Trihydro's State of Knowledge and Advances in 1,4-Dioxane Groundwater Remediation
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12 noon– 1PM Mountain Time

This transcript was auto-generated by the webinar. Please forgive typos.

0:03
Good afternoon! My name is Amy, and I'd like to welcome you to Trihydro's 1,4-Dioxane webinar.

0:10
Today's session is titled, State of Knowledge and Advances and 1,4-Dioxane, Groundwater Remediation. We're excited to get started, but first I'd like to share a few housekeeping items.

0:23
All attendees are in listen only mode. If you have questions at any point, please use the question box in your goto Webinar Attendee panel. We've dedicated a portion of today's session for Q&A and we look forward to addressing questions after our speakers present.

0:40
If we don't get to your questions, and our time together, will answer them directly via e-mail after the webinar.

0:47
Additionally, you'll have the opportunity to complete a short survey, when you exit the webinar. It should take just a minute, and your processes are very important to us, and help us create valuable webinar experiences for you in the future. Finally, please be aware that due to the number of people viewing this webinar across the country, we may experience right, bandwidth issues, and thank you for your understanding, during this time of increased online activity. And remote work with that, let's move on. We have three speakers today and I will introduce each as we go. Our first speaker is Fritz Krembs, Senior Engineer and Geologist from Trihydro Corporation.

1:29
Fritz has 17 years of experience and environmental consulting. He is Trihydro's subject matter expert, on 1,4-Dioxane, as the team lead and in situ remediation, an ITRC.

1:44
1-4 dioxane team has expertise include conceptual model development and evaluation, Remediation, technology, selection, design and implementation remediation hydraulics, and we're in meeting the remedy optimization. Right.

2:04
I'll turn it over to you.

2:07
Well, thanks so much, Amy. I'm just going to present a few introductory remarks here to, to get us started. On the history, physical properties of the 1,4-Dioxane, and, and this compounds current relevant, is, just going to get to those things up, for our external speakers. She was going to speak to ... and bio degradation. And yes, we'll speak to advanced oxidation processes. So in the interest of time, we will, we'll jump right in here. This first slide is from the, the Ongoing I

TRC Teams won four Dioxane Factsheets. Those released this past February. So this, this graphic is taken from there. On this slide, I'm going to start with the bottom. one for vaccine is still used, is still present in personal care products, other types of products that involves surfactants.

3:07

Also used in some manufacturing processes. So, so, all of That's true. That being said, manufacturers are working to cut down on the amount of work for vaccine in their in their products. Most importantly though 90% of the historical production in this country went to produce a 104 dioxane as a stabilizer for 1 1 1 TCGA that solve. It was introduced in theaters around the seventies, TCU is getting phased out due to health concerns. 111 warranties. A phased in this graphic here shows the production over time. So, key point here is the vast majority of use of more than four dioxane was to stabilize stabilized solvents.

4:00

one point I would quickly want to make about 111 TCGA. That compound is relatively unstable in the subsurface so it will undergo and a biotic hydrolysis reaction in 411 D C. That process happens over the course of years to maybe a decade. So seventies era releases there may well not be any 111 TCGA left but there could be 111 D C. So not having TCH, your site does not necessarily mean that, it was never used, 111, ... might be a better indicator.

4:43

So, now, speak to the chemical properties of 1,4-Dioxane, a little bit figure, Many of you have heard this, but just want to touch on these quickly 1. 4, dioxane is very hydrophilic is essentially can be mixed with water in any ratio, IE it is miscible. So the relevance of that particular property are that it's easily leached into the groundwater from firm surface. Releases additionally, it has a low organic carbon partition coefficient, so it is not a ....

5:19

Typically thought of not being absorbed to soil particles will hear some more on this in a little bit. So, it has generally lower retardation. coefficient, typically can travel at the same rate as as flowing groundwater. Whereas other solvents may move more slowly, has a relatively lower Henry's constant. So therefore, it is difficult to strip this compound into the gas phase. That's good because vapor. Intrusion issues are relatively less of a concern with 1,4-Dioxane, but it does challenge airstrip in, in situ processes or ... is a groundwater remediation technology. Those typically do not work so well for the word for word for the same. Additionally, as one for dioxane is a zero waste stream is being treated with an airstrip.

6:12

Or that airstrip or may pull out the other VOC, is 1,4-Dioxane to pass through because it it's just so soluble and has a relatively low hemorrhage.

6:24

Lastly, one more dioxane is classified as a likely human carcinogen. The toxicology still evolving and there's also some other potential acute effects. Actually point on this slide is the current EPA regional screening level or RSL zero point four six, which equates to a one cancer risk so less than a part per billion. That is in the range of endpoints that may be looked at for these remediation technologies. So, another order of magnitude lower than GCE or benzene is as well.

7:06

Spoke to the chemical properties, and those can line up to cause 1,4-Dioxane to be quite persistent in the environment. Because it's soluble, not typically thought disorder so much. I can move with groundwater can potentially for mom for March Blooms.

