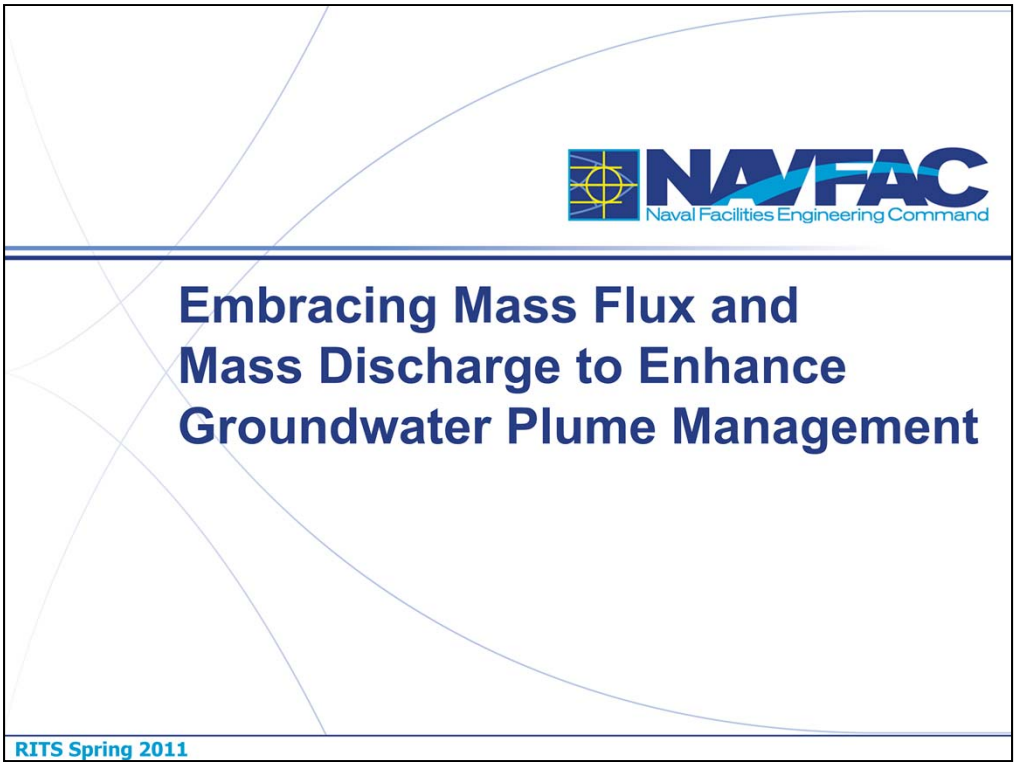

The question came up well if you can get mass out of the ground, but you can't get all of it out then what good does it do? So we thought "obviously it's good but what does it really do? Does it improve the plume condition?" Well we started saying "well obviously if we take a bunch of mass out of the source then more than likely the amount of mass going into the plume would go down." So the argument was by cleaning up the site you would reduce the mass discharge—how much mass was coming off of that source area or that site. And then we started thinking about well if we want to know that, we'll have to measure it. And if we measure it, we're probably going to really look at mass flux. I'm going to define those two terms in a minute but so we started working on trying to understand how these sites were behaving in terms of mass flux and mass discharge as opposed to concentration—which we think about all the time so the idea here is we're going to think about embracing this concept. It's another way to think about a site—another way to interpret the data—another way to think about how to formulate conceptual models and things like that--not throwing concentration out the window because that's important as well and its related, but to start to think about making use of and considering these concepts mass flux mass discharge.

Objectives of this Presentation

- Primary objective is to provide an introduction to the use of mass flux and mass discharge in site management
- Questions to address include:
  - What is mass flux and mass discharge?
  - Why these are useful metrics?
  - How can mass flux and discharge complement concentration-based measures?
  - What methods are available to measure mass flux and discharge?
  - Basic calculations of both mass flux and mass discharge
  - How to use existing site data for estimates
  - Regulatory considerations with mass flux and discharge estimates

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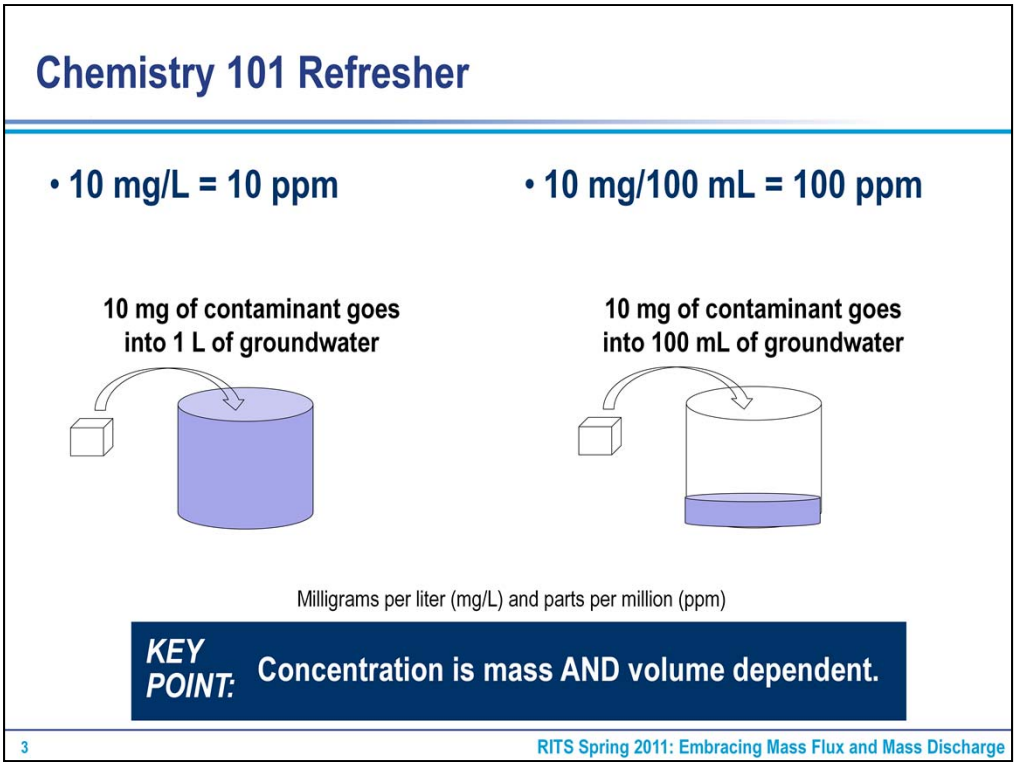
Introduce the topic, go over some basics, think about how it can be used, what are the benefits of collecting this kind of data or interpreting your data in that respect and this idea of how can we link remediation and cleanup of a heavily contaminated source area how we link that to the plume that is there obviously because mass was discharging out of that for years and we feel that the link is mass discharge and mass flux.



Alright, so to start with very simple concepts, we're all used to concentrations: 10 ppm 10 milligrams per liter well we can get that number by taking 10 milligrams and putting it in a liter of water that's our concentration concept it's a mass per unit volume—likewise we can get a different concentration by the amount of water it's in. the point here is the volume of water that this mass is in makes a difference.

Chemistry 101 Refresher (cont.)

