved into water, or for the original fuel itself. And once we do this now,

34:03 we can count—we can develop risk-based action levels and then treat TPH in the same way we do

34:09 as benzene and other compounds and assess risk in the field. So now, what drives risk? TPH or is

34:15 it HOPs, these degraded compounds or BTEX. Let's look at that real quick. So,

34:21 here are these—our current carbon range weighted TPH action levels for soil. So our action level first

URL: <https://youtu.be/MaX0UIX-w8I>

34:27 for benzene in soils. They have a gas station site, there was—gasoline was released to the soil, and you test it. You would test

34:34 for BTEX and other compounds. We have action levels for those. The action level for benzene and

34:39 soil was 0.3 milligrams per kilogram. We also have risk-based action levels for gasoline,

34:48 kerosene, we just got middle distillates, but this will be the example for kerosene and then for

34:55 diesel fuels. Actually, sorry, that's a mistake in this slide. It should say TPH is diesel fuels and the last one

35:01 should say residual fuels, heavy oil. So it's the TPH values, and the main point here is they're way

35:08 above the value for benzene. So you would think benzene would be the main thing of concern. But

35:14 actually, when you go out to gasoline station sites and such, and test the soil, you may or may not find much benzene left in the soil. So TPH may or may not—or benzene, may not drive risk.

35:28 So, as far as TPH versus BTEX is the fuel risk driver when you're looking at soil. For gasoline,

35:34 if it—probably a lot of sites, benzene does drive clean up at sites—gasoline contaminated sites. If

35:40 you clean up the site to address benzene, you're going to take care of all your problems. That's if you're using a 10^{-6} risk, one of the main cancer risks for benzene. If you use say a

35:49 10^{-5} risk, 100,000 cancer risk for benzene, your benzene action level goes up tenfold.

35:56 In this case, you may not have a problem with benzene at this site because still have a lot of other stuff left inside like the flaming pit example I showed you. Same thing for,

36:06 for kerosene, the modern formulations, there's really no BTEX in it. So in that case,

36:11 anytime you have a kerosene release, you're not going to find BTEX or PAHs in the soil. So all your risk and cleanup are going to be driven by TPH, not BTEX. Same thing for diesel.

36:24 And again, the reason this happens is that even if there was—were trace levels of benzene in soil,

36:30 the dose is so low that the risk is going to be pretty low, even though the toxicity of benzene is pretty high. And that even though toxicity of these TPH compounds in comparison is

36:40 relatively low, the dose is so high or the concentration in soil is so high that it's going to be the risk-driver, not benzene, not BTEX.

36:52 Looking at air, we've done quite a bit work looking at the TPH and carbon range compounds in air. Here are action levels for benzene in air is

37:02 0.36 micrograms per cubic meter, it's probably below background for most urban areas. 37:08 In the screening levels for, see—gasoline, kerosene, and diesel, alright, you see a lot higher. So what,

37:18 1000 times higher or something. So you would think again, maybe benzene is the main thing we need to worry about when we're looking at impacts to air or vapors coming off of fuel releases. In reality,

37:29 what we see this thing from fresh fuels, we tested vapors above gasoline, diesel, and JP-8. And there

37:36 was actually high benzene in the fuel, in the vapors from diesel and JP-8. So there is some BTEX in

37:43 there that is going into there, we were surprised at that. So maybe in that case, benzene does drive the risk if it's very fresh fuels. But if you back off to a 10^{-5} risk,

37:53 say for benzene, then your TPH is probably going to be driving risk in reality, even for contaminated air. Give me the TPH data, we could make a good call on it

URL: <https://youtu.be/MaX0UIX-w8I>

38:02 without even looking at the BTEX data. What's the problem? We look at field studies and we get
38:07 the soil vapor samples from sites all around Hawai'i. We don't see that much BTEX in the vapors, even
at gasoline sites in comparison to the—all these aliphatics and stuff.

38:16 The aliphatics tend to drive risk. So again, what drives risk in terms of you know, for
38:21 indoor air most of time is the TPH and this is light-range, mid-range aliphatics, not the benzene.

38:31 Then for tap water, this of course, is a big issue recently. Here's our action level for benzene and tap
water,
38:38 5.0 micrograms per liter. Again, the TPH is a lot less toxic—less toxic, maybe 50 or more times
38:44 less toxic and the action levels are equivalently much higher. So again, you might think what
38:50 benzene is our main concern at the site. When we go out and actually look at data in the field,
38:57 maybe at gasoline sites, especially when it's fresh and the plumes are still volatile. Then
39:04 you do see a lot of benzene in the water and BTEX and that's going to be driving risk
39:09 at those sites. For kerosene, diesel releases, depends on the formulation of the fuel but
39:15 especially for more modern formulations of kerosene and diesel you're not going to see much BTEX in
the groundwater, in the water period. It's going to be mostly these other aromatics and such.