7:26

Additionally, 1,4-Dioxane has been thought to be recalcitrant to biodegradation. Spoiler alert we have an internal expert joining us in just a few minutes who's going to share a lot of her and her collaborators research showing that that's not the case. That view is a bit outdated at this point, but depending on what guidance documents you're looking at, you may hear about recalcitrance to bio degradation, so, so that can owners or situations be true life. Surely speak to that, but 1,4-Dioxane can, potentially, form for large, losing in groundwater.

8:09

Last few, a few minutes that I have here are going to speak to a few different points related to the relevance of one for X in. This graphic is Grandma one of Dave Adamson's papers. She was a contributor, this is as well, and they looked at the EPA's ... three-d. data set. I made this really nice map showing the red circles, where 1,4-Dioxane was detected. In public water supplies. They were used by consumers at concentrations above the, what they call the restrooms concentration.

8:44

That is a toxicological irrelevant value. It was, I believe, point 3 5 in this study. So, sub parts per billion. So, in this very large dataset, 7% of the public water supplies that were sampled had 1,4-Dioxane above this, this risk based threshold. So this is definitely something that is individuals are encountering different locations across the United States. What? Interesting side note ... were in that study, Those were detected far, less often than one for assay, So the ..., They're getting all the Press Water four Dioxane, and in this study President, in 10 times more public water supplies.

9:31

Another incidents of relevance is even though the US EPA has not promulgated a nationwide MCL, that has not stopped many states from for having enforceable standards on the books In their regulations. This map is from the TRC Factsheets. It's also going to be included in the In the forthcoming tab Greg. I won't get into what all the different colors mean, but the vast majority of states have some sort of limited to one for X same in groundwater, many of which are enforceable. So there are many incidences where, because of state standards, one for vaccine has emerged.

10:14

Lastly, we'll speak to one of several studies. Again, This is by Dave Adamson and Shelley, other collaborators. In this particular dataset, they looked at the California Geo Track or database, so very large. Publicly available database. GSI's really done some very, very neat work in this area of Environmental Data Mining. But, anyway, what this study came up with was looked at all the universe of say it's about 2500 or so different impacted sites that have VOC analytical data. Well, over 2000 of those didn't analyze for 1,4-Dioxane. So 80% don't know if it's there or not. 500 or so did or closer to 600 of those sites with 100 for vaccine detections.

11:05

It was commonly associated with 111 TCGA, or 1 1 DC I'm sorry, 111 warranties. Yeah. So that relates to the use as a stabilizer and that solving another interesting finding was that there were a number of sites where TCE was detected.

11:26
Mount those other two CA or their degradation products, along with 1, 4 dioxane many different theories about why this would be, you know, some have speculated the dioxane may have been a stabilizer for TCE. That's not really been proven. Yeah. But as a possibility, another possibility is that sites that use GCE may have also used 111 TCAS, so multiple solvents used at the same industrial size. Regardless of the reason there is this association in this in this large dataset between TCE and more than four dioxane without.

12:08
Without the detection of those, those other compounds. So with that, have discuss the prevalence, the chemical properties of more than four Dioxane, and we'll, we'll pass things on to the next speaker to speak disruption and bio.

12:25
Thank you, Fritz mentioned we're holding questions until the end until if anything covered parked a question, please submit that in the attendee panel at any time. Now, I will introduce doctor Shaily Mahendra and she will share insights with us regarding 14 dioxane, bio degradation, and ... biodegradation treatment train.

12:48
Doctor Shaily Mahendra is a professor in the UCLA Department of Civil and Environmental Engineering. She received her PHD from the University of California Berkeley.

12:59
Her research expertise is grim biogeochemical processes and natural and engineered system degradation of one poor dioxane path and many other emerging contaminants, applications of molecular and isotopic tool, energy, positive wastewater treatment, and enzyme bulk, or water treatment and bio remediation.

13:25
Haley has received several prestigious awards for her research and teaching, research and teaching, and she serves as an editor of the Journal of Hazardous Material and J H M letters failing. We look forward to learning more.

13:44
Thank you, Amy. And I want to express my thanks to Trihydro organizers for inviting me to share some of my research kind of myth busting here about dioxin Fate and transport and implications for remediation. So, let me start out by saying, thank you. Was a really good setup and identifying the conventional knowledge, the conventional understanding that dioxane is so hydrophilic and has a very stable molecular structure. So it's hard to degrade, but you know, all is not lost yet. This, this can still happen, and I'm sharing some of my new data. Up until a decade ago. Yes. It was largely considered not solvable and non biodegradable.

14:31
So here it is. It can be solved and the benefits, the implications, but environmental engineering and science professionals are that it can remove contaminants of concern co. Contaminants like chlorinated solvent and other organics that are found together with dioxane.

14:47
So, option definitely has that advantage. There are no bonds formed of bonds broken, so there is no reaction products or talks potential toxic reaction product.

14:58
And many absorbance, such as clays, and Biochar and granular activated carbon, can be relatively inexpensive, as compared to more energy demanding technologies, But on the flip side, there are limitations of soybeans. You know, it ultimately, it's a it's a game of musical chairs, there's only so many spots where a molecule can get attached. So, there's a limited capacity. When the molecule is attash in this case, dioxane, it can also be detached if the chemical equilibrium shifts towards more dissolved species rather than solid adsorbed species. And then once you do have dioxane and co contaminants, adsorbed on the media than it needs to be regenerated or, you know, disposed landfilled and other considerations. So, it's important to recognize that we are now seeing something that's considered infinitely soluble in water. There are commonly available things that can temporarily adsorbed, actually. And then, there's a place for that in the in the world of remediation.