- **Example 1**
  - Flow Rate = 10 L/day
  - Concentration = 1 mg/L
  - M_d= (10 L/day)×(1 mg/L)
  - M_d= 10 mg/day
- **Example 2**
  - Flow Rate = 1 L/day
  - Concentration = 10 mg/L
  - Md= (1 L/day)×(10 mg/L)
  - Md= 10 mg/day

gallons per minute (gpm)

KEY POINT: **Mass flux and mass discharge are concentration and flow rate dependent.**

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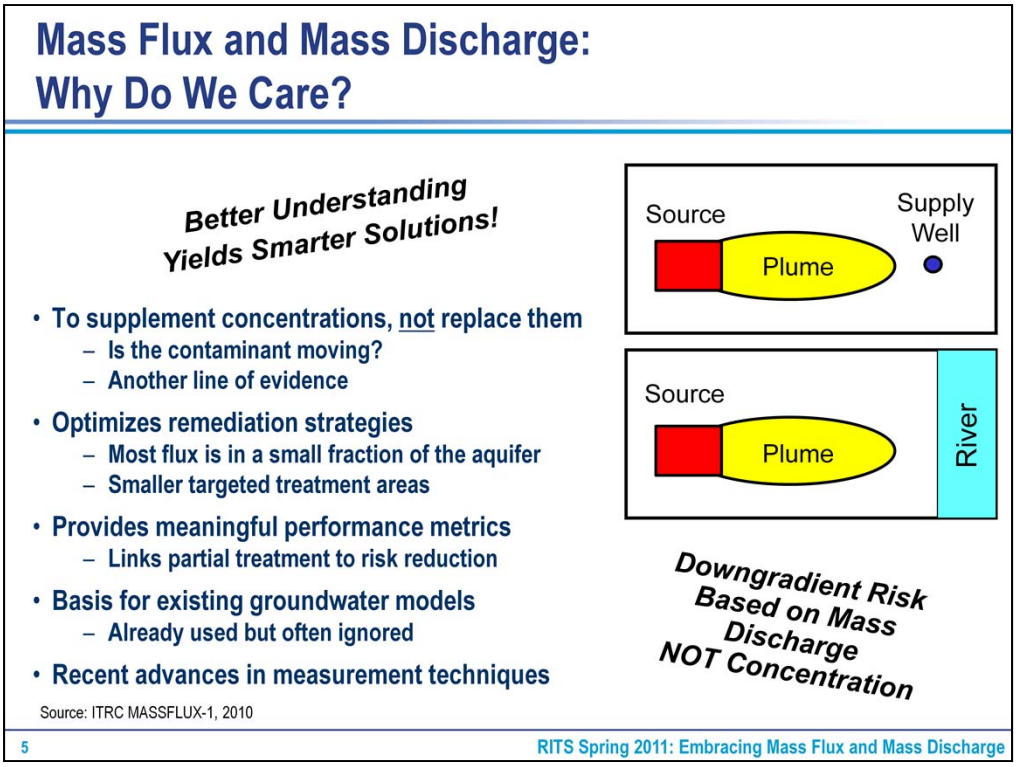
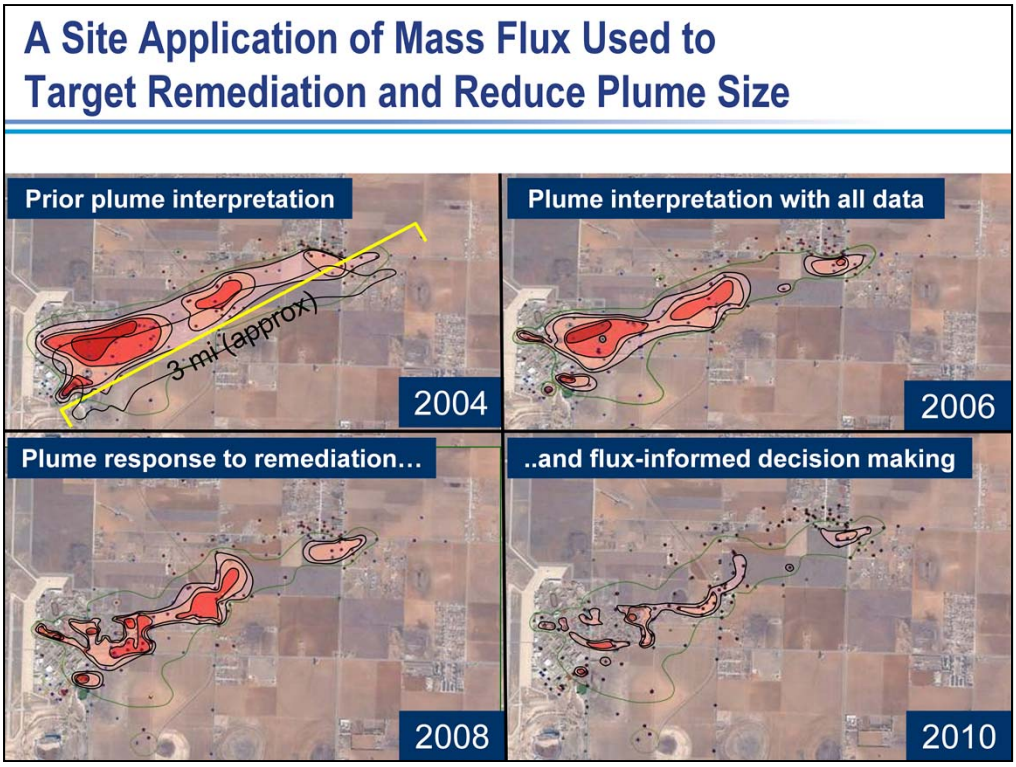
A big volume of water lower concentration, dilution really, but in the flux mass discharge world what really matters is it moving, is it flowing. Is the water migrating through your contaminated area picking up mass and generating a plume? So then we have to introduce the flow 10 L/day vs. 1 L/day, order of magnitude difference in flow and in these two systems we also have orders of magnitude difference in concentration in the opposite direction—here's the case of high flow, low concentration and low flow, high concentration. Well they both deliver the same amount of mass. The amount of mass is getting delivered to a plume or maybe to a river or a well. Well in these two cases they're the same but the flows are quite different so concentration matters but so does flow, if we don't consider flow at all the scenario I think about is a site where the concentration is way below MCLs but the groundwater velocity is almost zero. Compare that to a site where the groundwater flow is much higher even though the concentration is lower. One is going to have a very different plume than the other. So what controls that plume is groundwater flow and concentration.



