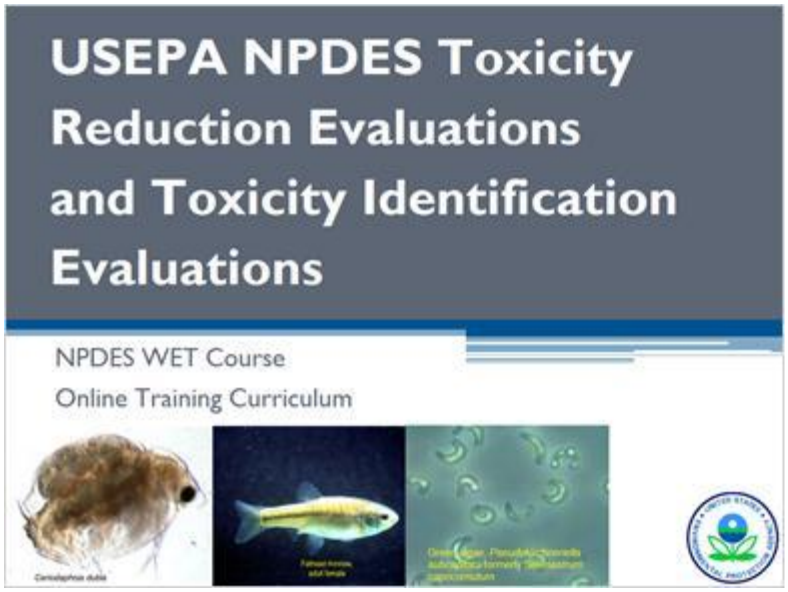
Module 9: USEPA NPDES Toxicity Reduction Evaluations and Toxicity Identification Evaluations



Notes:

Welcome to this presentation on the United States Environmental Protection Agency, hereafter USEPA, National Pollutant Discharge Elimination System, or NPDES, Toxicity Reduction Evaluations and Toxicity Identification Evaluations. This presentation is part of a Web-based training series on Whole Effluent Toxicity sponsored by the USEPA Office of Wastewater Management's Water Permits Division.

You can review this stand-alone presentation, or, if you have not already done so, you might also be interested in viewing the other presentations in the series, which cover the use of Whole Effluent Toxicity, or WET, in the NPDES permits program.

Before we get started with this presentation, I'll make some introductions and cover two important housekeeping items.

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Notes:

First, the introductions.

Your speakers for this presentation are, me, Laura Phillips, USEPA's National WET Coordinator with the Water Permits Division within the Office of Wastewater Management at the USEPA in Washington D.C., and Jerry Diamond, a USEPA HQ contractor and an aquatic toxicologist with Tetra Tech, Incorporated in Owings Mills, Maryland. Second, now for those housekeeping items.

You should be aware that all the materials used in this presentation have been reviewed by USEPA staff for technical and programmatic accuracy; however, the views of the speakers are their own and do not necessarily reflect those of the USEPA. The NPDES permits program, which includes the use of Whole Effluent Toxicity testing, is governed by the existing requirements of the Clean Water Act and USEPA's NPDES permit implementation regulations. These statutory and regulatory provisions contain legally binding requirements. However, the information in this presentation is not binding. Furthermore, it supplements, and does not modify, existing USEPA policy and guidance on Whole Effluent Toxicity in the NPDES permits program. USEPA may revise and/or update the contents of this presentation in the future.

Also, this module was developed based on the live USEPA HQ NPDES WET course that the Water Permits Division of the Office of Wastewater

Management has been teaching to USEPA regions and states for several years. This course, where possible, has been developed with both the non-scientist and scientist in mind, and while not necessary, it is recommended that a basic knowledge of biological principles and Whole Effluent Toxicity will be helpful to the viewer. Prior to this course, a review of the USEPA's Permit Writer's online course, which is also available at USEPA's NPDES website, is recommended.

When appropriate a blue button will appear on a slide. By clicking this button, additional slides will present information regarding either freshwater or marine USEPA WET test methods. When these additional slides are finished, you will be automatically returned to the module slide where you left off. The blue button on this slide provides the references for USEPA’s WET test methods that will be presented throughout this module.

Now that you know who we are and we’ve covered the housekeeping item, let me turn this over to Jerry to go over Toxicity Reduction Evaluations and Toxicity Identification Evaluations.

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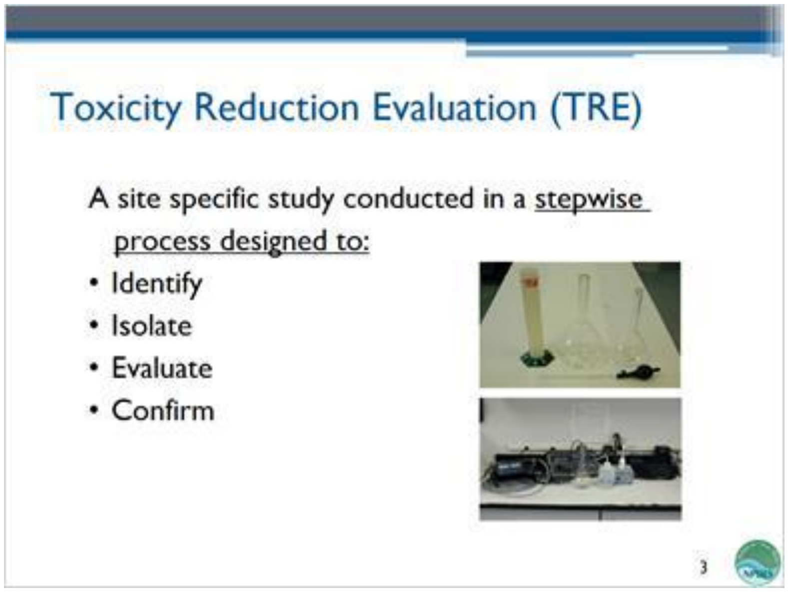

Notes:

This module reviews the Toxicity Reduction and Toxicity Identification Evaluation process that is used under the USEPA NPDES permits program to enable permittees to identify and reduce toxicity that is observed in Whole Effluent Toxicity, or WET, tests. A Toxicity Reduction Evaluation, or TRE, is a site-specific study of the effluent or wastewater at a treatment facility. The TRE process is generally a stepwise process that attempts to identify the class of the potential toxicant and, if possible, isolate the chemical causing toxicity. Once the identification/isolation process has confirmed the potential cause of toxicity, the evaluation step helps determine what needs to be done to reduce or treat the chemical or chemicals causing toxicity in the effluent. If the evaluation step is completed successfully, the TRE should confirm that the actions chosen to reduce toxicity are successful. There are potentially many ways to reduce toxicity depending on the cause and these will be covered later in the module.

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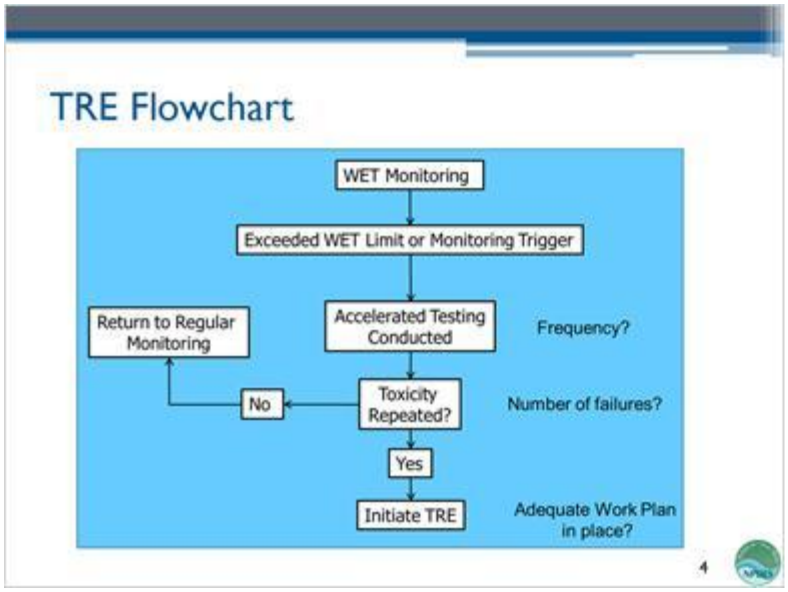

Notes:

Let's take a moment to review how the need for a permittee to conduct a TRE may arise. In the TRE flow chart example illustrated here, the discharger has conducted WET monitoring in accordance with their NPDES permit. During the WET monitoring, the NPDES WET permit limit was exceeded. NPDES WET permit limits are established to prevent excursions of state WET water quality standards, so an exceedance of a WET permit limit can result in permit requirements such as triggers. These permit triggers are actions to be taken by the permittee to identify and resolve the toxicity in order to come back into compliance with their permit. Therefore, based on WET conditions in the NPDES permit, the permittee is required to conduct accelerated WET testing. Accelerated monitoring requirements can vary from state to state, but there's usually a requirement for more frequent WET testing over a fairly short time period, often just a few weeks, to determine if the toxicity is persistent. If the effluent toxicity is not measured at a level that exceeds the permit limit based on the data generated by the accelerated WET testing, the permit usually allows for a return to the previous WET monitoring frequency schedule. If toxicity is still measured in exceedance of the WET permit limit based on the accelerated WET testing data, then the TRE process is initiated. The right side of the slide contains a few pertinent questions with regards to certain steps in the process, in order to highlight the recommendation that answers to these questions should ideally be clearly spelled out in the WET conditions of the permit. The final point of this slide, and one that will be reiterated in the next couple of slides, is that it is extremely important to have an adequate work plan that includes a schedule and reporting requirements in place throughout the process, but particularly once a TRE is initiated.