16:06
So I'll be sharing some of my research. This was published two years ago in environmental pollution. So this is a Langmuir isotherm of granular activated carbon in that studies. We have conducted some columns studies. We shared in forthcoming publications, but also the teleconference next year. So, dioxin is really well about 35 or so, milligram per gram of GAC would be the, this option capacity. So, that does work.

16:35
In addition to get, there certain zeolites natural or synthetic zeolites that can absorb and four dioxane. The two examples here, GSM five, which is more commonly used in the hydrocarbon industry for cracking and separation purposes. Also titanium silica based zeolite T S one we've published on both of those are pretty effective at absorbing dioxane as well as co contaminants like chlorinated solvents. Relatively speaking T S one, and GSM five, their capacities are about 85 and 65 milligram per gram as compared to 35 milligram per gram per granular activated carbon.

17:19
It's they're probably 2 to 3 times higher capacity, and that could really help extend the operational lifetime before you need to swap out the Sorbent media in in-situ or exited treatment system.

17:34
So as I said, the once dioxane and co contaminants are served on the material, then you need to deal with it in ways that you can generate them. Their current, heat intensive, physical chemical technologies, like steam, regeneration, and other chemical regeneration. Sometimes biological regeneration of sorbent materials is also a practice, definitely for other contaminants. And I'll walk you through some data that would demonstrate that that can also be done four dioxane.

18:05
So, when you have sorbent media, and then you start growing biofilms on it, the media is obviously pretty amenable for sales to attach. It serves as a really good surface and retention. It can help slow the migration routes in the in the system such as permeable reactive barriers or other media. The chlorinated solvents are much more hydrophobic than die offs in itself. So, the

same media that we are employing for dioxins option but also be useful much better for chlorinated solvents. and when you're regenerating biologically the solvents, it can serve as a real time extending the capacity of this option.

18:48
And by degradation process, unlike plane also, option, actually can convert dioxane into something else. Ideally, less toxic, sometimes, and I'll share some results all the way to CO two. So, there is no dioxin left to be these. Or if the chemical equilibrium shifts in a way that assumption is less favored.

19:09
So, just like I said about a couple of decades ago, when I started my PHD, dioxin was really considered to be not biodegradable.

19:18
It's not as common as, say, petroleum hydrocarbons and other things. But, there are increasingly available studies, both lab based and field based studies that provide evidence. So, we are working towards getting that critical mass that yes, under certain conditions, with certain types of aerobic bacteria and fungi, Dioxin can be degraded and there are some mixed communities which have been partially characterize in industrials, sludge settings. environmental settings.

19:49
A biotic treatment and biological treatment drains have been reported that are enhanced by degradation field efforts, which involve by stimulation with substances like methane and propane, which induce core metabolism, and then there have been efforts of bio augmentation with the kind of organisms. On the bottom you see on the very left that pseudo no cardio dioxane, ... 11 90, something that I isolated and characterized and continued to work with. There's a fungus here. There's lots of microcosm studies. MMA is becoming increasingly acceptable.

20:27
A quick note: to distinguish the metabolic versus co metabolic processes, would be referred to metabolic it's more like growth supporting. So, the reaction that takes dioxin and converted to CO two. That provides energy and carbon for the growth of the cell itself, so that's desirable, the cell is happy. In nature, sometimes the same enzymes that what produced by these bacteria by these organisms to degrade something else for their benefit can also accidentally degrade contaminants such as 1,4-Dioxane, chlorinated, solvents, and others. So, the reaction definitely proceeds, but it doesn't really support the growth of the sale. And that's what we referred to as non growth supporting a cool metabolic, but it is very relevant in environmental engineering and other industrial applications.

21:20
What happens when dioxin is biodegrade it? So, this is a condensed pathway that's carried out by CB 190, and many other aerobic ... oxidase expressing bacteria. As you can see, some relevant enzymes in the early part of the reaction, that catalyze these reactions are one oxygen aces, and they break this cyclical ether bond structure, and once it unraveled, the rest of the reaction becomes pretty easy.

21:48
Good thing is there is no smoking, and there's no wild chloride of dioxin that's been identified yet. Under metabolic conditions, there is some accumulation of H E a beta hydroxy ...

22:00
acid under cool metabolism, which is in some studies, suggest slightly more toxic than dioxane itself. But, you know, compared to some of the other MDMA and MTV and other things still somewhat manageable in the overall scheme of things. Something not to be ruled out.

22:20
But, under metabolic conditions, you can achieve complete conversion to carbon dioxide.

22:25
Some dioxin can be mineralized and some critical intermediate gli oxalic acid, really common metabolic simple organic compound actually serves as the switch where a certain organisms that can use it will metabolize dioxane, the others probably called metabolized. I have seen and that has to do with energy generation, energy recovery.

22:51
So, what we did was, I showed you, dioxin can be storm to show it to dioxin can be bio, degraded. What if we combine these two?