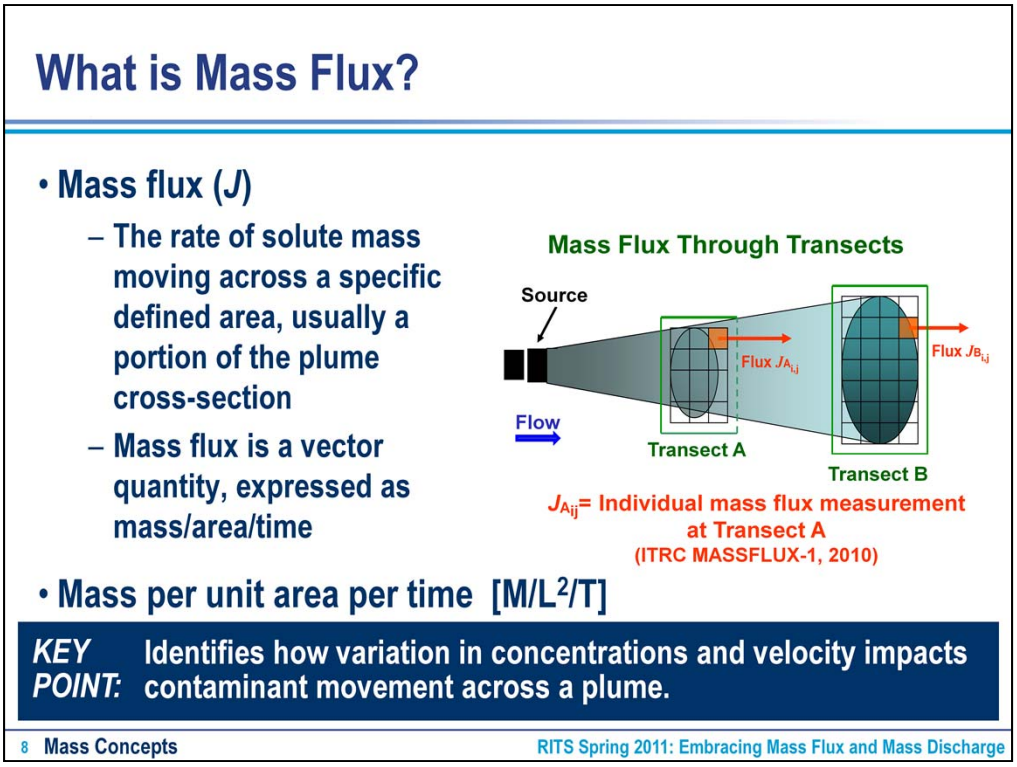
Conceptually I like to think about some region we consider the source where most of the mass is and another region really that dissolved the groundwater plume that evolved from that source area over decades probably. The threats are to downgradient water supplies, downgradient water features and the link between those or the thing that ties those together is a mass balance of the site the mass in the source, the mass leaving the source, the mass going into the plume and how fast is it moving. If you really want to know what's going to impact these downgradient receptors then we need to understand the story of the mass balance. And even another level beyond that is how has that changed over time from the day it was released to thirty or forty years later. That mass discharge has not been constant, it's been changing and, therefore, the plume reflects that. So why do we want to use this; there are several things I want to hit on several times throughout the talk I think but we can optimize our remedial strategies—we can focus on the high flux zones.



Why spend a lot of energy on low flux zones when there's a big hotspot over here you're not addressing well enough or not focusing on it enough—because that's whats going to make the plume shrink maybe, I may be getting into an MNA type mode. The main point here is that the original conceptual model may have looked something like this and we've all seen some gross scale contour plots of contaminant plumes. They're very simplistic, not highly resolved, and they're usually 2-D rather than 3-D. So we had something that looked kind of like that we knew we had a problem with some high resolution data gathering maybe focusing on what are the hotspots and what almost always happens, I'll show some examples in this talk is that the plume magically shrinks, and well the plume doesn't really shrink you're just getting a higher resolution data set and it says what your footprint is, where the heart of the contamination is or the hotspot is usually much smaller than the original imagined thing. Based on that refinement of conceptual model or refinement of where real mass discharge sites are or high flux zones then we can really begin to target remedial efforts, which was done in 2009 and this is 2010 and so the idea is that by understanding this site better, having a better understanding of where the mass discharge/mass flux is occurring then we can start having a bigger impact a faster impact on the remaining plume so that's kinda the argument that I'm going to continue to make throughout the talk.

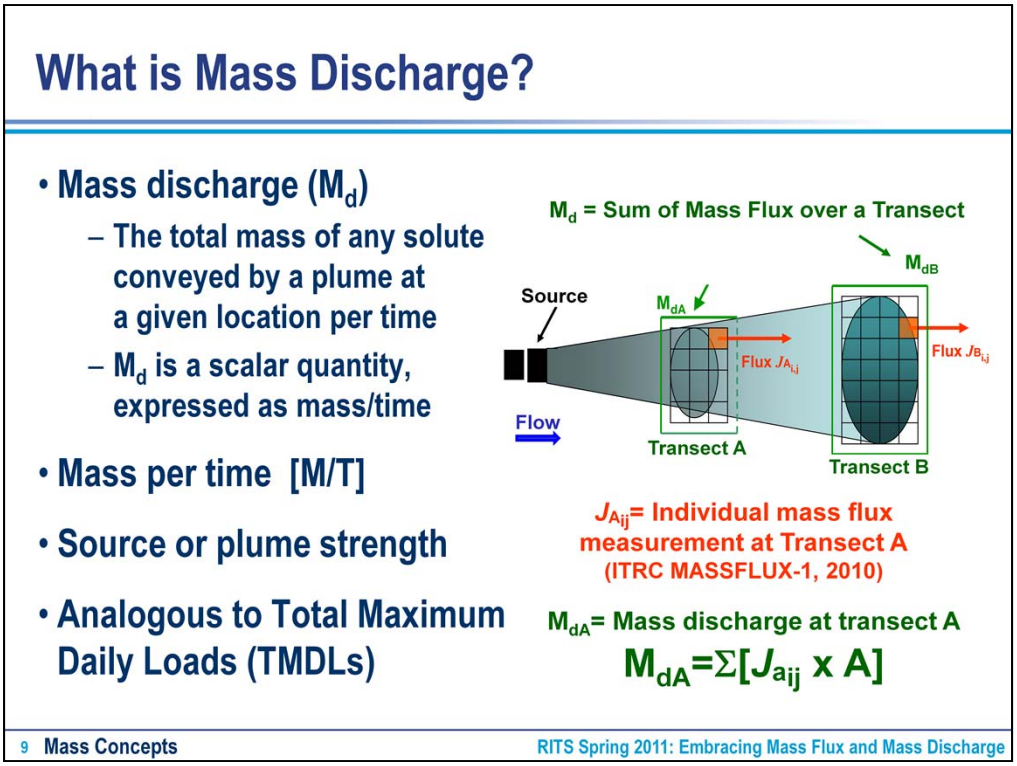
Presentation Overview

- ► Mass Concepts
- Measurement Methods
- Applications
- Advantages/Disadvantages
- Regulatory Considerations
- Case Studies
- Summary