39:25 And so the TPH components driving risk, not the BTEX
39:35 So that's the fresh stuff. How about for petroleum contaminated groundwater
39:41 is degraded, and most sites we look at the petroleum is heavily degraded. So if you went out and tested
for BTEX, if you went out and tested for individual carbon ranges in the water,
39:50 you wouldn't find anything. It's just a lot of degradation, partially oxidized compounds.
39:56 So that—in this case, we need to look at the weighted toxicity of not just the TPH, the carbon
40:02 ranges, but also the combined—these carbon ranges and BTEX, and mixtures as a whole.
40:07 What's the weighted toxicity of that, and this we do in the same manner. If we know the proportions of
individual carbon ranges that make up the TPH, and the proportions of, you know, the BTEX, and PAH
compounds
40:18 that make up the BTEX component dissolved in water, then just like the chocolate chip cookie, we can
calculate a weighted toxicity factor for all these—that mixture in total.

40:29 And then we can calculate a weighted toxicity factor for degraded petroleum associated with these
different fuel types: gasoline, JP-5, or diesel fuel.

40:40 That's a big thing we're looking at now and recently, really, for quite a while. Some people have been
looking at this for the last 20 or 30 years. So it's
40:50 a chemistry and toxicity of degraded—sorry, degraded petroleum in water. So take your BTEX
40:58 and TPH, degrade both of them, they turn into hydrocarbon oxidation products, HOPs as the
41:04 Californians call them, just a combination of these acids, esters, alcohols, ketones, and phenols.
41:09 There's a lot of research published on the toxicity of individual compounds and these
41:15 mixtures. And when the laboratory tests your water sample now, that it's going to report it in the
41:20 absence of silica gel clean up, which pulls out all the polar stuff, so you don't clean up the sample.

URL: <https://youtu.be/MaX0UIX-w8I>

41:26 In the lab report, this still is TPH, and in this case it's representing all the degradation compounds.

41:33 It's not a very good lab test, it's not very precise. But right now, it's the best we have.

41:38 And we can argue quite a bit—we have—I do quite a bit with my friends in the oil companies and other such about the chemistry and toxicity of this. There's a quote from Aristotle, at some point

41:50 there's such a tight range of what the weighted toxicity could be. It's like calories in the cookies between the

41:55 chocolate and the flour. I like Aristotle's quote here, "It's the mark of an instructed mind to rest easy with the

42:00 level of precision, that the decision, precision— that the decision requires. Not to try an

42:06 exactness that is unnecessary for the problem." So what we really need to get, detailed information on what specific compounds degradation products are. We can estimate based on the original mixture of what

42:16 the weighted toxicity would be. At least it's a starting point, which is good enough for most sites.

42:24 So here's some example screening levels, where we calculate a weight toxicity of carbon range plus BTEX. This is the HOPs action levels in our upcoming guidance.

42:34 And again, benzene, I just threw this in here for comparison, again 5.0 micrograms per liter. One thing, but the TPH action level, let me skip back, real quick.

42:46 It was originally 390, 339, 211, and 189. These action levels for gasoline, kerosene, and diesel.

42:53 When you degrade the stuff, the benzene action level goes from 339, or whatever it was, it

42:58 actually falls down to 190. That's because we're including degraded benzene in the mixture now.

43:03 So the mixture is actually more toxic, the TPH, because all the benzene is included in your TPH measurement now. For kerosene and diesel, the risk-based action levels tap water actually

43:14 go up a little bit because we're including all these low toxicity degraded xylenes in the water and calculating the weighted toxicity.

43:27 So in terms of TPH versus BTEX for contaminated drinking water, I know that was a lot of details

43:33 to go through, but get the general idea, I hope. But say if you have a fresh spill of gasoline it

43:39 already has a lot of BTEX in it, then yeah, BTEX is probably going to drive your risk. Don't even bother testing for TPH if it's fresh, test the BTEX. If you clean up the water to

43:48 meet BTEX action levels, then you're done. Not very many fresh plumes out there that you'll see.

43:54 For kerosene, it depends on the formulation. For more modern formulations of kerosene and diesel, again,

44:00 there's no BTEX, very little BTEX in the fuels. So you have to test for TPH, and TPH is what's

44:07 driving risks, not the BTEX. For degraded plumes, of course, now all these compounds are oxidized, your benzenes' oxidized. If you test for benzene in the water, you're not going to find the

44:17 degradation products. It's just going to come out lumped in with your TPH. So for degraded plumes,

44:22 the TPH, or in this case HOPs, we'll call it that, are always going to be driving risk, not benzene.