22:58
So, I'm showing data in which I have time on X axis in days and concentration of dioxin, on the Y axis. On the left figure, it's wastewater. So, we have tens of milligram per liter and groundwater, single digit milligram per liter, that's kind of groundwater example, we had access to back then when we did these studies. So, when, via dioxin exposed to biogas, media, rapidly sorbet and then it sort of flattens out, as you can see in the open diamonds, on both plots, in the triangles, these biogas, or these ... systems had see below 90 biofilms growing on it and they continued to metabolize dioxins, so the lower concentrations were achieved, and the other benefit was that it was not reversible. Dioxane is converted to CO two, so there's nothing left to re contaminate finished waters.

23:53
So there is evidence that you can combine two processes that we thought didn't occur in nature at all. Not only they do individually, but together they are even better. So that's an advantage. And if you do subsequent washes, EBRD gag eventually, would dissolve Dioxane. So you can have a slug of dioxin released. If it's not replaced, and regenerated in time by augmented, get, can continue to produce really low concentrations and basically regenerate the carbon in situ or in real time but also converted to CO two. So there's less risk of reversibility absorption.

24:34
Like Fritts mentioned, dioxin is found in contaminated sites along with chlorinated solvents because of their history of use and disposal.

24:44
Some of the work that we published was not very encouraging, but it is important to note that many of these donated solvent, especially the degradation products of tri chlorinated. compounds, tend to be inhibitory four Dioxane by degrading bacteria. So you could have the best dioxane integrator out there. But sometimes, things like ..., one to D C E, can actually inhibit those microbes. So yes, all is not lost, but it is important to understand that, and take that into account in predicting rates and conceptual site models.

25:24

Again, Biofilms can come to our rescue. There have been other evidence, again, from my work, and other people's work, that if bacteria are growing attached, rather than Planktonic conditions, and biofilm attached growth is more relevant to subsurface contamination anyway. Then those biofilms, they produce these extra polysaccharides. They're able to trap some of those inhibitors, in this case, excellent Chrome, but it also applies to chlorinated solvents, and other organic inhibitors. And that allows 1, 4 dioxane biodegradation to proceed better than what you would normally expect, given those concentrations. So there's ways that inhibition can be mitigated by attached bacteria.

26:08
So in the next 5 or 6 slides, I'll show you a cascade of curves that look like this. So, let me just orient you on that. On X axis, we have time in days. On Y axis, I recognize this as higher concentrations, but just to, to get the proof of concept, just to get the message across, I'm sharing these sets of data, others are in our publications, and we'll also share that. At Battelle next year, one of my students has won the Battelle Student Paper Award. And so I don't want to steal his thunder. So those would be in the PPB levels, which are more relevant to many contaminated sites.

26:46
And there's a little more complexity to that. So I'll let him explain that, But this is, this is what I can show to convince you. So, you'll see two sets of curves blue, dark, blue, navy blue, and aqua blue, and then dark light, red, and maroon ish colors. So the red curves are a biotics options.

27:05
It's a darker color is when dioxin is the only contaminant in these lab based studies, and a lighter red is when dioxane as well as about 2500 PPB. TCE was also present.

27:20
on the blue curves. Again, dark Blue Navy blue by augmented with See below 190. The ... itself, and dioxins this all contaminant, and in the lighter one, it's TCE.

27:30
So, as you can see, in planktonic cultures in the slide that I showed you previously, TC present ..., one to ... presence, really was strongly inhibiting Dioxane bio degradation. In this case, the attachment, the option, kind of pretty much rules that out. It negates any inhibition. So that's a good thing.

27:51
Second thing to notice is that the capacity off of granular activated carbon is almost regenerated. The red curves over multiple cycles, they have depleting capacity for more ...

28:05
option, but biologically activated or augmented carbon can achieve a much larger, almost, you know, original amount of capacity for Us, option of dioxin. So we're reporting measurement of dabbling, same story here, ..., the curve looks very similar to that with TCE.

28:27
Blue plots are lower than red plaza by augment. It is better than a biotic. But also the presence of the contaminant ..., in this case, is not providing any inhibition due to this option and the bio degradation.

28:44

Things get a little tricky with one when DC and we knew that in planktonic. So pretty much it was a deal breaker. Everything shutdown bio degradation here, there is inhibition, but, but not as much. Again, Blue Curves, the by Augmented Curves, handle the degradation of Dioxane much better, even in the presence of one Monday CE, as compared to the same competition. That happens for this option site: four dioxane, as well as 1 1 ... even in the a biotic systems.

29:15

So, overall, biological is better, for regenerating the capacity, and also preventing inhibition.

29:23

Let me put them all together, I think it was really pivoted by whether 1 1 disease present or not the others were not that harmful. Anything you want to see this is 2500 PPB of TCE and 2500 PPB, ... and .... So, pretty large amount of inhibition, but by augmented conditions, did really well as compared to a biotic.

29:53

And all of them thrown together all these curves. It looks messy, but I'm just overlaying all of them.

30:00

Again, the take home messages, by augmented is better, with respect to preventing inhibition, and regenerating the capacity of the carpet.

30:11

So, how do we know what is really happening with biological? So, we need evidence. We need markers. We need monitoring tools, we need a smoking gun, that everything I just said that was, taking place biologically is indeed a biodegradation and not an artifact.