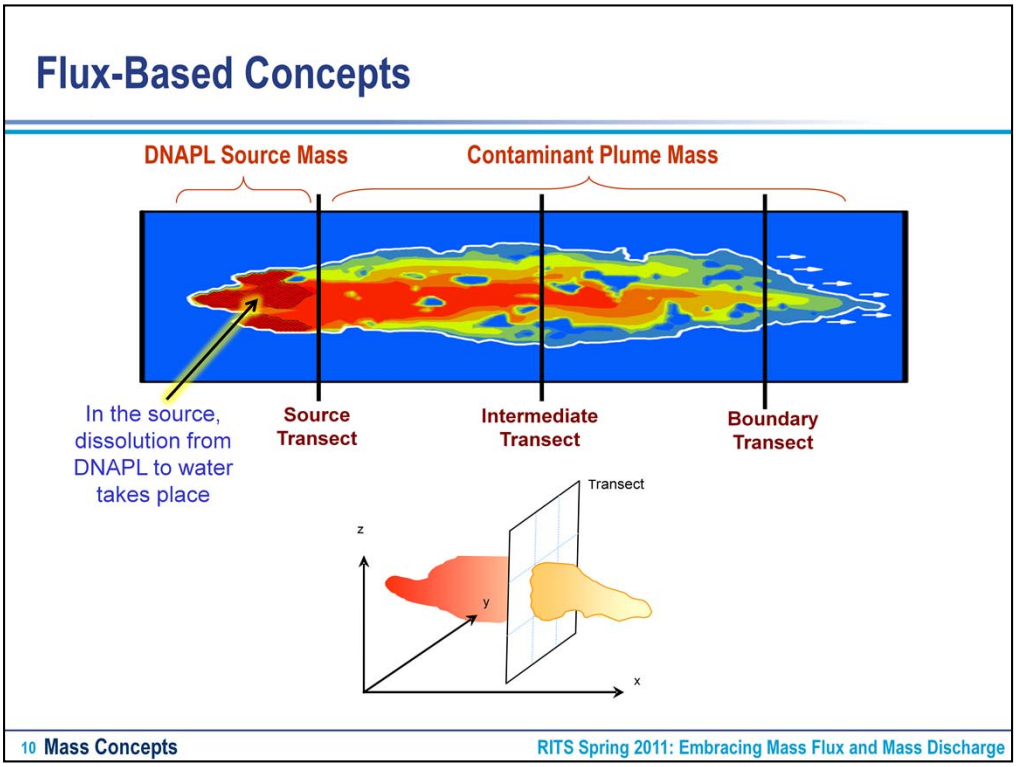


So I said I'd define these terms more rigorously definitively. These terms: mass flux and mass discharge are used sort of loosely back and forth all the time and I want to correct that even though I'll from time to time slip up and say mass flux and mean mass discharge. So we'll start with mass flux. The important thing to get our hands around is that the mass flux is how much mass is going through a unit area per time. one of the units we use quite a bit is milligrams per meter squared per day. And so that's really kind of a local measure.

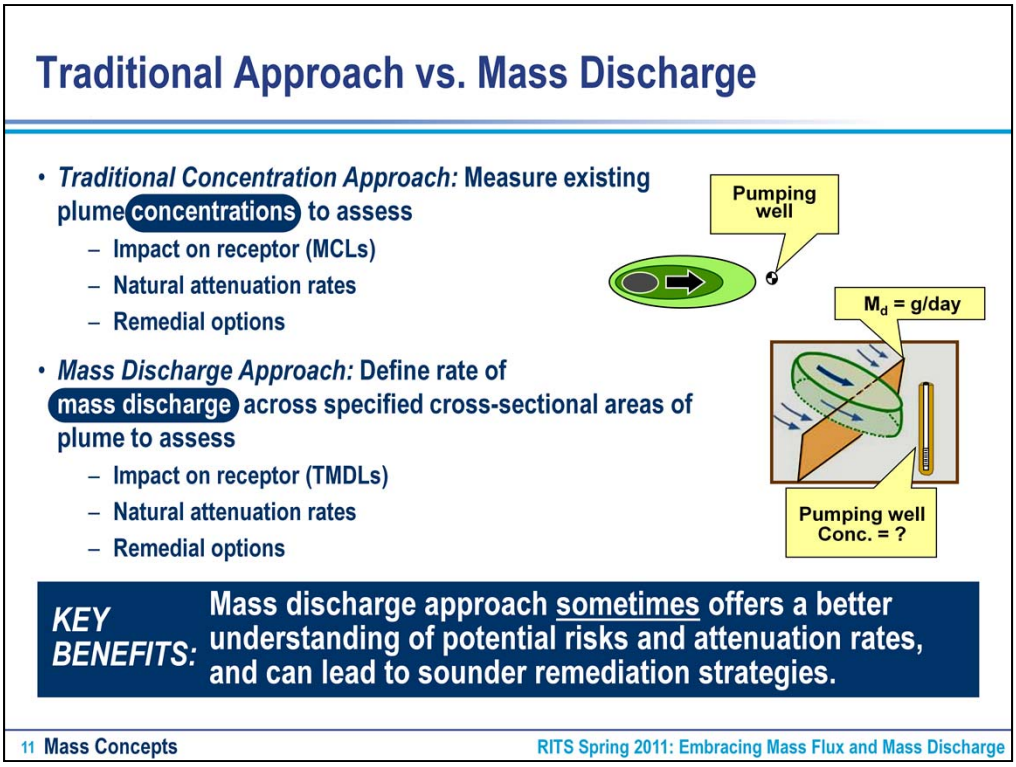
I could say the flux here is one mg per day per meter squared and the flux over there is 0.001 mg per day per meter squared. One is much higher than the other and that starts to map out the distribution of our mass flux and so we're going to think about our site as a source and mass moving through some control planes down gradient and sort of to facilitate that I want to think of our room the same way as this map. I'm going to imagine that there is a NAPL or a DNAPL in this case, a source area that you guys represent and so it's very complex. You guys might be pools, you could be ganglia, you could be a blob, you could be trapped residual, some of you might feel like a trapped residual, but there are all these complex distributions or pieces of that NAPL distribution. Why is it so complicated? Well it's because DNAPL goes down and it hits these layers and spreads out in pools and penetrates and complex distributions. We're not so worried about the details of that more worried, I am, about the fact that groundwater is flowing from behind you, its flowing through you through the area you're sitting in, the source area, and its coming out and going that way. And there's a big plume out there because of the source that's sitting here so we're really talking about the plume being the dissolved phase mass that was in the NAPL, that you represent, and is now in the large plume that is downgradient and this control plane right here I'd suggest is the control plane across the wall here and of course all the mass is going through there and it's not uniform, there's some hotspots there're some high groundwater flow zones coming through here—very complex and so there may be some hotspots through here and 80-90% of the mass is going through a small window and less and less across that distribution and of course mass flux is that area if you carved out a one square meter area right here and you'd ask yourself well how much mass is going through there per day for example and it certainly matters if the mass through here is 1 gram per day and the mass through over there is 100 grams per day but which area are you going to treat? The plume is responding to the high flux high mass zones and so what the plume is really responding to, mainly, is the mass discharge.



What's the total mass coming off of all of this source area? What's the total mass as a function of time-- that's here. And so as distinguished from mass flux, where you have a local measure, it could be high here and low there, mass discharge is something we integrate over an area so we usually talk about the plume mass discharge. In that case, we would integrate over this entire control thing. We'd just add up all the mass and then that would be the mass discharge and then you'll get numbers in terms of grams per day. [You would get] how many grams per day are coming out of this source area and going into the plume. In the dissolved groundwater, its partitioning into that, and then migrating downgradient. There may be sorbed mass in that plume as well, but in terms of mass discharge we're really talking about the movement of mass, how much of that TCE, for example, is moving in terms of grams per day. We really want people to start thinking about this and think about "what's that number for my site, the site I'm working on. How many grams per day are moving out of that site. Well why would I want to know that?" Well if you want to do any kind of mass balance and ask yourself how much mass is in the source now or was in the source how much mass is in the plume, 500 kg are in the plume 100 kg are in the source and 1 kg / day going between those two. Now you can start thinking about how that source has been behaving over time and how it's likely to behave. Predicting how it's going to behave in the future without remediation--that information can be useful. Also, [it helps in] prioritizing. If you've got a site that's one gram per day of TCE coming out of there and I say "Well there's this site over here that has 1000 g per day, 1 kg per day, maybe we might want to think about that when we're thinking about impacts, where to place our resources, and what to do first. I'll just mention that Chuck Newell has a recent paper that came out where they described distribution on sites using distribution sizes mag one to mag 10 and they really characterized that in terms of mass discharge. It's almost easier to just put it in terms of mass discharge itself—to say is this site a one kg / day site, a 1 g/day site, a 1 mg/day site, and there are sites that belong to all those categories but it's a way to put your site into perspective of sites that are out there.