44:34 So last slide I have is how are TPH and HOPs tested for, and it's—

URL: <https://youtu.be/MaX0UIX-w8I>

44:40 really that's where we are now. So we've gotten back—we have a much better idea, at least a starting
point on how to calculate looking—at assessing the toxicity of these mixtures of fresh
44:50 and degraded petroleum compounds. At one point again to make, is TPH action levels we publish, they
apply
44:58 to the total concentration of TPH-related compounds in the mixture. So you have to add in these separate
ranges that the laboratory reports. Ideally, the laboratory would just report a single
45:09 concentration for both TPH or HOPs if they're looking for degraded compounds. And that's what
45:15 gets compared to the action level we have. So we have action levels right now for gasolines, middle
distillates, heavy fuels. So you test the groundwater, you get a total TPH
45:25 number from the lab, and you compare it to the appropriate fuel type that was released there.
45:31 So site-specific carbon range data and action levels, they can be useful for vapor intrusion investigations
because the vapors above different fuel types really vary,
45:41 especially from middle distillates we saw in the fields. That would be useful for degraded road sites. It's
not really useful for cases like Red Hill. It is useful to try to
45:50 get site-specific carbon range data for the fuel itself, and then we can get a better idea of what went into
the groundwater. We're working on that now. All in all, we definitely still need better
45:59 test methods, now that we know what to do with the TP, for both TPH and for these degraded
compounds.
46:07 So I know there's a lot of information about different points. But just a quick summary, to get back to
46:12 the main points: no BTEX, no PAHs doesn't mean no risk. And methods are available to assess the risk
46:18 posed by TPH compounds and the non-BTEX, PAH stuff. TPH always needs to be considered in any
petroleum
46:28 release site, even if benzene other compounds are detected. A lot of times, it's going to drive risk,
46:33 not your other—these individual compounds, as we said here, even when the other compounds
46:40 meet their action level, especially benzene. So if you look at Red Hill, there's no benzene in the
groundwater. There's no benzene intentionally in JP-5 jet fuel. So of course,
46:49 if you just look at benzene, like my flaming pit example, it's going to pass a risk assessment. You have to
look at the TPH component, all the dissolved other hydrocarbons and related degradation
47:00 products. We definitely need better test methods for TPH and HOPs. There's people working on that.
47:07 And then the carbon range data-specific action levels, site-specific, this issue came up. They're mainly
47:12 useful for testing parent fuels associated with, you know, large fresh releases, whether it's crude
47:18 oil, or jet fuel, or gasoline, or something, and for testing of indoor air and soil gas,
47:24 otherwise these default make ups that we use are good enough for most sites, default compositions and
action levels associated with it. And the site-specific action levels,
47:35 you know, they're allowed, but they—they're going to fall within a pretty tight range, we already know
what the range would be for an individual site, unless someone wants to argue about the individual
47:45 original make up and toxicity of degradation compounds and such. So that was it, any questions,
47:54 comments, and ideas? If anyone who's new to this, totally understood everything I just went over then

URL: <https://youtu.be/MaX0UIX-w8I>

47:59 come talk to us, we'd love to hire you. It's kind of like looking at a car, the individual pieces and parts aren't that complicated. But when, you know, it's all put together, you just look

48:08 under the hood, it can look kind of complicated. But when you dig into it, it's not that difficult.

48:13 And this—the whole issue with TPH, like this quote from Neil deGrasse Tyson is we never really knew what to ask for early on. Now, we're starting to understand it more, we have

48:22 really for the last 20, 30 years, getting better. And now we know what questions to ask. So we can start

48:29 looking at better ways to assess things. So with that, and I'll take any questions,

48:34 and you have my email. I'd love to chat about stuff like this, and how to improve our guidance, also.

48:44 **[Keri Kodama:]**
All right, thank you so much. That was a really excellent talk. I've learned a lot. So I'll open the floor to questions. So

48:52 the audience is free to either type your question into the chat and we'll read the question to Roger.

48:59 Or you can raise your hand and then I'll give you unmute permissions and you can ask your question.

49:05 So please go ahead.

49:10 Okay, so we have one already from Michael [Parke]. So, "Thank you for a thorough review. Are action levels

49:17 regarding toxicity based on individual compounds, or are they based on potential cumulative effects?"

49:22 **[Roger Brewer:]**
That's a good point. For the action levels, of course for BTEX and such, are based on individual compounds.

49:31 But what we often do for individual compounds is we set our target risk really low. As if

49:37 we assume there's three, or four, or five other compounds there that have the same health risk, they do address cumulative risk, individual compounds. For TPH, because it makes such—

49:48 up such an overwhelming mass of what's in the air, or the soil, or the water, then we don't address

49:54 cumulative risk for the other individual compounds, they're assessed separately. The TPH

49:59 action level is the same cumulative risk of all the compounds, hundreds included under TPH, and HOPs.

50:09 **[Keri Kodama:]**
Okay, another chat question from Cristin [Bruce]. "Can you share documents capturing the diesel impacts with high benzene in the overlying vapor?"

50:19 **[Roger Brewer:]**
Yeah, and that's in a paper we published in 2014, the reports 2012. So see—if you send an email then I'll send you the paper and the report.

50:27 Otherwise, they're posted to our EAL, Environmental Action Level web page, some links there.

50:35 I was surprised at all the benzene in water and of course in the vapors. And of course the first thing the geologists field people do is blame the laboratory, that they screwed up

50:45 the analysis. We actually sent three separate samples of vapors from bit—from diesel fuel

50:52 to laboratories and they all came back with similar levels of benzene.

51:02 **[Keri Kodama:]**
Okay, chat question from Aurora [Kagawa-Viviani]. "Given aliphatics want to be in vapor, and many

URL: <https://youtu.be/MaX0UIX-w8I>

51:09 households smelling and experiencing headaches— did DOH do any vapor testing? Any idea of the TPH
51:16 components that could have been producing those effects?"