30:27

So, in some of my previous work done in collaboration with lethal risk going at UC Berkeley and others at Joint Genome Institute, we sequenced the whole genome of CB 190 strain using the sequences available for potential monarchs, the geneticists, and there are about 2000 of those. We picked some of the ones that we thought were relevant, selected those, and design the primers for QPCR. Went ahead and validated them in pure culture studies in microcosms, and directly in field experiments. And I'll show you some data about M&A, which would be of more interest. Other things are in our publications, and I think dry hydro has included many of the publications that are referenced here in our talks as part of the webinar handouts.

31:17

So, unlike what we know about biomarkers for chlorinated, solvents, reductively chlorination, it's, it's about the individual kind, the group of strains are really strong, small boutique type of screens, ..., the Hello, ..., yellow, vector, and the gang. If they are present, it's a really good chance that chlorinated solvents would be reductively detail oriented.

31:42

We tried to do that, We tried to focus on the identity of the organisms that are known to metabolize, or co metabolize 1,4-Dioxane, and we found that they were spread kind of uniformly all over the tree of life within the clade of bacteria.

32:01

Then, we'd rather said, Instead of focusing on the identity of the bacteria, let's just focus on the gene. The functional gene biomarkers and they tend to be a lot more concentrated.

32:13
The organisms, that cool metabolize dioxin after growth on things like methane and propane and toluene and phenol, they were still spread, again, in a much smaller area: part of this tree of life. But all the ones that have been reported to metabolize dioxane, are on the single branch, this purple one over here. So, we talk, it's a great way to go after just focus directly on the function rather than the name of the organism that may or may not be the one relevant at any given site, which is carrying out Dioxane biodegradation.

32:49
So, we used that. We did a bunch of lab studies and microcosms, like I talked about. But we were collaborating with Golder Associates on a different site where they had historical evidence that dioxane was going away. It was a mixed contaminant plume.

33:05
... were not detected, but there were other organic compounds. And then, dioxin concentrations ranged from 85 to 500. Depending on where this collected the samples from, they had other tools due to investigate The site, tried to understand what's happening. But we really suspected that there was money that was natural attenuation taking place.

33:29
And we used that opportunity to do see, asked the question, Can the biomarkers I just developed using them?

33:36
The genome data or CB 190, can they serve to provide evidence of natural attenuation?

33:44
And looks like, yes, natural attenuation was definitely happening. The source for this site is somewhere in the bottom right corner, the plume migrates in the north-west direction and there were these data and data. Available over six years and the bloom was definitely shrinking.

34:04
So, when we sampled directly collected groundwater and extracted total nucleic acid and PCR them using the biomarkers right away the presence of these relevant genes tracked with the receding films where we thought that was strong biological, natural biological activity. There was no treatment done.

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That's where some of these biomarkers actually lit up and pretty well, so anything that has a red circle is the Dioxane ... itself. So, that is induced by dioxin, but it's the enzyme that, that actually biodegrades dioxane, the first step.

34:42
L D H is another complimentary biomarker, which responds to the degradation product of dioxane, whichever the functional groups. So together, they work as a really good team, and provide pretty solid evidence of biological degradation. And those green circles, all over our, where both of them were detected significantly above our detection limits at that time.

35:05
And over the years, we have worked together with microbial insights and other collaborators to work on better sampling methods, and sample processing methods, and lowering the detection

limit by changing the chemistry of blood PCR reaction. So, we're able to do that much more accurately than earlier.

35:25
And, putting all those data together, not just, from this site, several other studies, where are the point where we can actually take this copy numbers, fold, change, of copy numbers of Dioxane, Monarchs nation, at the height dehydrogenase, coding genes, and plot them against the amount of dioxin integrated.

35:44
So this could be on its way semi quantitative, quantitative estimation of bio degradation rates that are found in natural attenuation, as well as some enhanced bio degradation efforts. So that would serve as a pretty solid, confirmatory and quantitative method to can confirm the bio degradation of dioxin in the environment.

36:10
So, I just wanted to summarize. And, you know, point out some key takeaways as, I hope, I've convinced you, dioxin can be sorbet and bio degraded independently and together.

36:20
And when you buy augment ..., it outperforms E by R to get you achieve lower concentrations of dioxin, in the in the .... And also the on real-time regeneration of the sorbent is also achieved.

36:38
In addition to get there are some zeolites that have even higher adsorption capacities even in the presence of COC's so then, they can also work really well, over multiple loading and bio regeneration cycles.

36:51
Innovation was mitigated because of its option itself, as well as the extra cellular polymeric substances secreted by the bacteria. As they were performing biofilms on the sarbanes and individuals' C V OC, especially TCE and ... had little effect on the removal, but mixtures with ..., slowed down the removal rate. But overall, so much better than what you would see in the absence of sarbanes. So that's definitely better.

37:24
Few more points about the biomarkers: Now, we do have a set of genes, DX, ambient, ELD edge. And I recommend using both rather than just one as biomarkers, but really conforming dioxin, biodegradation. We have successfully validated them in a large number of samples now, so we have a pretty good quality, you know, amount of confidence.

37:44
That expression B, to be perfectly honest can be influenced by environmental factors. So we just need to take that into account when interpreting those biomarker data.