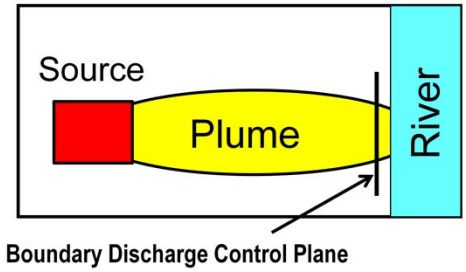


I made this point a few times: there's a source area, there's DNAPL in that source area—it could be LNAPL could be sorbed mass whatever it's a source that's sitting there, not moving, and the point is that mass is moving with the water across the source transect near the source and we could always go further down and look at transects across the plumes—maybe in the middle or towards the front of the plume--and what you can start to do is think about how the mass discharge is changing along the plume itself. Why is that useful? Well if you had natural attenuation going on, how much of that mass is being attenuated as it moves down that plume. But you've got to be careful because the mass in this plume also represents a time history of the mass discharge that came out of it. I mentioned earlier that this mass discharge is not likely to be constant over time; it's probably been decaying over time. As you move further down here, say here, this cross-section could represent the mass that came out of here 20 years ago so think about that space time continuum. We're starting to look at that in some of our CERCLA projects and you can start to think about whether you can use that to kind of infer how the mass was discharged 30 years ago. Of course, degradation makes that complicated along with other things as well.



Traditional versus mass discharge; it's not that we're trying to argue that concentrations don't matter, most of the regulations are based on the concentrations—the MCLs and such, and they're important and need to be used for understanding risk and things like that, but I'm arguing that mass discharge can compliment them by helping us start to think about the site and still look at natural attenuation rates, more importantly remedial options: what are good strategies to target high mass discharge zones, maybe be more effective at reducing downgradient mass discharge that's going to impact monitoring wells.

Mass Discharge to Surface Water



$$C_{River} = M_d / Q_{River}$$

- The Mass Discharge at the river boundary control plane can be used to evaluate the risk to surface water (e.g., TMDLs)
- Concentration alone can not assess the risk. Need to know how the contaminant is moving in ground water

KEY POINT: Evaluation of mass discharge (M_d) can increase understanding of contaminant mass movement at site and be an important component of the conceptual site model.

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Mass discharge to surface water-- if we want to know the concentration in the river its truly important that we know the mass discharge coming into that river.

Comparison of Concentration to Mass Discharge

Scenario: Compound X has an MCL of 25 µg/L. A sensitive receptor is located downgradient of a suspected source area and can receive no more than 10 µg/day of compound X.

- **Case A**
  - **Conc. = 100 µg/L**
  - **Flow = 1 L/day**
  - **M_d = 100 µg/day**
  - **M_d *exceeds* loading criterion and conc. *exceeds* MCL**
- **Case B**
  - **Conc. = 1 µg/L**
  - **Flow = 100 L/day**
  - **M_d = 100 µg/day**
  - **M_d *exceeds* loading criterion while conc. does NOT exceed MCL**

KEY POINT: **Different concentrations, but same mass discharge**

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That depends on two things: the concentration and the flow of water. So I'll take my DNAPL room I set up, and change it slightly. Now imagine there's a river running through the middle, and now there's two sides. There's a DNAPL contaminated side on this side and there's one over on this side, where flow is moving this way and discharging towards the river. If they're both the same size, have a balance of mass, and the concentrations are similar, but the groundwater flow from one side is an order of magnitude higher than this side than [the other], immediately, 90% of the mass discharge is going to be coming from this side. Why? Because the flow is dictating that. Which one are you going to target to be protective of the river? Well if you're interested in the river concentrations than clearly the one with the high mass discharge is most important. But you're going to say well what about this one that lasts 10 times longer? Well in terms of reducing concentration in the river, we'll always focus on high flux site or zones within a site.

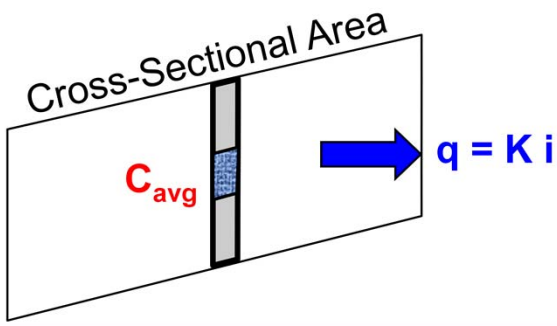
Another simple calculation is this: say a site has 100 ppb vs. 1 and flows alternating by two orders of magnitude. Again, it's mass discharge that is determined by those two parameters and so the point being that a site with very low concentration could still be delivering comparable mass, it really depends on what's going on with water flow—groundwater flow, in this case. So while groundwater flow is important, darcy's law is important, and the flow within that is related to hydraulic conductivity and the gradient, and so if we could have some measures of that, we can use that to estimate darcy flux, we may take samples from monitoring wells and such and we could estimate an average concentration in an area and then we can calculate the mass flux.

Relating Mass Flux to Concentration?

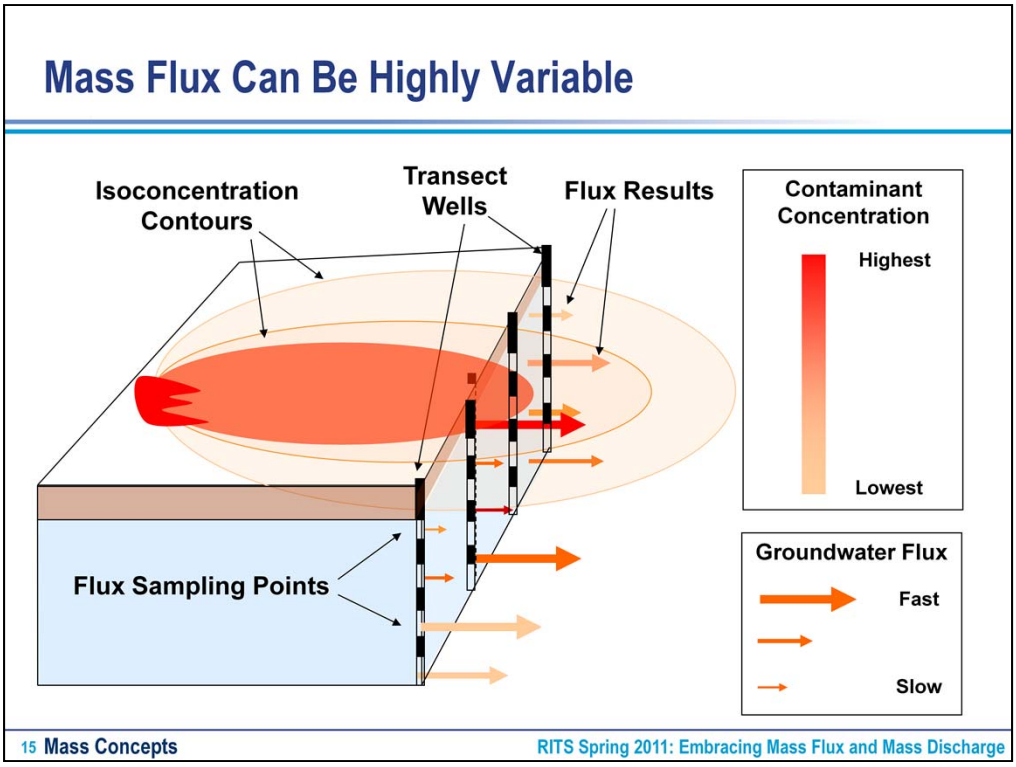
1. Specific Discharge: $q = K \times i$ [L/T] or [$L^3/L^2/T$]