[Roger Brewer:]

Well, if you look at our—the memo we published in February, in—I think in there we estimated
51:28 the carbon range makeup of the—of what would have gone into the air from the dissolved phase mixture.

51:33 So we know it would have been mostly, mostly the C8 and higher aliphatics from the—from kerosene.

51:43 So we have a pretty good idea of that. The original form fuel formulation we got from the Navy
suggested there were pretty high levels of xylenes, maybe toluene in the water. But

51:52 it turned out, you know, testing the fuel itself is preliminary data, we don't really see that much in there,
it'd be mostly these mid-range aliphatic compounds. You know, one thing about the vapors too,

52:01 I'll point out in the fresh samples we test over gasoline diesel, we find a lot of BTEX, which

52:08 is surprising even for diesel. But when we go to the field, and we collect soil vapor samples in the field,

52:14 we find very little BTEX, even at gasoline station sites. And that's a surprise because that's what you
think would be driving risk for vapors at gasoline station sites. But you just

52:24 don't see much, it's mostly these lighter range aliphatic compounds. So the theory is, is that the

52:30 aliphatic compounds, they go into vapors along with the aromatics, they go into the vapors when

52:36 the gasoline percolates down into the soil, but they quickly dissolve into water in the soil and the

52:41 soil moisture get kind of extracted from the vapors, and you're just left with a lot of aliphatics.

52:50 **[Keri Kodama:]**

Okay, another chat question from Cristin [Bruce]. "Why do you include organic acids in the total
petroleum hydrocarbon analysis?"

52:59 **[Roger Brewer:]**

See me, skip back to that.

53:06 Here it is. So this, if you look at our 2018 document up here, this is our risk-based or our case

53:13 studies of TPH risk we published. Says a attachment 5 to that document talks about the chemistry

53:21 of degraded petroleum and there's a geochemist I've known for quite a while, Dawn

53:27 Zemo. She published a paper in 2016. There a few others on the basic chemical makeup of degraded

53:36 petroleum—dissolved phase petroleum associated with middle distillates. And she broke it into these
four groups here. They actually assigned toxicity factors for each one of these groups,

53:46 which we discussed in the paper we published, and calculated a weighted toxicity, including the acids,

53:54 and is based on what they published in their paper. The initial degradation products,

54:00 as we hypothesized before, have a very similar toxicity to the original compounds that were dissolved in
the water.

54:13 **[Keri Kodama:]**

Okay, we still have some time for questions. Is there anyone else?

54:23 Barbara Bekins' put a comment in the chat, "One possible reason for seeing benzene and lighter

54:29 aliphatics over diesel may be biodegradation." And there's a link to a paper for people to reference.

URL: <https://youtu.be/MaX0UIX-w8I>

54:37 ["Forensic Fingerprinting of Oil-Spill Hydrocarbons in a Methanogenic Environment-Mandan, ND and Bemidji, MN," Environmental Forensics 8:1, 139–153]

[Roger Brewer:]

Okay, we don't really see a benzene at degraded sites, we only saw benzene

54:44 for diesel fuel with the fresh samples we were getting from the local gas station.

54:54 [Keri Kodama:]

Rob Scofield says, "Did you say you assume benzene is present in degraded middle

55:01 distillates for purposes of assigning the toxicity factor to middle distillate TPH?"

55:07 [Roger Brewer:]

Let's see. Did we? If it was in this, skip back to here.

55:13 If it was in the original fuel formulation, we use California LUFT Manual for 2015. They had a carbon

55:21 range breakdown of—for diesel fuel and gasoline. And for the diesel fuel, they had some BTEX.

55:28 No, actually—I think they did, yeah, and they're in their water. So we would have used that in our way to toxicity. Here, if you see under diesel fuel—diesel here, in this slide for soil, this—the

55:41 last pie in that column, soil under diesel, it's mostly TPH but for that thin blue sliver

55:46 is that the BTEX component in ethylene. That was in the California LUFT Manual's, the default for the make up of these fuels.

56:01 But actually, in the groundwater itself. Yeah, it's in our default toxicity factor for the

56:09 groundwater itself. We did include BTEX when you run the calculations for effective solubility as part of the—we're calculating weighed toxicity for degraded mixtures, or total TPH and BTEX.

56:22 I forget the exact percentage.

56:29 [Keri Kodama:]

Okay, I had a question from Tao Yan, "Are there literatures that verified the assumption that HOPs have the same toxicity

56:36 profiles as original petroleum compounds? Could they be more toxic, if the generation processes

56:42 generate metabolites as aldehydes or ketones?"

[Roger Brewer:]

Yeah, that's the—that's the big debate. The

56:49 discussion and you know, originally TPH was just ignored. And a lot of states still ignore TPH. The,

56:57 you know, these other this mixture of degraded non- BTEX compounds and groundwater. Some states, they

57:05 specifically just ignore it. So we wouldn't, we wouldn't think it is. What was the question again?

57:13 [Keri Kodama:]

So are there literatures that verified the assumption that HOPs have the same toxicity profiles as original petroleum compounds?