37:57
When we analyze DNA from groundwater ..., we were able to identify some indigenous previously unidentified dioxane metabolizing micro-organisms. Even if you can't isolate them, even if you can't put a name on them, but we know they have the right functional genes, that can carry out natural attenuation. So, that's important for assessing a site prior to setting up a treatment system. Monitoring it as bio remediation is in progress, but also post remediation after

active treatment seizes into the monitoring phase. So, all of those times have opportunities for using these biomarkers, for assessing biodegradation.

38:46
A last point, and this is something I get asked all the time, Can you have biomarkers for co metabolism?

38:53
As I said earlier, core metabolism is a biological accident. so you really can't design for it. But statistically because cool metabolism of dioxin has been shown by propane, oxidizing and told me an oxidizing and methane oxidizing, athene oxidizing bacteria.

39:11
So, if those genes can be amplified and confirmed, it's a reasonable probability that dioxin and ... are being biodegrade. But at best, it's indirect. It cannot be direct just by the nature of the co metabolic process but it would still be valuable as one of the lines of evidence to support dioxane Biodegradation.

39:34
With that, I wanted to just stop and just recognize all my collaborators and sponsors who supported us throughout this research.

39:44
I'm going to hand it over to the next speaker, then .... As mentioned, we're holding questions until the end, so if anything Shaily covered all the questions, please submit that on the attendee panel.

40:00
Now, doctor Jens Blotevogel ..., will share insights with us regarding information such as a biotic technologies that degree 1,4-Dioxane when bio remediation is challenged. Yens holds a PHD in Environmental Chemistry from Colorado State University, and a Diploma in Environmental Engineering from the Technical University Berlin. The Ancestry Search revolves around the three of emerging contaminants and conducting laboratory and field scale experiments to elucidate their degradation and both natural and engineered system.

40:40
Develop sustainable water, treatment technologies, thorough, radical model for contaminant degradation, prediction, and very advanced analytical method, with a focus on high resolution, accurate math.

40:57
Cometary.

40:59
Currently working on solutions for managing P 5, 1,4-Dioxane, nitrile, aromatic compound, perchlorate, and oil and gas produced water. ..., take it away.

41:13
Thank you, Amy. Yeah, so, shady has basically just presented to rather low cost options, ..., biodegradation, and if these processes work, then they often the goto processes that that we use of contaminated sites. However, there are cases where maybe harsher treatment technologies are necessary, for instance, when receptors are threatened or when these processes are inhibited.

41:41

By co contaminants such as chlorinated solvents, then, you have another option and those are advance oxidation process needs and cost wise they are certainly higher than what we've just seen, but again sometimes simply necessary, ah.

41:59
So, the classic offense oxidation processes use technologies and chemistry that generate or a tragic Colts.

42:11
And classically this has been provided by the use of hydrogen peroxide H 2 O 2.

42:19
And two hydroxyl radicals to be generated because these are the species that really oxidize the one for dioxin and mineralize it. P H 2 O 2 needs to be activated or in other words it needs to be split holistically into O H radical or two O H radicals. And you have a couple of different options here. The first option is ferrous iron and this is the Classic Fenton's reagent. Now ferrous iron occurs.

42:49
Natural, naturally in a lot of sub surfaces so you can actually do this process in situ to the only thing to consider is that first hiring is really only soluble at low PH and low PH is often something you can do in situ. So in this case, if you want to do the reaction at circum Neutral PH for instance, you can do that, you would have to add a collation H into your solutions, such as citrate to keep the iron into another. Combination for H 2 O 2 processes is the use of UV light UV itself is not very efficient for direct 1, 4 dioxane photolysis. There is emerging evidence that vacuum UV may be very efficient and also energy efficient. But in general UV is used in combination with catalysts such as TI O two and Photo catalytic processes or it can be used to split the H 2 O 2 and provide the hydroxyl radicals that I need it for events.

43:53
Oxidation of 1,4-Dioxane Now, with all thy driven processes, you do have to make sure though, that your water is quite free from turbidity, and iron, for instance, and other species that may take away in the end. Absorb UV light and take away from the power that is being provided. And then finally, and this is a combination that has become especially popular with 1,4-Dioxane because it is, it works very well and has been shown to lie at the door of chemical consumption Is the combination of H 2 O 2 with ozone. Does a process that as well established has been implemented it at very large field scales to treat large groundwater volumes, contaminated what's with 1,4-Dioxane, and again, another process here that can provide ...

44:47
for the oxidation of 1,4-Dioxane: These are again, the more classic processes that are there are also, somewhat more modern pro sulfate based processes per sulfate is a somewhat newer oxidant in the world of Finance oxidation processes that can be applied in situ. So it's a chemical that can be injected into groundwater and distributed that passively with groundwater flow for instance.

45:17
But just like H 2 O 2, it needs to be activated first, and then you have several options here. It can be active, great advice, terrorists iron can be activated by even zero valent iron, if you have a barrier at your site, for instance, can be activated by UV by PH and also as a combination by H 2 O 2. The difference here is that personal page Also solidity splits into two sulfate radicals. And,

sulfate radicals are likewise very effective for 1,4-Dioxane oxidation, all the way to mineralization. And, then, depending on the PH, can also generate O H radicals. So, the PH somewhat governs here which radical this is effective, but both do the oxidation of 1,4-Dioxane.