2. Average concentration: C_{avg} [M/L^3]

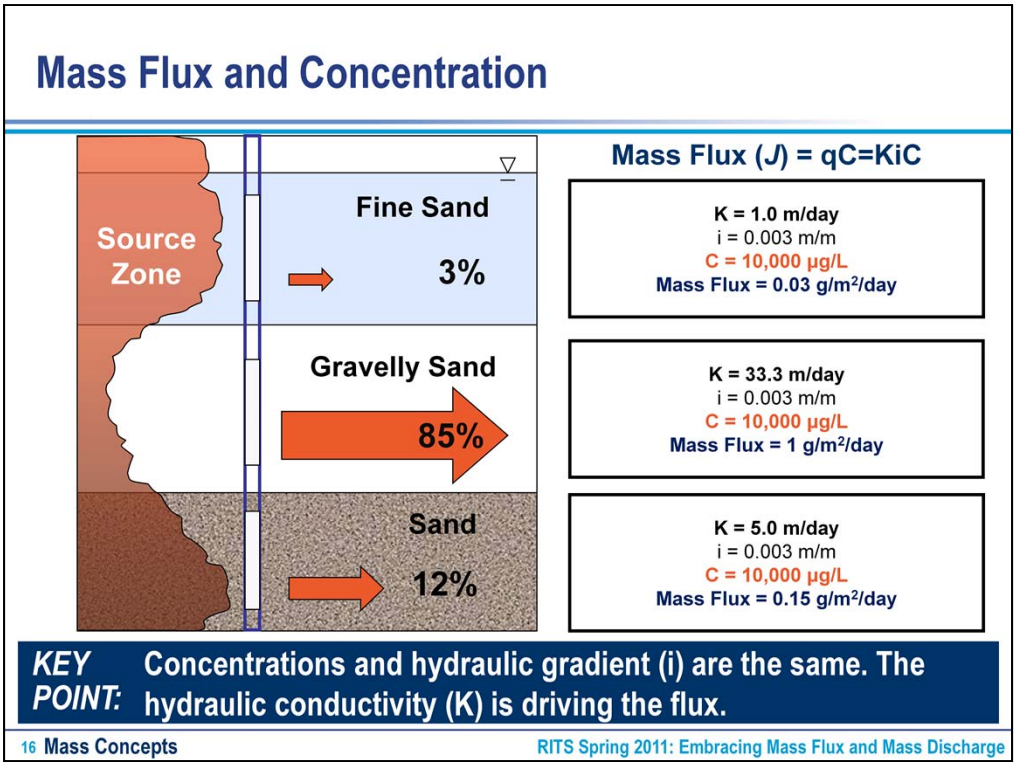
3. Mass Flux: $J = q \times C_{avg}$ [$M/L^2/T$]



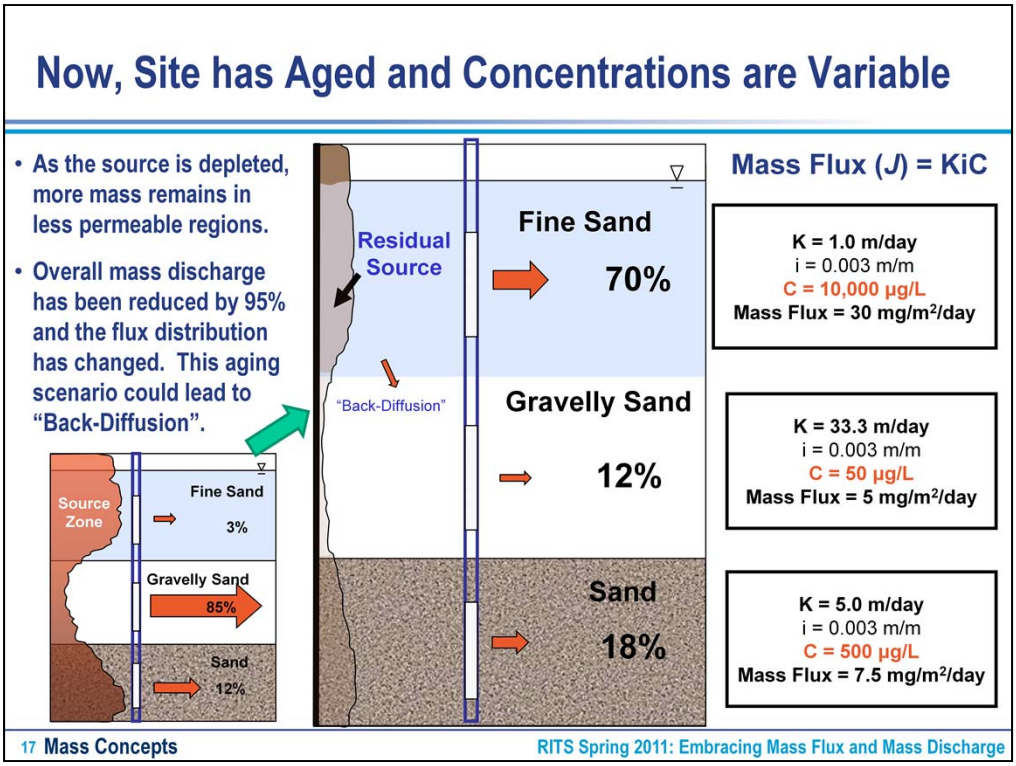
One equation that we should get at least a little bit comfortable with is darcy flux times concentration gives mass flux which is in units of mass per unit area per time. so I'm going to show a few calculations with this later on.



I mentioned this a few times already mass flux is not a constant, it will be—more than likely—variable across the control plane. Across the control plane of this room, we won't expect to see uniform conditions, there's probably some local hotspots. Why are they high flux zones? For a few reasons, the concentration is probably high and the flow is also probably pretty high. But there may be other zones out there, where we have high groundwater flow but low concentration so we don't really need to worry about that area, it may be seeing high flow but it it's a low concentration so it doesn't really matter. What we're concerned about are the larger highly colored areas, the high flux zones maybe is where we should target our remedial efforts.



Here's another nice example of a layered system, we've got a three layered aquifer model: a fine sand, a gravelly sand, and a regular sand. Those will have different hydraulic conductivities: one meter per day, 33 meters per day and 5 meters per day. Three hydrogeologically distinct layers with different hydraulic conductivities—all of them have the same gradient. In this case, I'd like to think of it as a site that hasn't aged too much, in other words a young site, and the concentration in all three layers is about the same. So it's all 10,000 in this case. You can do the simple calculation and determine the amount that comes through in each case, each of the layers 0.031, 0.15…. there's no question that the major zone of concern is the gravelly sand with reasonably high concentrations. If you've got high flow and high concentrations, that's going to carry, in this case, 85% of the load. In terms of the plume generated by this, it's really being controlled by that high flow zone. Again, I think of this as a young site because this isn't going to last—you can't maintain that [high concentration] forever and so more than likely it's going to get depleted.