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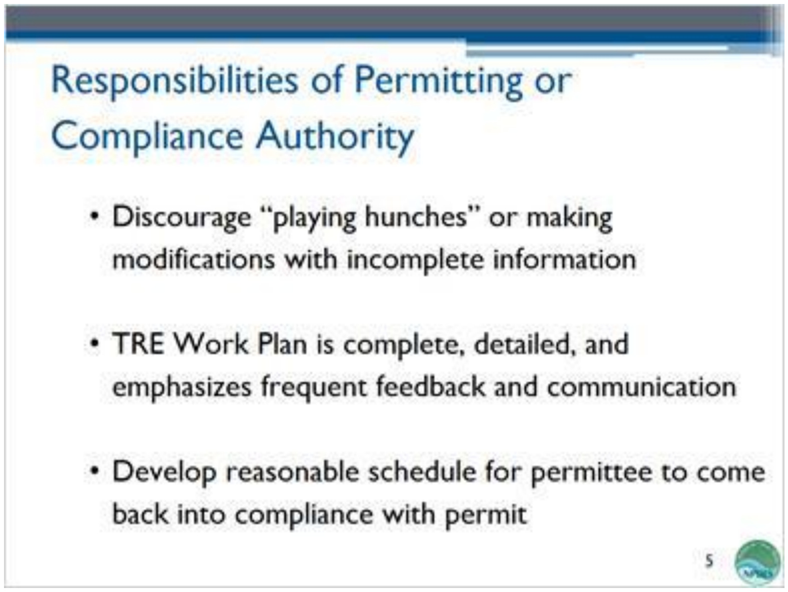
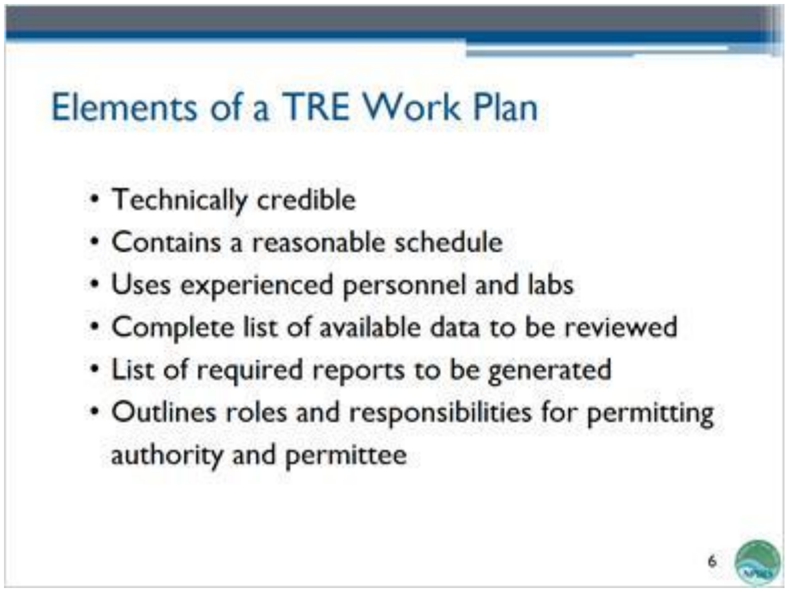


Notes:

It is important to understand that most of the work being completed in the TRE is being conducted by the permittee through their labs or consultants. However, it is equally important for the USEPA or state NPDES permitting authority to ensure that the TRE process is on track and that the permittee is going to resolve the toxicity problem in an appropriate and timely manner. One recommendation is that the NPDES permitting authority discourage the permittee from "playing hunches" or progressing forward in a treatment modification based on improper or incomplete information regarding the cause of toxicity. On occasion, a permittee may believe they have the answer, and they may take measures that can not only be costly from a financial standpoint, but also from a time standpoint as well. This is where the NPDES permitting authority can provide key recommendations to the permittee towards ensuring that all available information and possible strategies are considered in the evaluation (the complete picture).

Another important recommendation is that the permittee have a TRE work plan that is sufficiently detailed and includes frequent communication between the NPDES permitting authority and the permittee. TRE work plan requirements vary from state to state; however, one common aspect is that the TRE plan includes a schedule and reporting requirements to ensure that the effluent toxicity is reduced or eliminated so that compliance with the permit is achieved in the required time frame.



Notes:

Based on USEPA's national NPDES permit experience, a TRE is most likely to be successfully completed if there is a good partnership between the people who know the facility, including what's coming into the facility, and the experts on toxicity issues, including how to determine the causes of the effluent toxicity. A TRE often will involve the use of several disciplines, including wastewater treatment engineering, chemistry, process engineering, toxicology, and perhaps hydrology. Therefore, it is important that there are experts on the team that cover these and other disciplines as needed to ensure a successful TRE. The more experience TRE team participants have, the better. This is especially true for the toxicologist on the team, because they can help link water quality characteristics to toxicity for different USEPA WET test species.

Regardless of the facility, a TRE almost always starts with a review of the available data. Relevant data includes influent and effluent chemical and physiochemical data, facility treatment data, and WET test data, including the physicochemical data collected during the WET tests and the raw toxicity data from the lab. Often, a thorough review of these data can be very useful in helping to determine what might be causing toxicity in the effluent. Facility treatment information that is often very useful in conjunction with the WET data are parameters such as effluent chemical oxygen demand (COD), biological oxygen demand (BOD), mix liquor solids, volatile solids, and removal rates of COD and BOD based on influent and effluent concentrations. The work plan should include the data and other information available for the evaluation, any interim reports or other deliverables to be sent to the NPDES permitting authority, and the roles and responsibilities of the TRE plan's team members.

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Notes:

A TRE consists of six steps, but all six steps may not be required depending on the facility site-specific situation. The acquisition of relevant information and data, step 1, is a necessary first step in any TRE. Step 2, evaluation of the facility performance, is nearly always needed in a TRE. Step 3 is the Toxicity Identification Evaluation, or TIE, and is optional. There are multiple ways to resolve an effluent toxicity issue, and it may not always be the most expedient strategy to focus first on identifying the exact cause of the toxicity. While knowing the exact cause of toxicity may be optional, the evaluation of the source of toxicity, step 4, is almost always a critical step in the TRE process. The toxicity source evaluation is particularly important where a facility may have multiple sources, such as a municipal wastewater facility or a large industrial facility with multiple waste streams. Step 5, the toxicity control evaluation, is always required within the six-step TRE approach. This step evaluates how the effluent toxicity will be controlled based on either an identification of the toxicant(s) or the source of toxicity. Finally, the toxicity control implementation plan and follow-up WET and/or chemical monitoring, step 6, are incorporated into the TRE plan to confirm that effluent toxicity is controlled and there is permit compliance.

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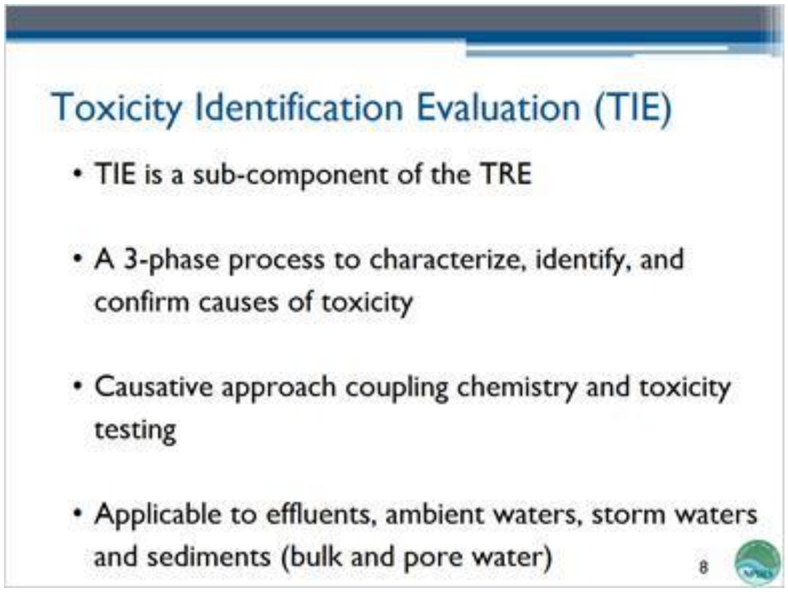

Notes:

As noted on the previous slide, one optional step in the six-step TRE approach is to identify the exact cause of effluent toxicity. This is commonly referred to as a Toxicity Identification Evaluation, or TIE. Although not necessary, a TIE can often be very helpful in a TRE, because toxicity can be more certainly controlled if the identity of the toxicant(s) is known. The TIE is a three-phase process that characterizes, identifies, and confirms the cause or causes of toxicity. A TIE couples effluent chemical analysis and WET test results. Although it may take some effort to identify the exact cause of effluent toxicity, particularly in a very complex effluent situation, using experienced WET testing laboratories and consultants can help ensure that the TIE is not an expensive, time-consuming venture. TIEs are applicable to evaluating toxicity of permitted effluents, ambient waters, storm waters and sediments, including bulk sediment or pore waters.