46:10

The only thing to consider here is that sulfate radicals are a little less unspecific compared to O H radicals in the oxidation of for instance, natural organic matter and they are thus more they are longer lived. So, once injected, you can achieve larger radii of influence with this.

46:33

And, since I just mentioned it, the oxidation of organic matter is something you always have to consider when you inject strong oxidants into the subsurface because it will take away from your oxidizing power. And so before you go to a field type and implement this process, you want to test the soil oxygen demand. And make sure that the chemicals that you are injecting are actually working on the contaminant you want to remove.

46:58

Then, finally, as with all injection based remediation processes, heterogeneity of the sub surface, of course, challenge these processes. The contaminants are no pay zones for instance, they are hard to reach by these species, but to a certain degree it can be very successful.

47:18

A somewhat newer option for advance oxidation processes is electro chemical treatment, and this is technology that we've been working on over the past few years, and it is a technology that solely relies on current electrical current that is being provided and does not require any chemical edition.

47:38

So, an electro chemical treatment in general, you can do advance oxidation processes at the anode, such as ..., but you can also do advanced production processes at the cathode, such as reductively chlorination of chlorinated solvents. We just heard that these are very relevant one for dioxin contaminated sites because they may inhibit biodegradation processes. Electro chemical processes can basically break down and eat organic contaminants solid. They have become somewhat popular with P, fast, destructive PFS treatment to the very flexible in the implementation. they can be installed as ex situ treatment in form of a reactor. And we've done this, but they can also be implemented in situ treatment. And I'll give you a little flavor of that on the next slide.

48:28

The one thing to keep in mind is that water is a great Redux buffer. And so, when you provide electrons and electrical current with sufficient power into an aqueous phase, most of the electrons are basically wasted in the generation of oxygen at the anode and hydrogen at the castle.

48:47

So to make this process more efficient, we thought we're going to team up with ... team at UCLA, and combine this technology with bio degradation, where the oxygen can be used by aerobic bacteria such as cardiac to help with the degradation of 1,4-Dioxane.

49:06

And so shady and I have been developing this new technology, call it by electro chemical treatment for 1 4, dioxane. And the idea here is that when you combine these processes, you do still have the direct anodic, oxidation of 1,4-Dioxane, just based on electro chemical processes.

49:24

And you can, at the same time remove inhibiting ... such as chlorinated solvents. But in this case, first of all, you have the oxygen that's being generated. That can be used by CV, 1094, metabolic 1, 4 Dioxane, bio degradation, and also that.

49:41

The electrochemical processes opened the Ring of ... and provide growth Substrates, intermediates, basically that much easier for C V 1100, 90 to grow on, basically, you know, to gain energy from then from 1 to 4 dioxane itself. And so the overall idea of one-off DIDS, how we intend to implement this technology as we are using mesh electrodes, that very much look like Windows screen can be implemented on or they can be mounted on vinyl sheet pile and sunk into the subsurface.

50:13

So you basically get a reactive barrier and you can run this treatment passively in situ or in a buff brown reactor, for instance, if you prefer more control. But there are very many ways in which this can be implemented.

50:27

And so to illustrate how effective this treatment is, I'm showing some results here of our research. Seeing results here from electro chemical flow through reactors. On the right-hand side where I plotted the normalized one for an oxygen concentration as a function of distance through the reactor from the left to the right. And these three black dashed lines. Those are the electoral pair.

50:51

So I measure the actual pairs where the water flows through and if you compare the dashed lines then you can see that electro chemical, a biotic electro chemical, oxidation is effective for 1,4-Dioxane and it increases with increasing applied voltage. That's no surprise.

51:09

But once we inoculated these reactors with ... culture, then you can see when you look at the solid lines, that the degradation efficiency at both applied potential increase dramatically. So we're looking here at results for an experiment that had a starting concentration of 100 milligrams per liter 1,4-Dioxane, which may be orders of magnitude higher than you have it at a contaminated site.

51:36

But we broke down these concentrations in the solid blue pace with by electro chemical treatment to be no our detection limit of three micrograms per liter within, basically, just a few centimeters or a few minutes to hours of treatment time. Certainly after the second electrode pair, so, meaning that, even if your site has much lower concentrations, these findings are still relevant. And the bottom line is that we can reduce 1,4-Dioxane by several orders of magnitude quite rapidly, likely to below the very strict sub PPB, regulatory limits that exist in many states.

52:21

The nice thing is 1, 1 ..., which is the hydrolysis product of 111 TCAS Fritz had explained. It is also the strongest known biodegradation and temperature. So if you have inhibition at your site, electro chemical treatment, removes 1, 1 V CE, just similarly effect efficiently to 1,4-Dioxane and potentially other organic compounds. Which would then enable biodegradation of one for the oxide.

52:52

So, to evaluate the efficiency of these processes, we look at capital costs and operational costs and the major capital cost driver are these electrodes. The electrodes we use are dimensionally stable electrodes.