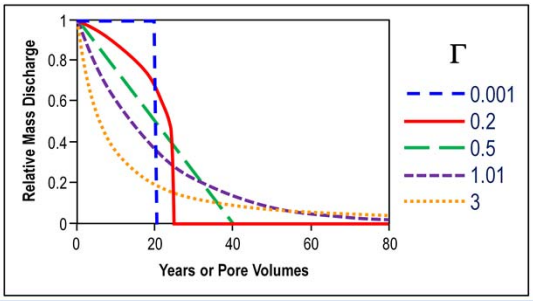
The concentration has been depleted from 10,000 down to fifty. Now that's a lot but if there was high flow through there and a finite amount of contamination, eventually it will decline. Everything else is held the same—hydraulic conductivities, but now the concentration's different. Still 10,000 back in that fine layer that hasn't been removed by dissolution, this one has been substantially reduced and this one has been moderately reduced. We'll do the same calculations to determine the mass flux and we'll see the opposite—the fine sand is now the main culprit, the main zone that's delivering mass. Now I see this as an aged site, an older site where most of the high flow zones have been removed by dissolution—and now we're down to this low permeability recalcitrant mass remaining. We could even talk about a scenario of back diffusion where this low permeability unit that has diffused into that mass as a result of the original spill and now is coming back out, because the gradients have reversed, and the mass is coming back out into a higher flow zone. I'm starting to see some evidence of that at some sites where the persistence of the mass discharge of that plume is being influenced by those low permeability zones that release mass over time. This mass discharge is probably not constant over time.

Changes in Mass Flux and Discharge Over Time

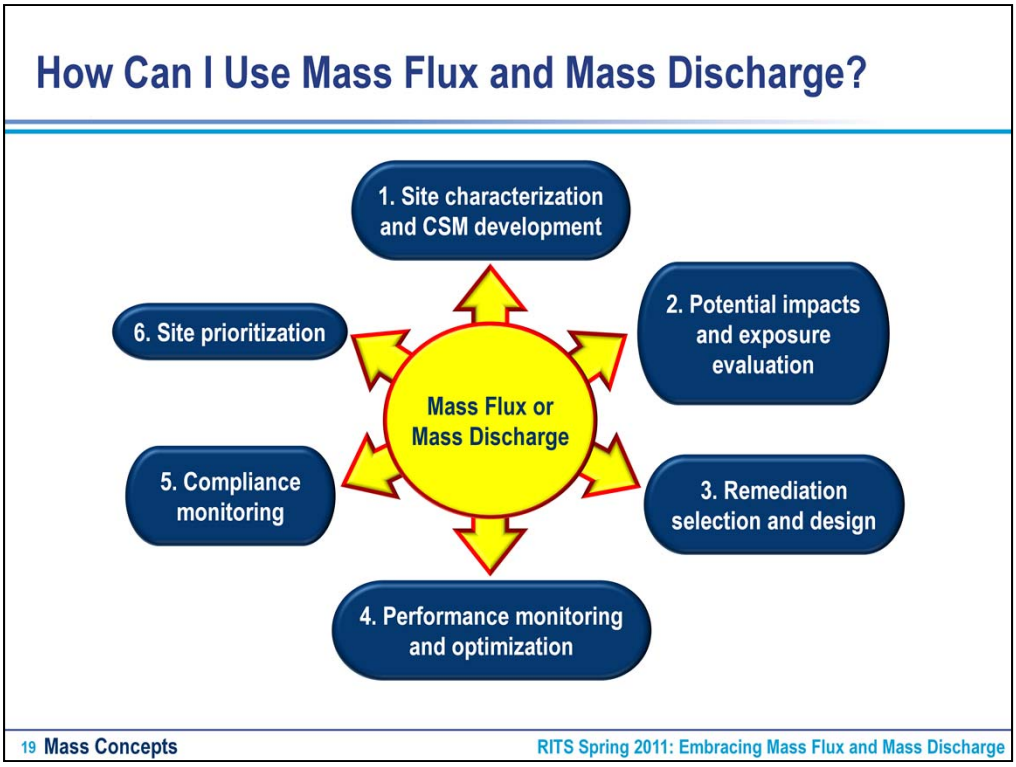
The **Source Strength Function** at DNAPL contaminated sites is a function of the architecture of the DNAPL source area and the complexity of the water flow field.

Source Strength Function Models

Power Law Model
Note G = 1 is exponential



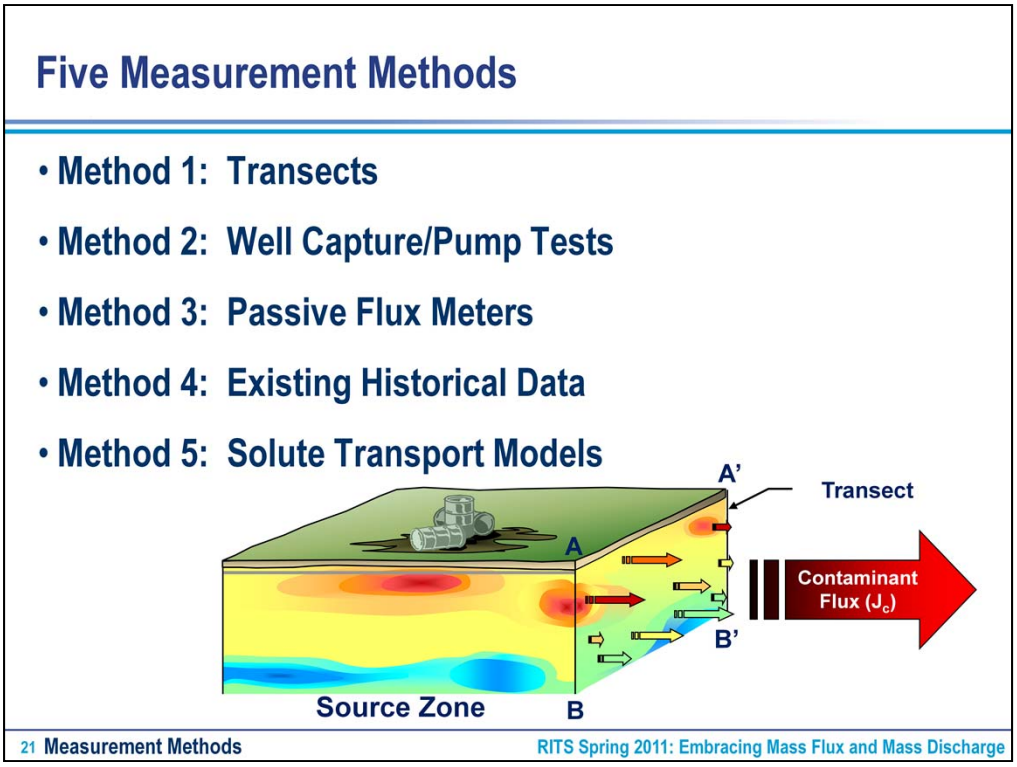
We've developed what we call "source strength functions" that describe how mass discharge changes over time, simple models--not to take into account the complexities of the DNAPL structure—but simpler ones that kind of act as an analog for more complex processes. This graph shows a power law model—raised to an exponential power that is good because it gives a wide spectrum of site conditions. One of them is a zero model a power zero essentially says that the mass discharge was constant for a time and then went to zero. That's not too realistic but some sites behave like that, maybe you have a large DNAPL pool and it's just going to sit there and release mass at a fairly constant rate until the pool is gone. More realistic are some exponential curves that are more of an exponential decay. You start with a high mass flux and it decays asymptotically towards zero, it bleeds forever. We are, through a serta project, trying to see if these models are reasonable for DNAPL sites and so we're trying to fit these to historical data sites from some of the past DNAPL sites. TCE is mainly of interest, other DNAPLS that are higher solubility than TCE are also of interest because we want sites that age, the PCB solubility limit is low they just don't age they age very slowly, so conceptually I'll mention the age of the site: we've kind of defined this idea of the age of your site. Is your site 10% old? That means that ten percent have gone or is it like 95% aged. We've got a couple of sites where over 90% of the mass has already left the source zone, the plume is miles long—that's a highly aged site: you mainly have a plume problem at that point. There's source still left but it's much smaller than historically. So I've got a pitch to you, if you've got a site that has historical data with good groundwater concentration trends with time—ideally if you've got 20 or so years of data I would be interested in talking to you about that.