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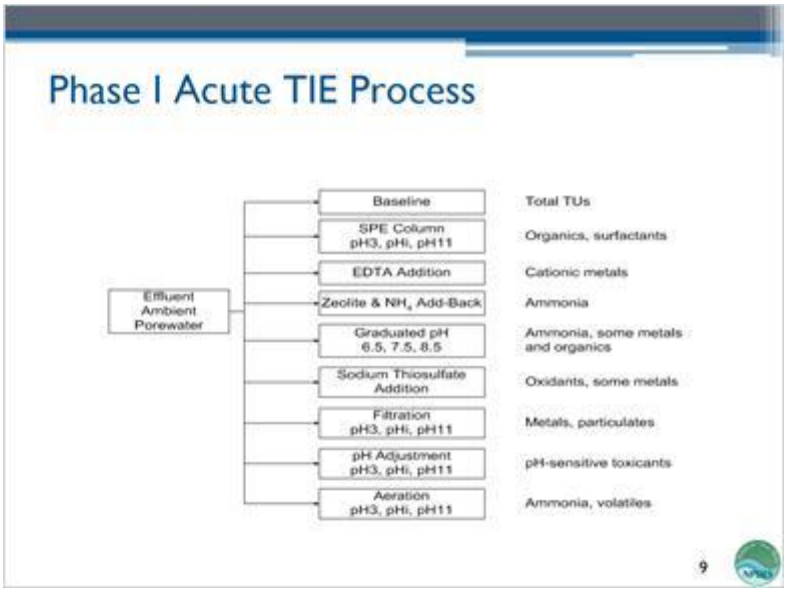
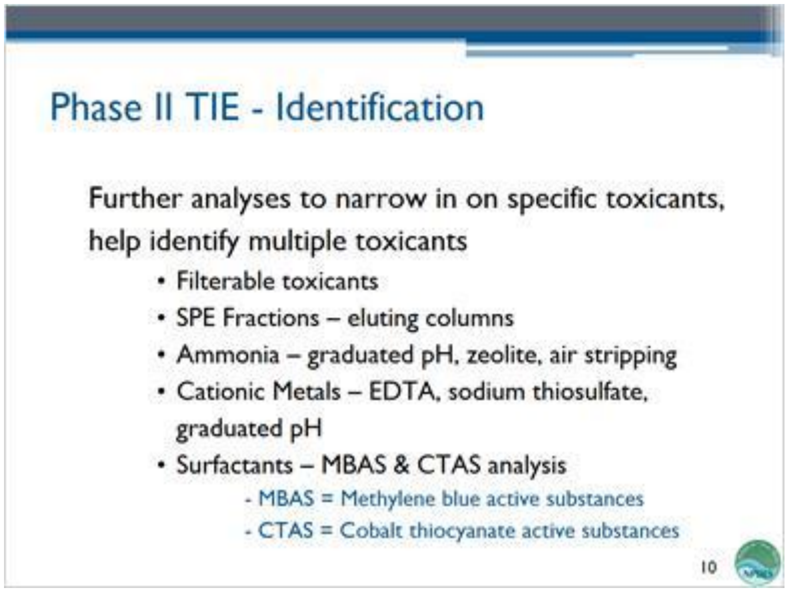


Notes:

The TIE flow chart illustrated on this slide is from the USEPA Phase I TIE guidance manual. Although this guidance was published in the early 1990s, it is still very relevant. Also, many labs have added to the options presented in the TIE Phase I document based on an increasing array of specialized columns and other types of treatments that are fairly specific for certain chemicals.

When conducting a TIE, an effluent sample is separated into several sub-samples, each of which is subject to a different benchtop treatment. This is called fractionating the effluent. Each of these different treatments is designed to remove or treat different types of chemicals. Once the treatments are applied, each treated sample is tested to determine whether toxicity was reduced as compared to the baseline effluent sample. As noted on this slide, there are multiple treatment options that could be applied, including SPE columns, EDTA addition, and so forth, all of which are discussed in USEPA's Phase I guidance.



Notes:

After conducting Phase I of the TIE, the type of chemical that may be causing toxicity, for example, metal, non-polar organic, oxidant, etc., should be identified. Phase II of the TIE process attempts to identify the specific chemical or chemicals causing the toxicity. The identification of the chemical(s) is accomplished using more in-depth analyses that often require more chemical analyses of the effluent and working more with certain effluent fractions based on the Phase I TIE results. For example, if air-stripping reduced the toxicity in the TIE Phase I, then ammonia may be responsible for the toxicity, because ammonia tends to volatilize when using air-stripping. TIE Phase II analyses might then use additional treatments to determine whether ammonia is indeed the cause of the toxicity.

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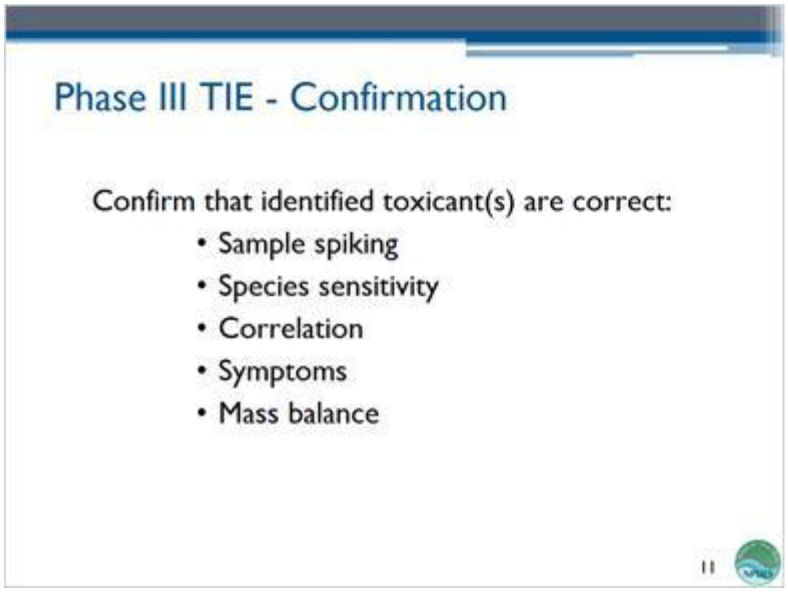
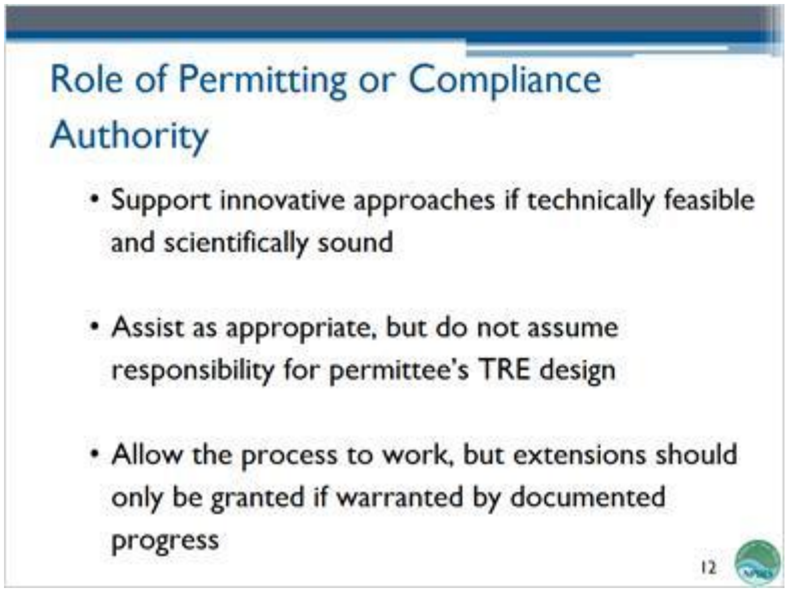


Notes:

In Phase III of the TIE, we confirm what we believe is the cause of the toxicity as determined in Phase II. In Phase III, different analyses including some statistical analyses may be conducted to confirm the cause of the toxicity. There may or may not be a need for more chemical analyses or toxicity testing at this point. Other lines of evidence such as more in-depth treatability information may be used in Phase III to confirm Phase II conclusions. USEPA has guidance manuals for Phase II and III and the TIE procedures listed here are discussed in more detail in the USEPA TIE manuals.



Notes:

As previously mentioned, the role of the NPDES permitting authority in TIEs is to support innovative approaches that are technically feasible as well as scientifically sound, and to discourage approaches that are not results-oriented, are costly, or require too much time to resolve the toxicity. In some instances, the discharger may need to use novel approaches to identify the cause of toxicity. The NPDES permitting authority can assist the permittee by providing technical information, where appropriate. However, conducting the TIE/TRE is the responsibility of the permittee, not the NPDES permitting authority. The role of the NPDES permitting authority is to allow the TIE/TRE process to proceed and to confirm that the permittee is making good progress towards completing the TRE.