57:21 [Roger Brewer:]

Yes. So that one—yeah, some of the literature is gonna say it's not toxic at all. And of course, that's not true,

57:27 because water is toxic itself. So that, that right now, the literature out there,

URL: <https://youtu.be/MaX0UIX-w8I>

57:32 this Zemo et al. paper from 2016, is one of the more useful papers, I think, it's been published.

57:39 And they look at four stages of degradation. And as it gets more and more degraded, by their take,

57:46 it becomes less and less toxic, you know, only by a factor of four, even the heavily degraded stuff,

57:51 they would still say it's still toxic. So could it be more toxic? Well, that's, I know, some,

57:57 some risk assessors have argued that, but for the mixture as a whole, which is what we're interested in, we know some individual compounds might be more toxic. But what we really want to

58:06 know is for the mixture as a whole, what's the toxicity, and I haven't seen any detailed studies

58:12 that go in depth more than Dawn Zemo's paper. And even in her paper, she didn't calculate

58:18 weighted toxicity, we had to do that in the— our 2018 document that I have noted here.

58:25 So if you happen to know of any, definitely, we should chat about it, track those down.

58:35 **[Keri Kodama:]**

There's a question from Kyle Kajihiro, but first, Cristin Bruce put a quote from Dawn Zemo, so just connecting that, "Our work

58:44 demonstrates that the metabolites identified in groundwater at biodegrading fuel release sites

58:49 are in classes ranked as low toxicity to humans and are not expected to pose significant risk

58:55 to human health." That was from September 2016, Integrated Environmental Assessment [and Management 13(4), EOI:10.1002/leam.1848].

59:01 **[Roger Brewer:]**

Right. Yep. That's the case—you know, a lot of the cases when you have contaminated groundwater degraded, for one thing, it's not—it's going to degrade faster

59:08 than it migrates away from the source area, you know, Red Hill was obviously an exception to it. So there, they are fairly—they're low toxicity, nobody would argue with that these, TPH components.

59:19 But, so it all comes down to what the dose is. So it may be low toxicity, but low toxicity

59:26 doesn't necessarily mean low risk, it's something you have to think about on individual sites.

59:32 So definitely the action levels related are going to be much higher than they would be for individual compounds like benzene or when you're looking at chlorinated solvents.

59:45 **[Keri Kodama:]**

Okay, so Kyle's question was, "Where can we find the list of fuels used in Red Hill and the description of their components and their degradation products?"

59:54 **[Roger Brewer:]**

Yeah, for there— So right now, the data we have—information we have is right, they're mostly storing JP-5 at

1:00:00 Red Hill, jet fuel. And, I think there are maybe a few other fuel types they stored there in the past.

1:00:07 So we know the basic make up of JP-5 jet fuel, you can find that on the internet. But the—

1:00:13 what we need to do to assess risk, and I thought this might come up. But sorry, down here—

1:00:25 is we need more detailed data than what you find generally published. So here's—is my wish list,

1:00:32 say for Red Hill. If you're—if you want—if you're assessing the risk posed by the fuel itself,

1:00:40 say you're drinking the fuel itself, or contaminated soil, which we assume most of petroleum is,

URL: <https://youtu.be/MaX0UIX-w8I>

1:00:46 is going to be the pure fuel, then you need a lot of data, you need your standard BTEX. You know, what's the composition in terms of your BTEX, naphthalene, you could add in some

1:00:55 other components as needed, especially—especially the carbon range information. Each one of these carbon ranges I have listed here has a different solubility, especially in maybe volatility.

1:01:05 So to understand the fate and transport of fuel, when it's released, you need a pretty extensive breakdown of the aliphatic and aromatic carbon ranges. It's only one laboratory,

1:01:16 Newfields, that I know of that can give us this kind of breakdown. And we're actually

1:01:22 sending samples to that laboratory to test and get this—get a breakdown of this detail

1:01:29 for JP-5 jet fuel from Red Hill. Once we do that we can calculate and get a much better idea

1:01:34 of what the dissolved phase TPH look like at Red Hill in the groundwater. And then, based on that,

1:01:42 we can estimate a much more accurate weighted toxicity. It's not going to be that different, it'll just be a little bit more accurate. If we're just concerned about toxicity of water—

1:01:51 of contaminated water and vapors, we're mostly interested in just toxicities. We don't need as detailed a breakdown of aliphatic-aromatic compounds. We just go back to these there's really just

1:02:00 four different groupings of aliphatics and aromatics with different toxicity factors, we can get away

1:02:05 with just those for the water. For vapors, all we need from a laboratory of testing is two different—

1:02:14 breakdown of these two different ranges of aliphatic compounds and just one of the aromatics because there's just three that are volatile. So that's what we'd like, the

1:02:23 data we want to get for Red Hill. We have it partial, we have enough data to look at,

1:02:31 you know, the water in terms of toxicity, except we don't know—we don't have a good breakdown of the aromatics to look at what the concentration might have been dissolved in the water at Red Hill.

1:02:46 **[Keri Kodama:]**
I have another question from Aurora [Kagawa-Viviani]. "What do we know about fuel additives beyond what is captured by TPH

1:02:52 that might have strong biological effects with respect to Red Hill?"