53:07

So, they work for several for months, definitely for several years sometimes they don't dissolve. So, you have an initial investment. You have to make into these electrodes. In the top right corner, what you can see when you compare all these columns is that if you use via an electro chemical oxidation as opposed to a biotic, electro chemical oxidation only, you can save over 90% in the cost.

53:35

And in this case you can also see that at the higher potential applied, we can make more savings here at more power. And then likewise, if we look at the operational costs, those are driven by energy consumption.

53:50

Again, we can reduce operational cost, through combination with bio degradation processes by more than an order of magnitude, or 1%.

54:02

And in this case, the higher potential is not necessarily more efficient than the nor potential. They're pretty similar. But again, bottom line, you bioelectric, chemical, oxidation, saves you over an order of magnitude and cost. Whether you use a lower voltage or a higher voltage, that depends on many sites specific factors. So if you do want to take this technology to the field, there is some pre-testing you want to do just as with other chemical oxidants two. And this is basically where we are with the development of this technology. We're at the field scale right now, and we're testing this technology on the path of scale up to a full scale implementation. And so with that, I'd like to thank my sponsors here and also that many students and postdocs who worked with me on this. And then I'll pass it back to Amy and I think we can go into the Q&A section.

55:01

And remember if you haven't already submitted your questions please go ahead and submit them in the Q&A or the question panel on your goto Webinar. Now it looks like we have a couple of questions that have come in. The first one I'd like to open up to the panel feel free to answer as you wish. Is any technology biological or a biotic considered best available practice her 1,4-Dioxane in water stream?

55:36

Depends, yes, no, no, not nothing specific. Depends on the concentrations depend on other site conditions.

55:48

I don't have my favorites, but, but I I wouldn't say one. There's one thing that would fit everywhere.

55:57
OK, thank you, Shaily. Another one opens for the panel, or the ... and degradation approach, or discuss being used at appeal scale? If not, would there be an issue?

56:15
I can answer that, too. Yes.

56:16
We do have some active projects that are going on at various DOD sites and some industrial sites where we have some exit reaction reactors piloting the via Augmented Sarbanes. And, yes, you're right.

56:32
We're learning a few things about scale up processes, taking the technology from the lab to flow through systems at the pilot scale. So, we hope to be able to share those those results in time for Battelle next year.

56:48
All right.

56:51
Shaily one more, another one for you. Are there any known circumstances where biodegradation of 1,4-Dioxane can occur under anaerobic conditions?

57:03
If not, what are poor minimum read level below? which bio transformation will not occur?

57:13
Again, very important question yes, many subsurface aquifers are anaerobic.

57:19
So, the important distinction is that some dioxane degrading bacteria can survive anaerobic conditions.

57:27
And, they will do other things, but they not degrade dioxin, oxidized dioxane under anaerobic conditions.

57:36
That said, I do think it is possible for dioxin to be enter a weekly biodegrade it. And if I may put my professor's hat on for a minute, it would be anaerobic oxidation rather than reduction. So, not something that happens with chlorinated, solvents, and metals. It will still be an oxidative technology. Dioxane will very likely go towards low molecular rate acids or even CO two. It's just that the terminal electron acceptor may not be oxygen, could be, nitrate, could be something else. With respect to minimum oxygen levels, we've done some studies in the lab, in microcosms, and also some via traps in monitoring wells. And I don't want to pinpoint a specific dollar level, but something in the range of three milligram per liter. So, saturation is definitely not needed 3 to 4 milligram per liter.

58:34

Based on my experience, so far, ought to be enough to power. Errol Big Dioxane by degradation under certain conditions.

58:43
Surely, if I may add an observation from our experiments, it's very hard to remove oxygen from water, and so, our objective in the control columns without oxygen, they were still run with somewhere between 1 to 2 milligrams per liter of dissolved oxygen, and we still saw aerobic biodegradation of 1,4-Dioxane, So you're absolutely right, can be well below saturation.

59:11
Thank you.

59:14
You go. I think we have time for one more question. Again, open to the general panel. Are you seeing many, one poor dioxin sites that are nothing but 1, 4 dioxane at a low PPB concentration?

59:33
Fritz, do you want to take that? I mean, I think my answer to that would be, would be, no, there's, there's typically something else out there. I mean these chlorinated solvents. They won four dioxane is associated with the certain we can be recalcitrant in the environment as well. So one for to actually do purely by itself would be relatively uncommon in my opinion.

1:00:09
Thank you. Fritz. If I may just add to that, the source may not be dioxane free of other co contaminants. But because Dioxane migrates faster than the associated chlorinated solvents under certain conditions, you could have the leading edges.

1:00:27
That would have I wouldn't want to say, pure for a contaminated plume.

1:00:32
But more dioxane and really low concentrations of T C and T C A. And some other chlorinated solvents.

1:00:42
Good point.

1:00:44
Right. Thanks for that insight. Well, we're reaching our end of our time. If you have additional questions, please be sure to fill out our exit survey. There's an opportunity there to request one-on-one follow-up. Time with us is helpful. Also, please be aware that a recording of today's webinar, along with the PowerPoint slides and handouts, will be delivered to your inbox tomorrow. Thank you for joining us today. Thank you so much all of our speakers today and all your valve valuable. Information you delivered. Everybody stay well.

1:01:19
Take care.

1:01:22
Thank you everyone.