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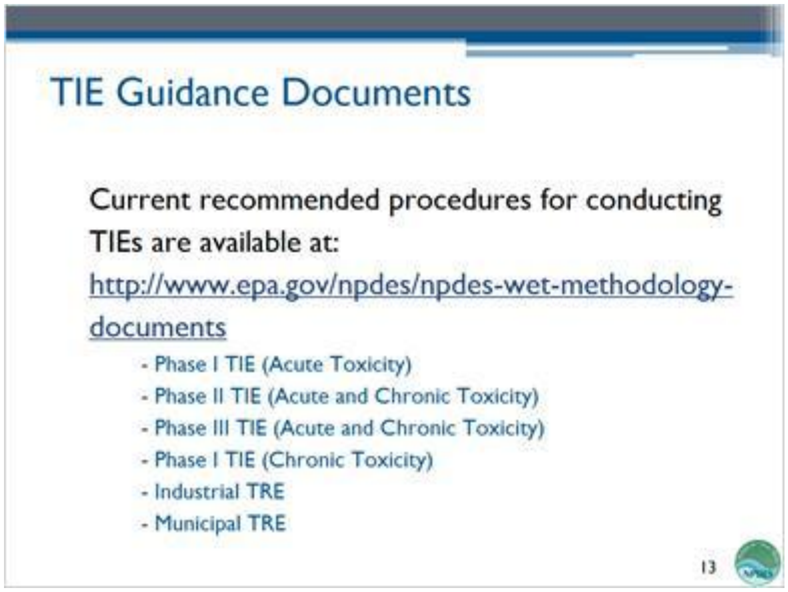

Notes:

USEPA TIE guidance documents, which are the current recommended procedures for conducting TIEs, are available on the USEPA Office of Wastewater Management's NPDES website listed on this slide. There, you will find a guidance document for each of the three phases of Toxicity Identification Evaluations, a Phase I TIE guidance document for chronically toxic effluents, and the guidance documents for conducting toxicity reduction evaluations for industrial and municipal effluents.

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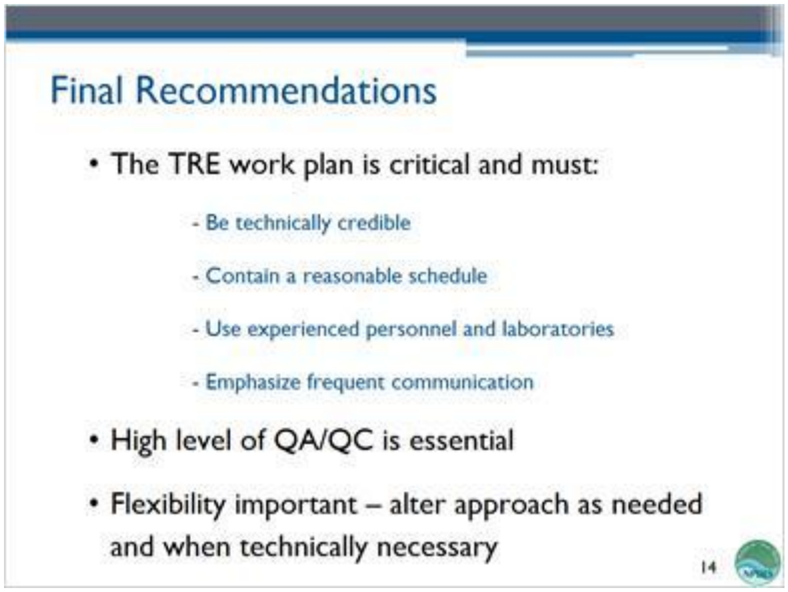

Notes:

Before we look at some TRE/TIE examples, we want to remind you that the TRE work plan is critical and should be technically credible, contain a reasonable schedule, and use experienced personnel and laboratories. The TRE work plan should also provide for ongoing re-evaluations of the plan as necessary. The work plan should encourage decisions that are guided by the site-specific situation, and should emphasize early and frequent communication between the permittee and the NPDES permitting authority. The focus of the TRE work plan should be on mitigating the effluent toxicity problems, reducing, abating or eliminating the toxicity, and returning to compliance with the permit as quickly as possible. In addition, a high level of QA/QC during the TIE and TRE process is essential for ensuring that the results aid in finding a solution to remove the effluent toxicity and return to full NPDES permit compliance. Finally, as the TIE and TRE process can be very challenging, the NPDES permitting and/or compliance authority should offer some flexibility for the permittee to alter the approach when appropriate and technically necessary.

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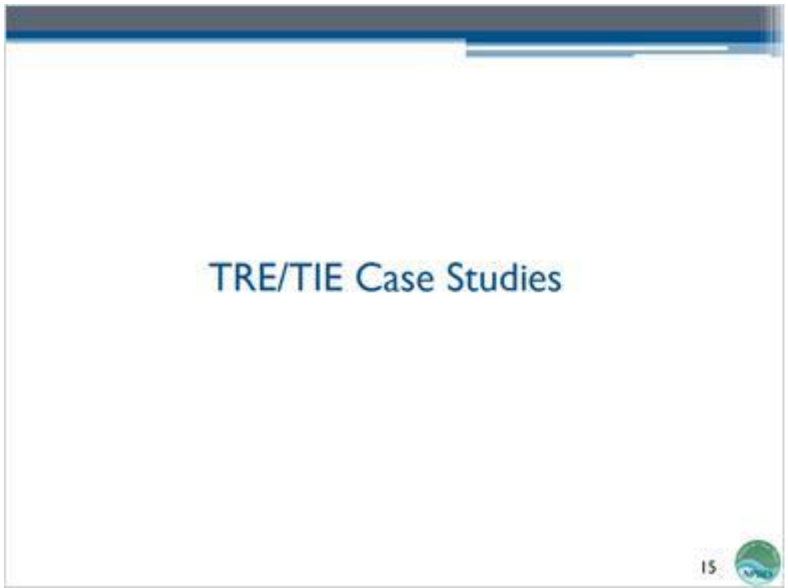

Notes:

Now let’s take a look at a few examples where the TIE and TRE process was used to successfully diagnose the cause of toxicity and address the issue so that the permittee was back in compliance with the NPDES permit.

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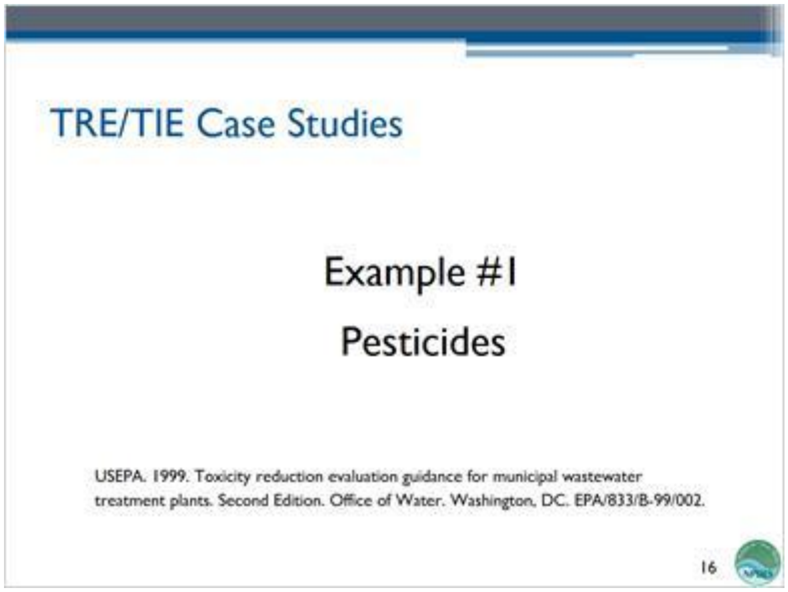

Notes:

In this first example, we will look at a municipal effluent that had a toxicity issue involving commonly used pesticides.

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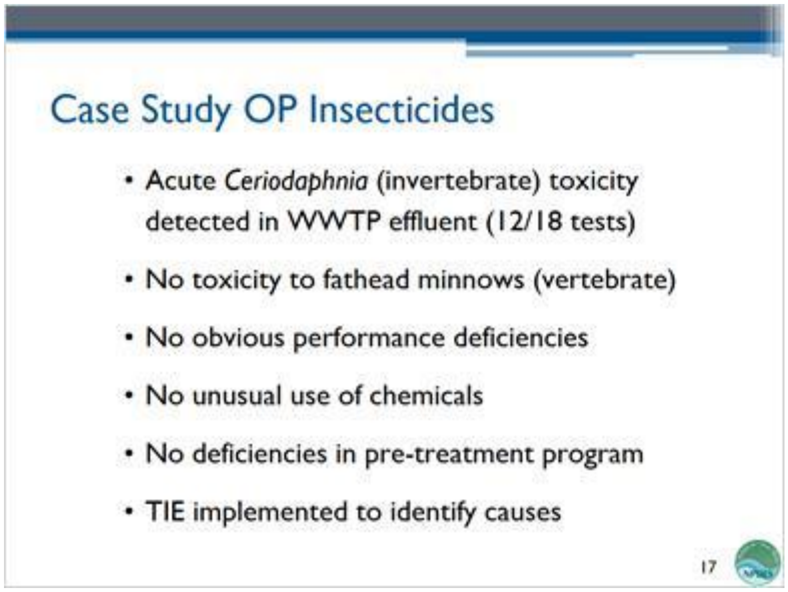

Notes:

In this example, a wastewater treatment plant effluent exhibited acute toxicity to *Ceriodaphnia dubia*, an invertebrate water flea, in 12 of 18 acute toxicity tests, and there was no observed toxicity to the tested fish, fathead minnows. As part of the TIE, the facility's treatment performance was reviewed, and no obvious performance deficiencies were noted. Furthermore, the facility met all the other water quality-based effluent limits in their NPDES permit. There had been no unusual use of new or different treatment chemicals, and no deficiencies were noted in their pre-treatment program. The wastewater treatment plant therefore initiated a TIE.