1:02:57 **[Roger Brewer:]**
Yeah, if you mean in terms of biological effects in terms of ecotoxicity, or humans, or—

1:03:05 **[Aurora Kagawa-Viviani:]**
Human health?

[Roger Brewer:]
Okay. Yeah, that's a good question. That's something we looked into early on, is trying to get more detailed information

1:03:13 on the additives that were in the fuel. And all we had was just published information

1:03:19 at the time of, of other additives that could be in the fuel and the main—one of the main issues that came up was antifreeze, it's this fuel system ice inhibitor that could be in—that are actually

1:03:31 in the fuel here in Red Hill. And that stuff is fairly soluble. So that's one other thing that

1:03:38 would likely have dissolved into the water and been a part of the mixture in the groundwater.

[Aurora Kagawa-Viviani:]
Can I ask a follow up then?

URL: <https://youtu.be/MaX0UIX-w8I>

- 1:03:48 **[Roger Brewer:]**
Yeah.
- [Aurora Kagawa-Viviani:]**
Okay, so what—was that analyzed for at all? I'm assuming that was the glycols?
- [Roger Brewer:]**
Yeah.
- 1:03:54 **[Aurora Kagawa-Viviani:]**
Glycol ethers?
- [Roger Brewer:]** Yeah. It was, you know, I think they did find low levels of it in the Red Hill Shaft. But I haven't seen the data for it.
- 1:04:06 **[Aurora Kagawa-Viviani:]**
Thank you.
- 1:04:16 **[Keri Kodama:]**
Okay, do we have any other questions?
- [Aurora Kagawa-Viviani:]**
Okay, I have one more then while we're at it. I can, I can turn on my video. Thanks so much.
- 1:04:30 I guess one of the things I've learned is that there was likely mobilization of I—sort of earlier
1:04:38 contamination with the slug sort of dropped into Red Hill Shaft. What do we know about what's—
1:04:48 about, about those I mean. I guess it would be classed under the additives and the other stuff,
1:04:57 you know, because previous whatever was sitting in there before from earlier releases.
- [Roger Brewer:]**
Oh, from early
1:05:03 releases, but you're presuming was JP-5 from earlier releases or some kind of jet fuel or kerosene. So
anything, as it goes down
1:05:12 percolates through the vadose zone then you're going to lose the more volatile stuff so your
1:05:18 lighter range aliphatics are going to be coming out of the fuel. And when it gets to groundwater,
1:05:24 the aromatics are going to go into the groundwater, the lighter range aromatics. So we know that would
have been mostly C8 and higher aromatics. Because, based on the new preliminary data
1:05:34 we have, there's not much xylenes and other stuff in the jet fuel there. So we have a pretty good handle
on what would have dissolved into the water and what would have gone into the air. And what would
have
1:05:43 been left in the fuel would just been degraded. First, it would, you know, the volatile stuff would have
come out,
1:05:48 and it would have degraded in place some. So you would have some of the degradation products
1:05:54 potentially leaching out of the fuel, hung up in the rocks, getting down into the groundwater.
- 1:06:01 **[Aurora Kagawa-Viviani:]**
Sorry, one more, and I'll let somebody else go, but has DOH, I guess, assessed not only
1:06:07 just the fuel that released, but what was in the shaft, and then post chlorination?

URL: <https://youtu.be/MaX0UIX-w8I>

1:06:14 You know, would there be any interactions with the chlorination steps or treatment steps along the distribution lines that could help explain what was being experienced by households?

1:06:25 **[Roger Brewer:]**
Yeah, I know that some groups were looking at that. I think Diana Felton was more involved in me than looking at that in the system.

1:06:34 I wasn't—I didn't look at that in detail yet. That's a good question. Really, in the

1:06:40 end? One question is what was coming out of the taps. So based on the formulation of the jet fuel

1:06:46 itself, JP-5, then we can make a pretty good guess of what was dissolved in the water. If there's any free product, we know that also in terms of just the hydrocarbons,

1:06:56 but then what was the other stuff? You know, there could have been some of the fuel systemized

1:07:02 inhibitors compounds in there and then other products produced as it went through chlorination.

1:07:13 I know people looking at into that a good research project.

1:07:19 **[Keri Kodama:]**
Okay, I had a question from Ernest Lau. "Are you researching and identifying the range

1:07:26 of fuels that have been stored in the Red Hill facility over its 79 years?"

1:07:31 **[Roger Brewer :]**
Yeah, I know our office is looking at that, in the—probably underground tanks group. I haven't looked at it myself in particular.

1:07:40 We know in general what they were—I mean, they're petroleum fuels probably mostly jet fuel, kerosenes, and such.

1:08:00 **[Keri Kodama:]**
From Catherine Rong, "There are some concerns over the use of Simple Green and cleaning, which

1:08:06 affects the solubility of hydrocarbons in the water. Would this affect the action level?"