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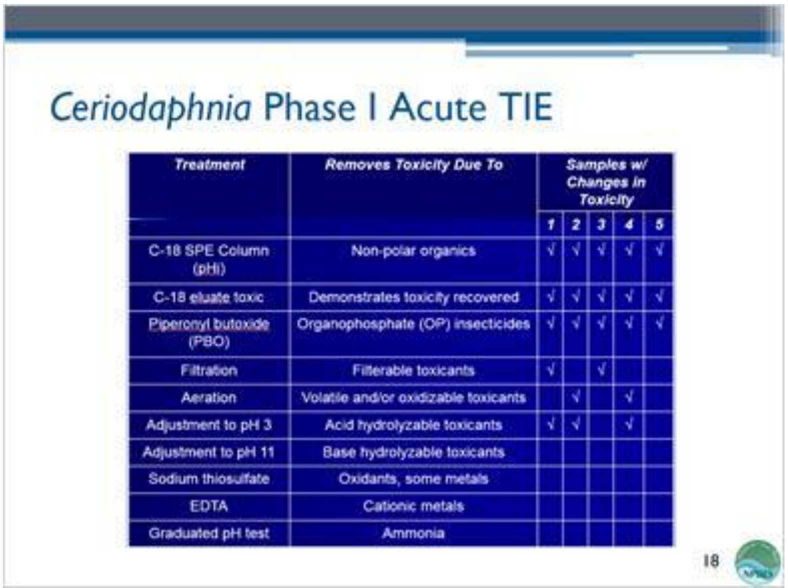
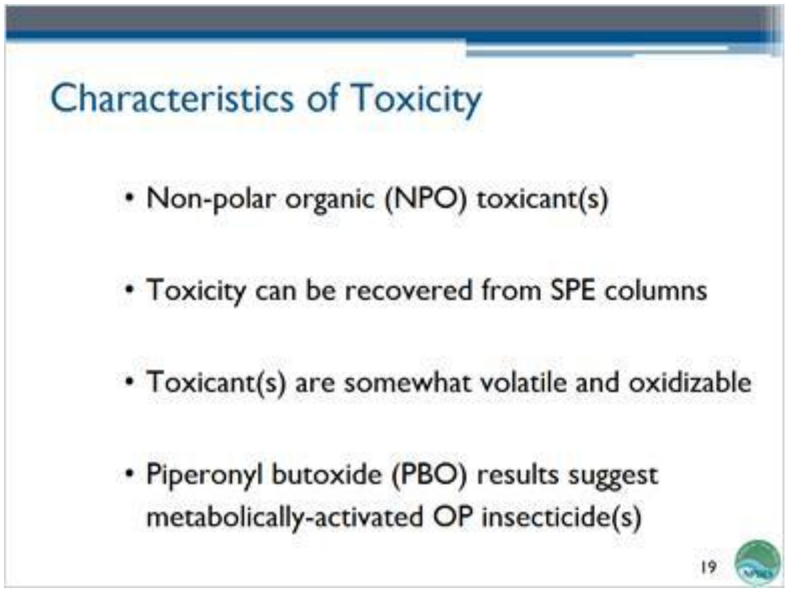


Treatment	Removes Toxicity Due To	Samples w/ Changes in Toxicity				
		1	2	3	4	5
C-18 SPE Column (pHi)	Non-polar organics	√	√	√	√	√
C-18 eluate toxic	Demonstrates toxicity recovered	√	√	√	√	√
Piperonyl butoxide (PBO)	Organophosphate (OP) insecticides	√	√	√	√	√
Filtration	Filterable toxicants	√		√		
Aeration	Volatile and/or oxidizable toxicants		√		√	
Adjustment to pH 3	Acid hydrolyzable toxicants	√	√		√	
Adjustment to pH 11	Base hydrolyzable toxicants					
Sodium thiosulfate	Oxidants, some metals					
EDTA	Cationic metals					
Graduated pH test	Ammonia					

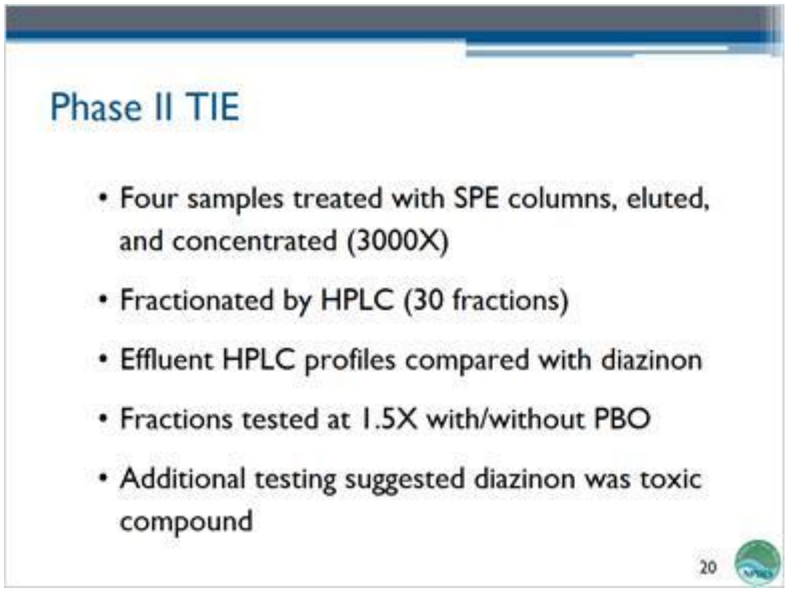
Notes:

This table shows the results of the Phase I TIE WET tests using acute exposures to *Ceriodaphnia dubia*. The first column shows the treatments that were used on sub-samples of the effluent, many of which were presented in the previous slides. One additional treatment, Piperonyl Butoxide (PBO), was used in this case. PBO specifically enhances organophosphate insecticides, making them even more toxic by increasing the likelihood that the aquatic organisms cannot metabolize these insecticides. The numbered columns refer to 5 different effluent samples collected over time that were assessed using USEPA WET tests. Testing multiple effluent samples helps ensure that the cause or causes of toxicity is adequately characterized. The checkmarks in each column indicate whether, for that sample, the treatment was effective at giving them information about toxicity. In most of the cases, the checkmark means that the treatment reduced effluent toxicity. In the case of the PBO treatment, the checkmarks indicate that the effluent was much more toxic when PBO was added. Treatments that did not provide any information or reduction in toxicity were not marked.



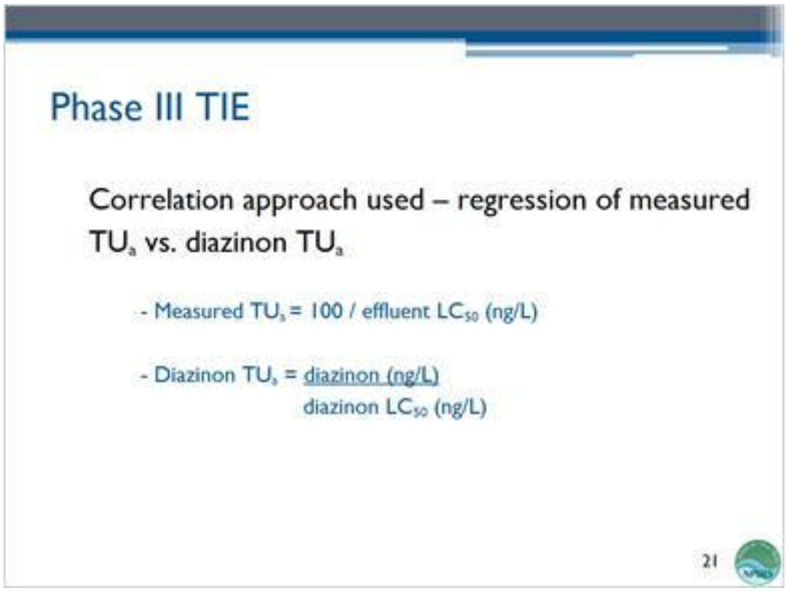
Notes:

Looking at the results in the table on the previous slide, the C-18 column reduced the toxicity, indicating that the toxicant could be a non-polar organic. Further testing using the SPE column demonstrated that toxicity could be recovered, further implicating a non-polar organic chemical as the cause. Other treatments used, including aerating the sample and lowering the pH to 3 before a return to the initial effluent pH, indicated that the toxicant or toxicants are somewhat volatile and oxidizable. The enhancement of toxicity in samples treated with PBO is very specific, suggesting a metabolically-activated organophosphate insecticide may be responsible for the observed toxicity.



Notes:

During Phase II of the TIE, a number of specific chemical analyses, such as High Performance Liquid Chromatography, or HPLC, were conducted to identify the chemical toxicant. Using HPLC, the organophosphate insecticide diazinon was identified. Interestingly, diazinon was not one of the chemicals being monitored by this facility in their NPDES permit. The facility had no knowledge that this chemical could be entering their plant, perhaps through storm water runoff from residential lawns or from commercial users of diazinon who may have discarded it down sink drains.



Notes:

Phase III of the TIE process is the confirmation of the cause of the toxicity. To confirm that diazinon was the cause of effluent toxicity, the correlation between effluent diazinon concentrations over time and the associated effluent toxicity results using acute *Ceriodaphnia* WET testing was conducted. To do the comparison, both the diazinon effluent concentrations and the WET data expressed as *Ceriodaphnia* LC_{50}s were converted to Toxicity Units, or TUs. For acute toxicity, the TUs are calculated as 100 divided by the observed LC_{50}. For diazinon, the TUs were calculated by dividing diazinon concentration in the effluent by the known diazinon acute *Ceriodaphnia* LC_{50} data. By converting the data to TUs, there are now two expressions of TUs that can be directly compared. If diazinon is the sole cause of toxicity, there should be approximately a 1:1 relationship between the two types of TUs.

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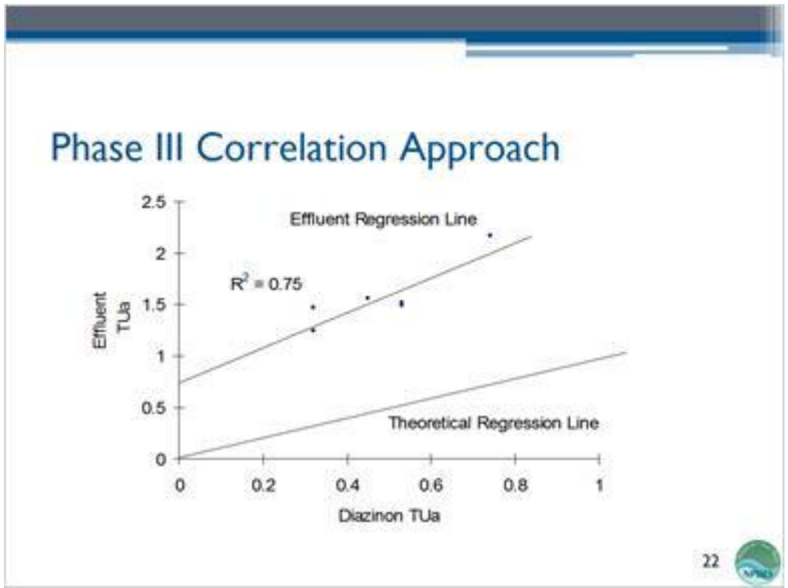
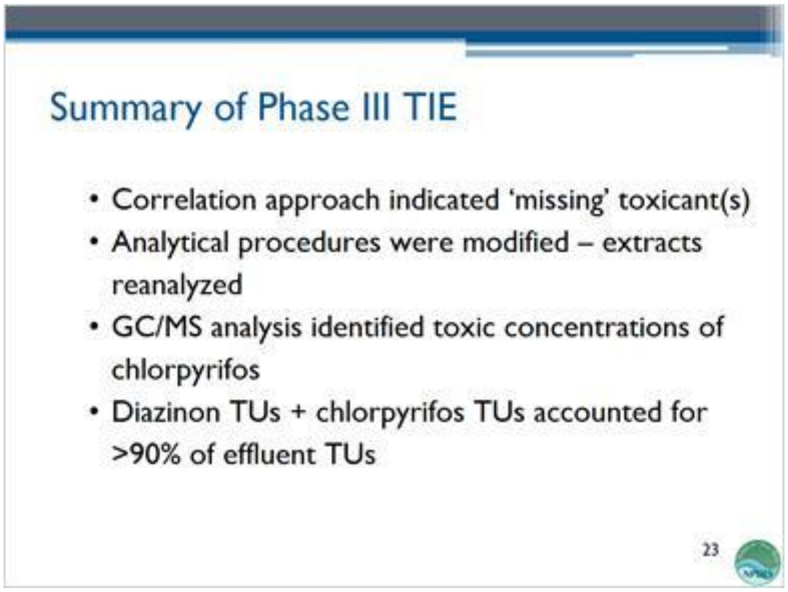


Notes:

During Phase III of the TIE, a correlation approach was used by plotting the effluent acute TUs on the y-axis and diazinon acute TUs on the x-axis. What this graph indicates is that there is not a 1:1 relationship between the two forms of TUs and, in fact, there was more effluent toxicity than would be expected based on the known diazinon acute toxicity to *Ceriodaphnia.* For example, at only half the diazinon concentration that should cause acute toxicity to this WET test species (0.5 TU_a on the x-axis), they observed 1.5 TU_as based on effluent toxicity testing (or an LC_{50}=30-40% effluent). This WET test result indicates that there must be another chemical causing the toxicity in addition to the diazinon.



Notes:

So the team went back to the lab and did more sophisticated chemical analyses and found that the effluent contained chlorpyrifos, another organophosphate insecticide, in addition to the diazinon. The TUs for diazinon and chlorpyrifos were combined and an almost perfect 1:1 relationship with acute toxicity results was observed. Chlorpyrifos and diazinon are organophosphate insecticides that respond the same way in Phase I TIE testing using PBO. By combining effects of both insecticides, they obtained a more accurate picture of the causes of effluent toxicity.

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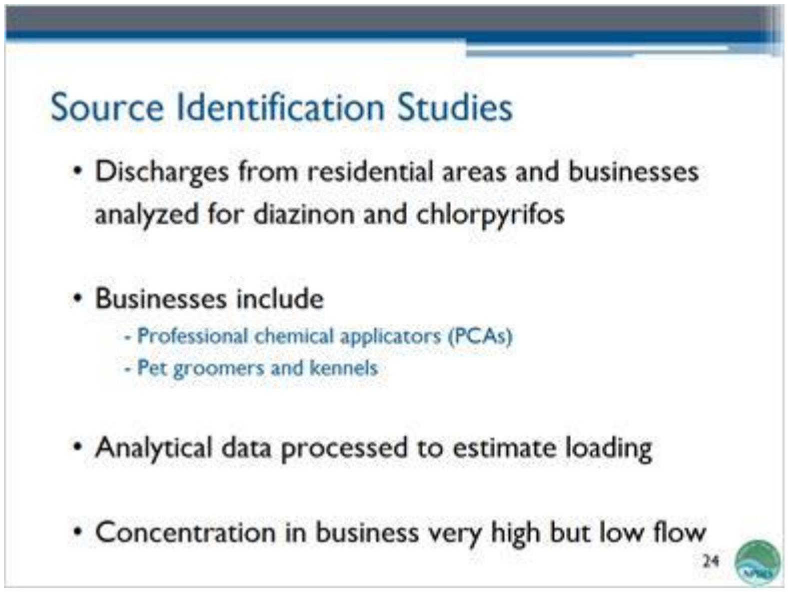
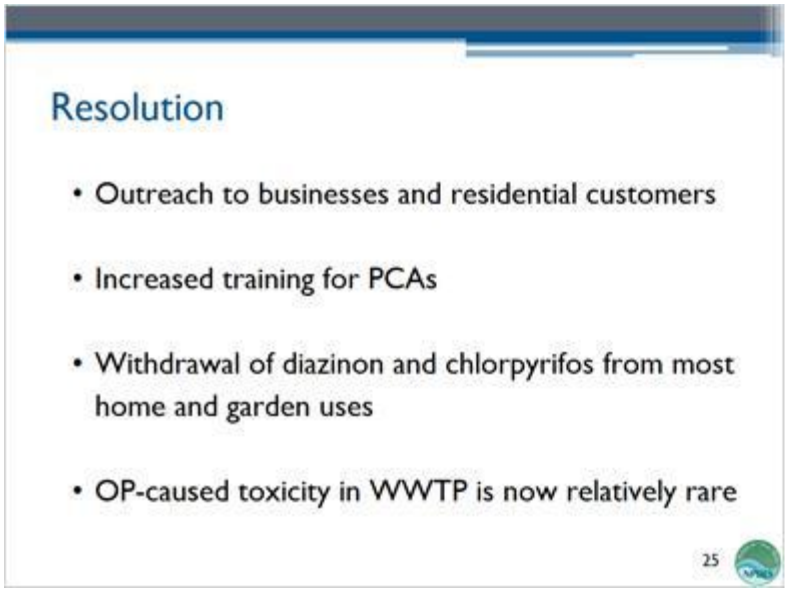


Notes:

Now knowing the causes of effluent toxicity, the next task was to determine the source or sources of the two insecticides. It was quickly confirmed that the major sources of these pesticides were residential areas and businesses, particularly those that dealt with pet grooming and similar types of activities where products were used that contained these pesticides. So what did they do to resolve the toxicity issue?



Notes:

This particular WWTP was already using fairly advanced tertiary treatment. Therefore, the toxicity issue was resolved by finding ways to reduce pesticide loading to the WWTP. The City implemented an intensive public communication and outreach plan to promote the use of safer replacement chemicals and reduce the usage and disposal of these insecticides. The public outreach program was a success and the WWTP came back into compliance with their WET NPDES permit limits.