1:08:13 **[Roger Brewer:]**
That's a good question, something we—and as people in our office looked into initially, because we think

1:08:18 Simple Green may have been used up—used in cleaning up the shafts, so it spilled. So it would have,

1:08:24 it would have enhanced the—maybe it might have enhanced the solubility, but it would have broken

1:08:32 up the fuel and carried it down into groundwater much faster. But, you know, the effects of Simple Green with

1:08:41 that, it's another useful, interesting study. We look into—in the toxicity of Simple Green itself.

1:08:50 You see a lot of emulsive—there's a lot of emulsification of the fuel in the water in the shaft. And that was one thought some people had

1:08:58 was that was because of the simple green emulsifying the fuel. It basically would mobilize it and get it down to groundwater faster, and carry it maybe through the system.

1:09:15 **[Tom Giambelluca:]**
Referring back to Ernie Lau's question and earlier question by Kyle Kajihiro about what fuels were

1:09:24 stored at the site. In the tour in December, as—if I recall correctly, there was—there's currently in

1:09:34 addition to JP-5, there's also diesel stored up at the facility. And I do recall two main fuel lines

1:09:42 going down the lower tunnel. One was for JP-5 and one—I believe the other one was for diesel.

URL: <https://youtu.be/MaX0UIX-w8I>

1:09:51 **[Roger Brewer:]**
Yeah, and I think that if you think about that in terms of the carbon range make ups, diesel has—it's
1:09:58 a wider spread. But ultimately that—the toxicity of dissolved phase JP-5 and diesel will be fairly
1:10:06 similar. You're still looking at the C8 and higher aromatic compounds, in general, just the
1:10:12 concentration might be higher for—I would guess it would be a little higher for kerosene than it would
for
1:10:18 diesel, that you would see in the water. And something we haven't looked at in detail. And so
1:10:24 what I want to do, and we're talking to the lab, is to get more detailed carbon range breakdown of these
fuels. Since we were unsuccessful in physical laboratory experiments to get a better idea of
1:10:35 what the chemistry would be in the dissolved phase hydrocarbons in this kerosene versus diesel.
1:10:43 Ultimately, I think it'll come down to the concentration more than the toxicity.
1:10:54 It'd be similar.
1:11:03 You know, somebody asked about Simple Green. I actually contacted the Simple—the company that
makes Simple Green.
1:11:09 They're real friendly. They actually have detailed chromatograms for some of their Simple Green
products.
1:11:16 And with marker compounds, if you're looking because they use it for testing—for cleaning food
equipment. So people go in to test the equipment or test the food, they actually have
1:11:25 chromatograms for key markers in Simple Green to look for when you're testing food to see if any
Simple Green got in the fuel. So if anybody's interested in that information, then send an email.
1:11:43 **[Keri Kodama:]**
Catherine Rong says, "What method does Newfield use for determining the carbon ranges?"
1:11:52 **[Roger Brewer:]**
You know, I got—I have an idea, but I won't even attempt to try to explain it. So you can—I can
1:11:59 put you in touch with them. In general, but some—I don't have a strong background in lab chemistry,
1:12:05 especially the analytical methods themselves. But they—the person that they work with is another
1:12:12 laboratory in Massachusetts, Alpha Laboratory. And there's a guy there, Jim, sorry Jim, if you're listening
in, I always forget your last name, starts with a known, and it's Italian. But he actually
1:12:21 wrote some of the original laboratory methods from Massachusetts back the 1990s on how to test—how
to break down the TPH component into aliphatics versus aromatics and dissolve these
1:12:33 samples—your water samples. But the—with that breakdown, it only gives you a small breakdown
1:12:41 of aliphatics and aromatics. And to get deeper into it, to break it down any more—even more ranges,
1:12:46 were detailed idea of it than Newfield's group there, Eric Steidman, if the ultimate is to do that. They're
1:12:55 the only laboratory I know of in the US that can do it, get this carbon range breakdown,
1:13:00 which is why—another reason why we need TPH, your weighted screening levels—that are individual
1:13:06 carbon range screening levels. But if you're interested, I can put you in touch with them.
1:13:11 I'd love to try the experiments again. Like I showed before with the glass jars with fuel on top of water.

URL: <https://youtu.be/MaX0UIX-w8I>

1:13:17 But they're—that's the only laboratory I know of that I would spend another \$25 or \$50,000 of your tax dollars attempting to run these experiments on.

1:13:28 But the other labs and system chemists listening in, what they initially thought they had separated

1:13:34 the aliphatics and aromatics in the water samples, but when we looked at the gas chromatograms that were supposed to be just aliphatics, then you could see spikes of aromatics all through it.

1:13:45 So they weren't able to successfully separate aliphatics and aromatic compounds in their analysis.

1:13:57 **[Keri Kodama:]**

Patrick Casey asks, "Are there records of AVGAS historically stored in the Red Hill tanks?"