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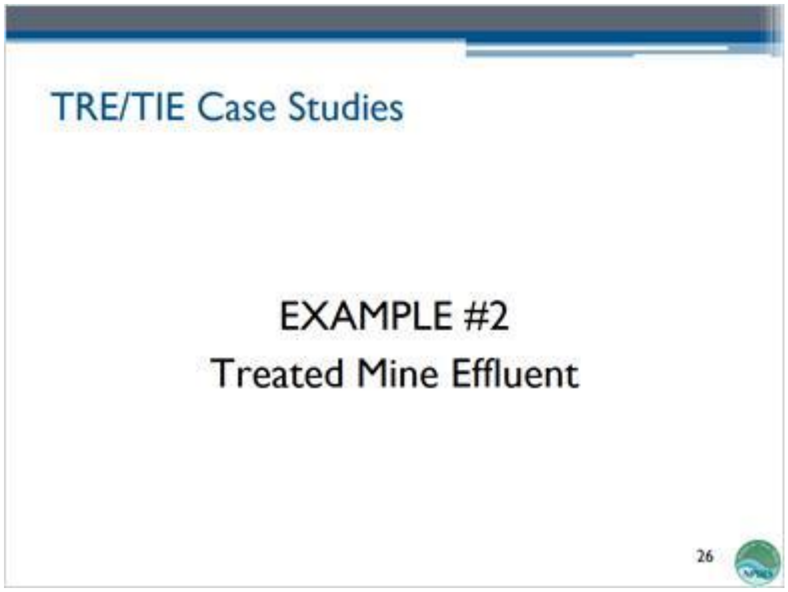
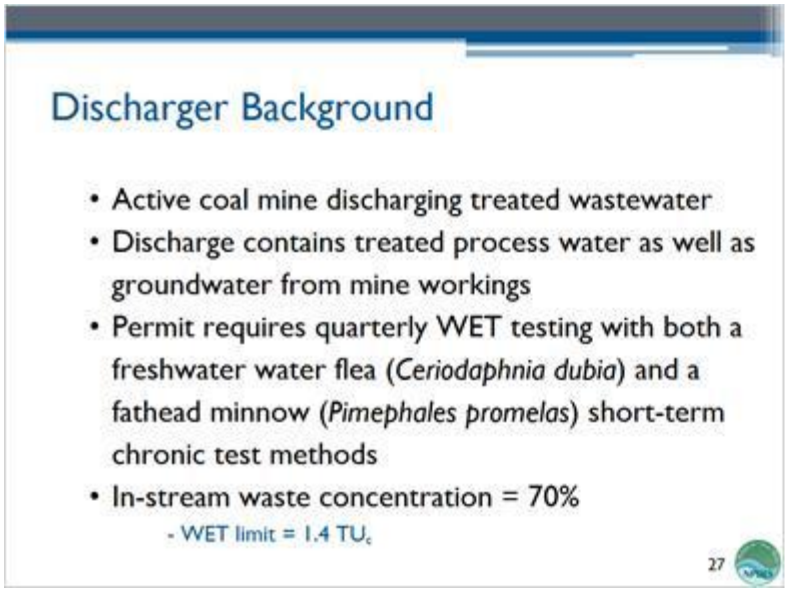


Notes:

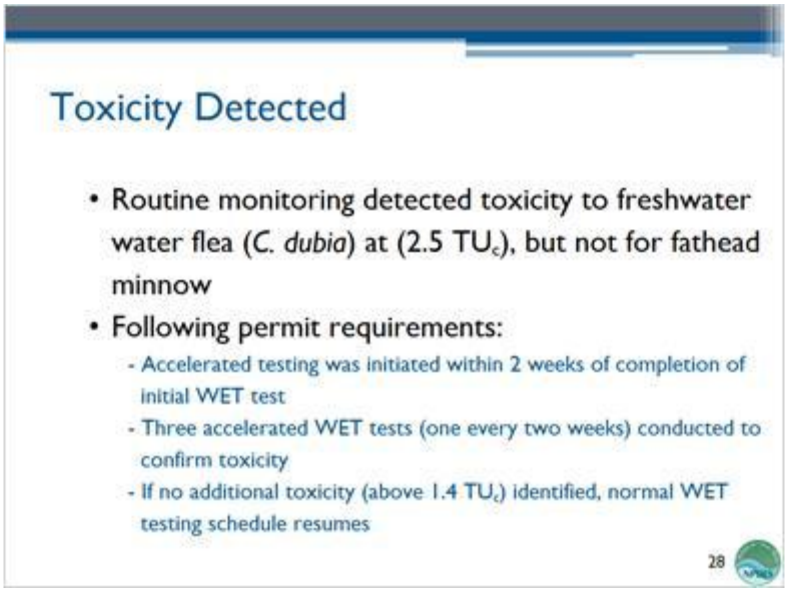
In this second example, we will look at an industrial effluent from a mine that had a toxicity issue involving dissolved solids.



Notes:

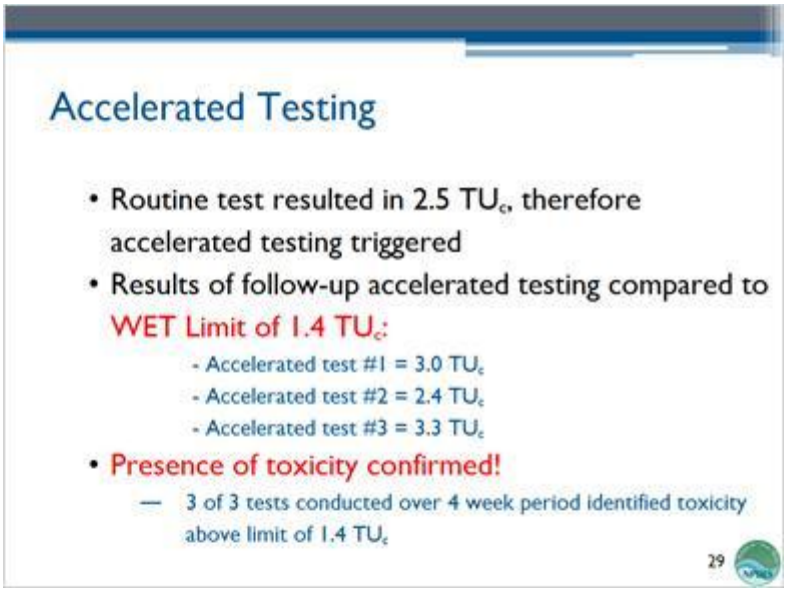
In this second TRE example, the industrial effluent discharge from a coal mine contained process water and groundwater from mine workings. The NPDES permit required quarterly chronic WET testing with both an invertebrate water flea, *Ceriodaphnia dubia,* and fathead minnows, *Pimephales promelas*. The in-stream waste concentration was fairly high at 70%, indicating little effluent dilution was available in the receiving waterbody. The WET limit for this facility was 1.4 chronic toxicity units, or TUs.

Module 9: USEPA NPDES Toxicity Reduction Evaluations and Toxicity Identification Evaluations



Notes:

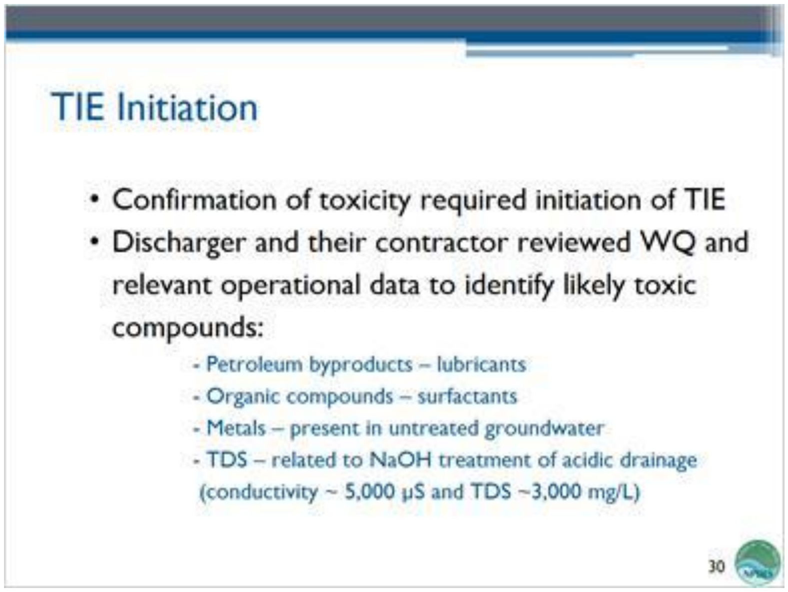
Toxicity was observed at levels exceeding their WET limit of 1.4 TU_c. Therefore, in accordance with their NPDES permit, accelerated WET testing was conducted to determine whether the toxicity was persistent, which can be helpful when trying to identify the cause of toxicity.



Notes:

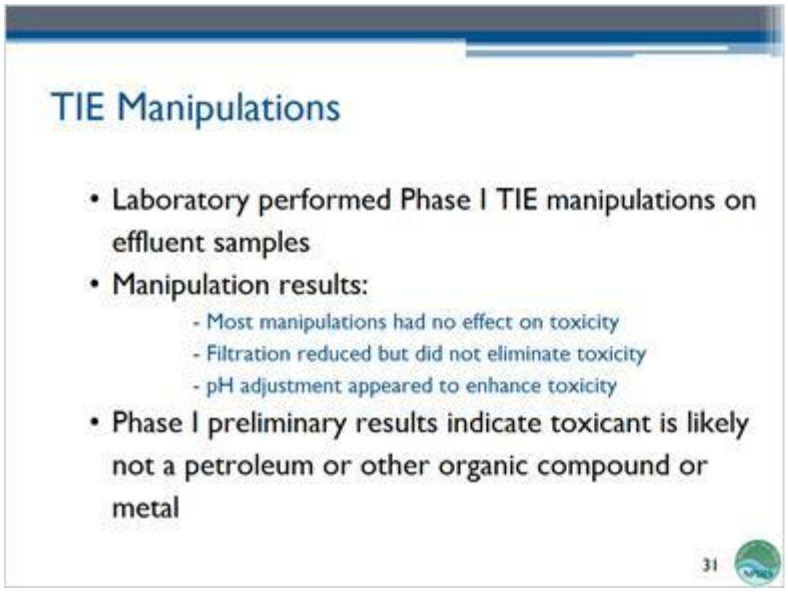
Results of accelerated WET testing indicated persistent toxicity in this effluent. Thus, toxicity was confirmed, and the permittee entered into a TRE to determine the potential cause of toxicity and how to reduce it to get back in compliance with permit limits.

Module 9: USEPA NPDES Toxicity Reduction Evaluations and Toxicity Identification Evaluations



Notes:

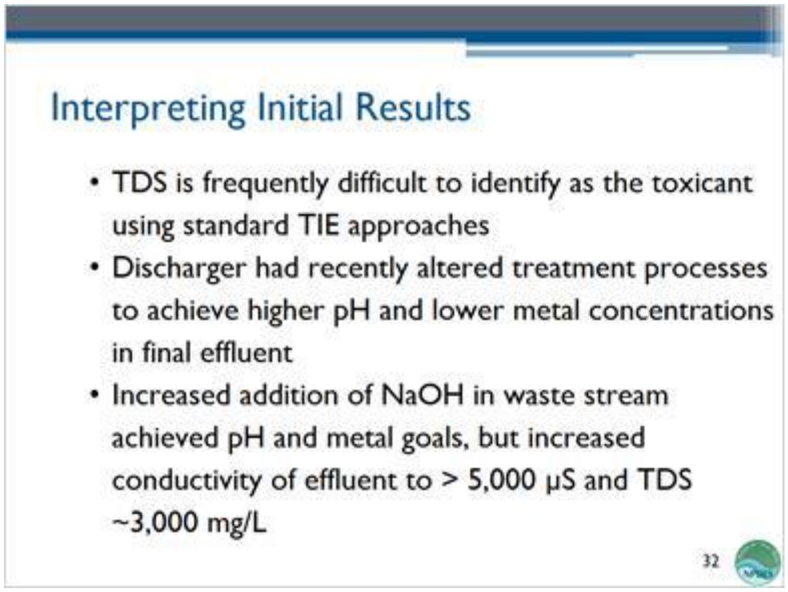
Based on the results of the accelerated WET testing, this industrial facility initiated a TIE in accordance with their NPDES permit. As a first step, water quality data for the effluent and the wastewater treatment process data were reviewed. Several potentially toxic chemicals were identified through this review, including petroleum byproducts, lubricants, and surfactants used in the mine, as well as certain metals and total dissolved solids, TDS. TDS, mostly in the form of sodium chloride, was enhanced in this effluent, because sodium hydroxide was used as a treatment chemical to meet the state's pH water quality standards.



Notes:

Following USEPA's Phase I TIE guidance, several treatments were used. However, in this case, most of the treatments did not reduce the toxicity of the effluent. Filtration helped, but it did not eliminate the toxicity, and pH adjustments appeared to increase the effluent's toxicity. The TIE Phase I results suggested that petroleum-related chemicals, such as polycyclic aromatic hydrocarbons or PAHs, as well as metals, were unlikely causes of toxicity, because the respective treatments for these compounds did not decrease effluent toxicity.

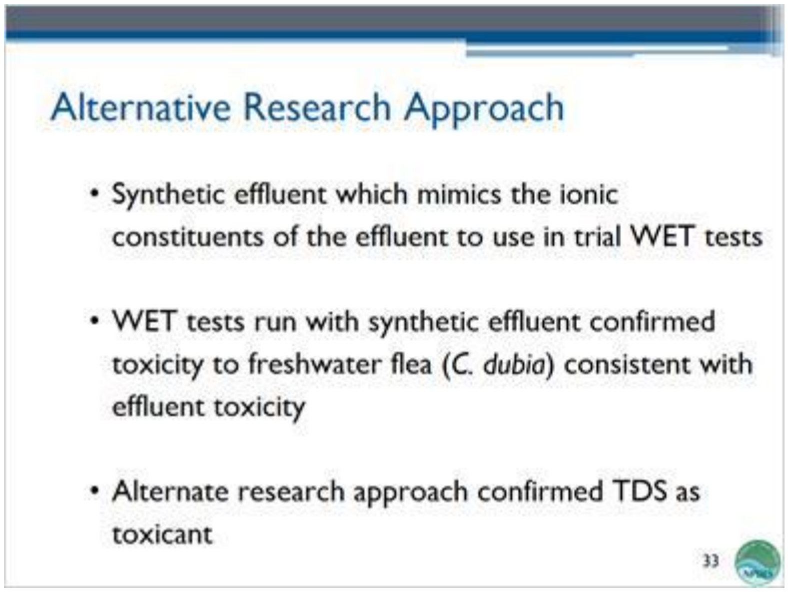
Module 9: USEPA NPDES Toxicity Reduction Evaluations and Toxicity Identification Evaluations



Notes:

The results of the TIE Phase I suggested TDS could be a cause of toxicity. TDS is difficult to confirm as a toxicant using the standard TIE approach, because TDS could be the product of ions (salts) that are not readily removed using the standard TIE treatments. Furthermore, any treatment that removes salts, such as special membranes, are not selective to salts and will remove many other types of chemicals as well. Another piece of useful information in this case is that the permittee recently altered the treatment by adding more sodium hydroxide, or NaOH, to increase the pH slightly and thereby lowered the metal concentrations in the final effluent. However, adding more sodium hydroxide only increased effluent conductivity and made the effluent even more toxic. The TIE Phase II analyses supported TDS as the cause of toxicity based on the conductivity toxicity data for *Ceriodaphnia dubia* in chronic WET tests.

Module 9: USEPA NPDES Toxicity Reduction Evaluations and Toxicity Identification Evaluations



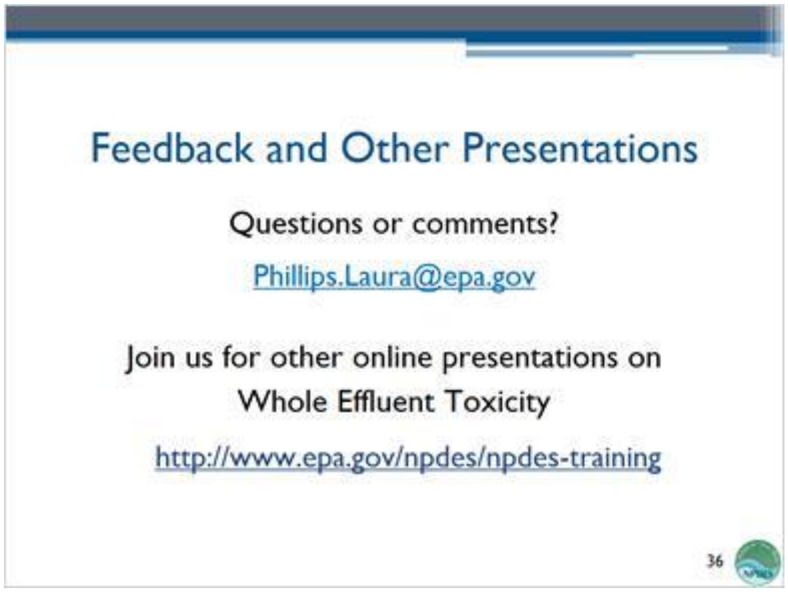
Notes:

To help confirm that TDS was the cause of toxicity, a mock effluent was prepared using known clean deionized water and salts to mimic the ion concentrations in the effluent. The mock effluent was determined to be chronically toxic to *Ceriodaphnia* in a very similar way as the actual effluent. This alternate TIE research approach helped confirm that TDS was the likely cause of effluent toxicity.

Notes:

Based on the TIE and TRE results, an alternative treatment process was recommended that would reduce the concentration of salts in the effluent but still meet all of the NPDES permit water quality-based effluent limits. As a result of this alternative treatment, the industrial coal facility was able to reduce its TDS to levels such that the permittee was able to meet their NPDES permit chronic WET limit and also decrease their treatment costs since less salt was needed for their treatment process. Hence, in this case, the TIE/TRE process benefited the permittee by lowering the facility's production costs.

Module 9: USEPA NPDES Toxicity Reduction Evaluations and Toxicity Identification Evaluations



Notes:

Thank you for joining us for this USEPA's NPDES Whole Effluent Toxicity training presentation. We hope that you have enjoyed it!

If you have questions or comments on this or any part of the USEPA's NPDES WET online training curriculum, click on the email address given on this slide to send a message to Laura Phillips, USEPA HQ National WET Coordinator.

Remember, you will find all of the USEPA's NPDES WET online training presentations, under the USEPA's NPDES training section found on the Office of Wastewater Management's NPDES website.

See you next time!