1:14:06 **[Roger Brewer:]**

I've heard of AVGAS being stored there, which is aviation gasoline. I forget the exact details. It's a—it's basically as I understand it, a

1:14:15 mixture of gasoline and kerosene. So I definitely heard of it. So what would happen if AVGAS hit

1:14:22 the groundwater, what would dissolve into the groundwater, you'd expect to see it? It would look something like a mix of jet—kerosene, and gasoline. So you'd see more, maybe C5, C8 aliphatics

1:14:33 dissolved into the water initially and also, I assume, there's BTEX in it. You'd see that dissolved

1:14:40 in the water along with the aromatics. Maybe if there were any heavier aromatics, you'd see some of that in there. So the toxicity would be somewhere between—

1:14:50 weighted toxicity of that mixture would be somewhere between gasoline and kerosene.

1:15:05 **[Keri Kodama:]**

Aurora, since you're a host, do you want to just ask your question?

[Aurora Kagawa-Viviani:]

Okay. Sorry, thanks. I have,

1:15:14 I guess I was interested in your professional opinion on what you see as a priority for

1:15:19 monitoring as the defueling gets carried out at Red Hill, because I understand

1:15:26 the risk for releases is highest during fuel movement. And, I guess priorities? I mean,

1:15:33 you know, what do we need to be measuring? Where do they need to be? Where does—do the measurements need to be made? And how frequently in order to not have—to have a much more, I guess,

1:15:47 rapid response? Or, to prevent what recently happened? And then as a follow up, you know,

1:15:54 how do we more—most effectively monitor? You know, the plume from what's already happening? So it's

1:16:03 sort of two questions there. What, what do we need to be monitoring, where, and how frequently?

1:16:09 **[Roger Brewer:]**

And I think, you know, what do we need to be monitoring. As far as where is they're installing a lot more monitoring wells around Red Hill, that's

1:16:18 been one of the issues that passed. And with the Navy, also, is them just getting money to install these

1:16:24 monitoring wells, they're not cheap. Environmental programs tend to be poorly funded to begin with,

1:16:29 but now they have plenty of money to put in more monitoring wells around Red Hill. So we're gonna learn quite a bit for that. So you can put in the monitoring wells and

URL: <https://youtu.be/MaX0UIX-w8I>

- 1:16:38 they're, you know, they're vapor probes underneath the tanks themselves/ And that's the way you initially catch a release, is from the vapors. And you know, they're already
- 1:16:48 doing this, you don't just test for BTEX, obviously, especially with jet fuel. You test for TPH and everything. But you know, what, what to monitor in addition to what they're not doing now?
- 1:17:01 I'm not, I'm not really sure. The main thing was to put in more wells. You just want to monitor the pipes themselves, the system itself
- 1:17:08 as you're defueling, just to avoid any releases. So you don't—you're not monitoring after the fact.
- 1:17:19 And then, what else do we— should we be monitoring for?
- 1:17:25 In the water? Not sure, we need more information on the additives. What's in the fuel, that's one thing that's been missing. And what happens to these additives,
- 1:17:34 to the ice inhibitors once they get in the groundwater.
- [Aurora Kagawa-Viviani:]**
Okay. Thanks. I guess I suppose,
- 1:17:44 would the monitoring wells that are being installed wouldn't have prevented detection
- 1:17:50 before, given this release, sort of went straight from the lines into the shaft?
- 1:17:56 So is there better monitoring, I guess, in place within the facility itself? That you're aware of?
- 1:18:02 **[Roger Brewer:]**
Yeah, that I'm not—I'm not sure of. I'm, I'm sure they're gonna be watching it extremely closely as they defuel these tanks. And how are they going
- 1:18:11 to defuel them? As you know, maybe it's like a gas station, you don't necessarily pump all the fuel out into another tank, maybe they just use it up. I'm not sure what their plan is and how
- 1:18:19 much the fuel they use. Maybe as far defueling is, they're just not going to refuel the tanks. If
- 1:18:24 they use the fuel in it, instead of trying to ship it somewhere else. I don't know the details of that.
- 1:18:30 **[Aurora Kagawa-Viviani:]**
Thank you.
- [Keri Kodama:]**
Have a question from Michael Fry. "Do commercial under the sink water filters remove TPH and BTEX?"
- 1:18:46 **[Roger Brewer:]**
Yeah, they should. If it's carbon, if it's activated carbon filter, it should remove the TPH and BTEX and it should pull out the
- 1:18:58 degraded compounds. Also, they can be polar. But again, I don't know as much about that.
- 1:19:03 I can definitely look into it to see what type of filters are most useful.
- 1:19:14 That's what in the laboratory they remove the degraded compounds by running the water through silica gel, that absorbs all the polar degradation compounds.
- 1:19:25 Which is why we don't want them to use that when they're testing water samples because we'll miss all the degraded compounds.
- 1:19:35 Now, I know people, again—I know a lot—have lots of contacts. So I have some contacts with some people who market and manufacture water filters. I can put people in touch with, if

URL: <https://youtu.be/MaX0UIX-w8I>

1:19:44 they're interested. Thanks also everyone.

1:19:49 **[Tom Giambelluca:]**

Roger, thank you very much for that really important and interesting presentation. Gets us all thinking a little more and understanding

1:19:59 the framework for understanding possible human health impacts of this contamination. So really

1:20:05 big thanks to you—and the work you're doing, for this presentation and for the work you're doing.

1:20:11 Transcribed by <https://otter.ai>