So how can we use mass flux and mass discharge? The ITRC came up with six methods that would be useful to have mass flux data. One is changing the conceptual site model, I just mentioned a few minutes ago, how old is your site? That would help define your conceptual model. Is it still delivering a lot of mass to the plume or has it decayed substantially. Remediation selection and design: if you know something about the mass flux distribution across the control plane, than you may be able to target some remedial control technologies--there may be some technologies that are better than others in reducing that mass discharge. Linked to that is performance assessment. If you have a mass discharge and its 10 g / day and then there's remedial effort and you measure the mass discharge and its 0.5 gram/day, that a direct measure of the impact you have on the plume. Will the plume go away? That depends on whether 0.5 gram is enough, but that is a performance metric. Rather than just looking at concentration look at mass discharge. Prioritization, I mentioned that as well. Compliance monitoring, I mentioned that as well is another use for that data although I think we're a ways from that. If you're going to want to quantify mass flux mass discharge at a site we'll need some techniques to do that.

Presentation Overview

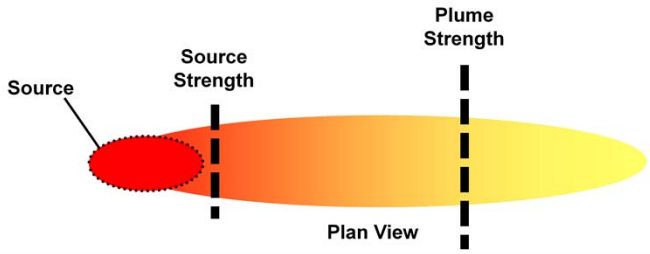
- Mass Concepts
- ► Measurement Methods
  - Transects
  - Well Capture/Pump Tests
  - Passive Flux Meters
  - Existing Historical Data
  - Solute Transport Models
- Applications
- Advantages/Disadvantages
- Regulatory Considerations
- Case Studies
- Summary



We'll go through 5 methods that are out there for quantifying or getting that information. The first method I'll call the transect method. The transect method is just what it sounds like; define a transect across the plume and you've got two of them and the source stream and maybe a mid plume control plane transect.

Method 1: Transects

- Permanent or temporary installations
- No special type of well or sampling points needed
- Use longer single screen wells or multilevel observations
- Approximately perpendicular to groundwater flow
- Hydraulic conductivity from pumping test, slug test, or soil type



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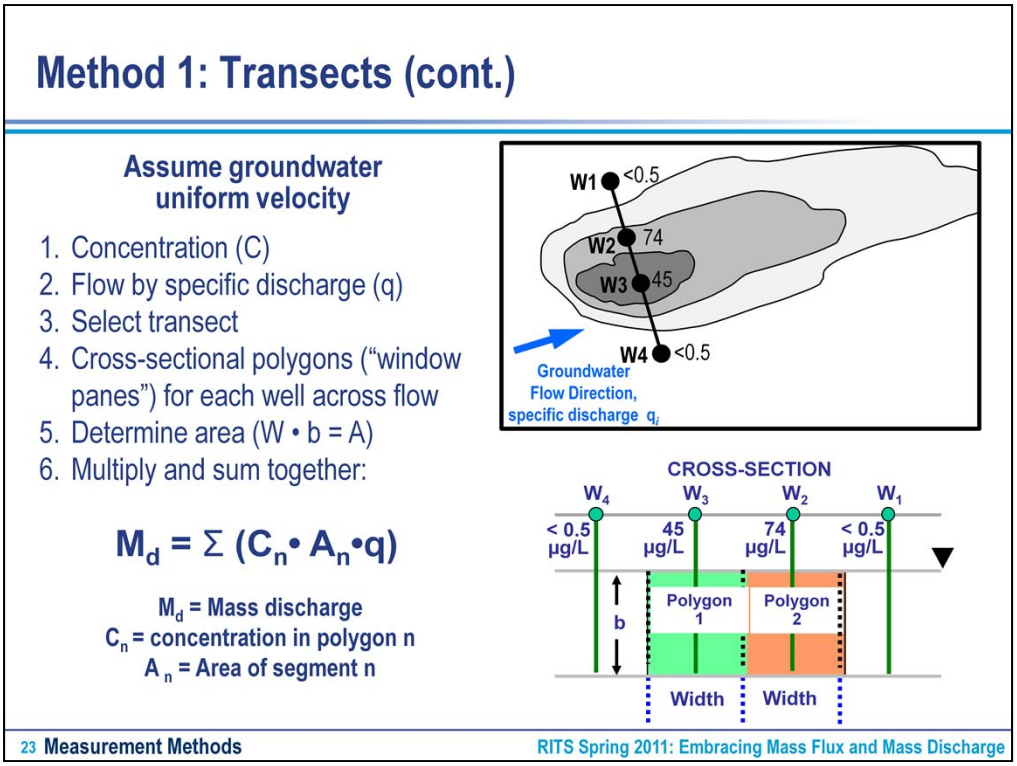
There are several ways you could do it: you could use a series of wells across that, multilevel samplers approximately perpendicular to the flow, they could be wells approximating the transect of interest—they don't have to be perfectly in a line.



And then we could define areas through that. So say we have four wells across the plume area. We collect groundwater concentrations from those wells and, conceptually, we think about the cross-section across those four wells and we define an area, a polygon, that that well represents, obviously it'd be the midpoint of the wells and vertically the screening intervals or the extent of the water table of the aquifer down. Well each of those polygons become the area through which the mass is moving and the concentration and area would be used along with the groundwater flow. So we would need to have some idea of the hydraulic conductivity and gradient. It'd be great if we could do that well by well but maybe more realistic is a single groundwater discharge value across the transect but it allows you to calculate the mass discharge by breaking it into pieces and then summing it up so it's easy.

Method 1: Transects (cont.)

- Pros
  - Commonly used – many applications
  - Direct measurement
  - Extension of accepted technology
  - Can use existing wells (if the wells form a perpendicular transect)
- Cons
  - High resolution data can be costly
  - Calculations can be time consuming

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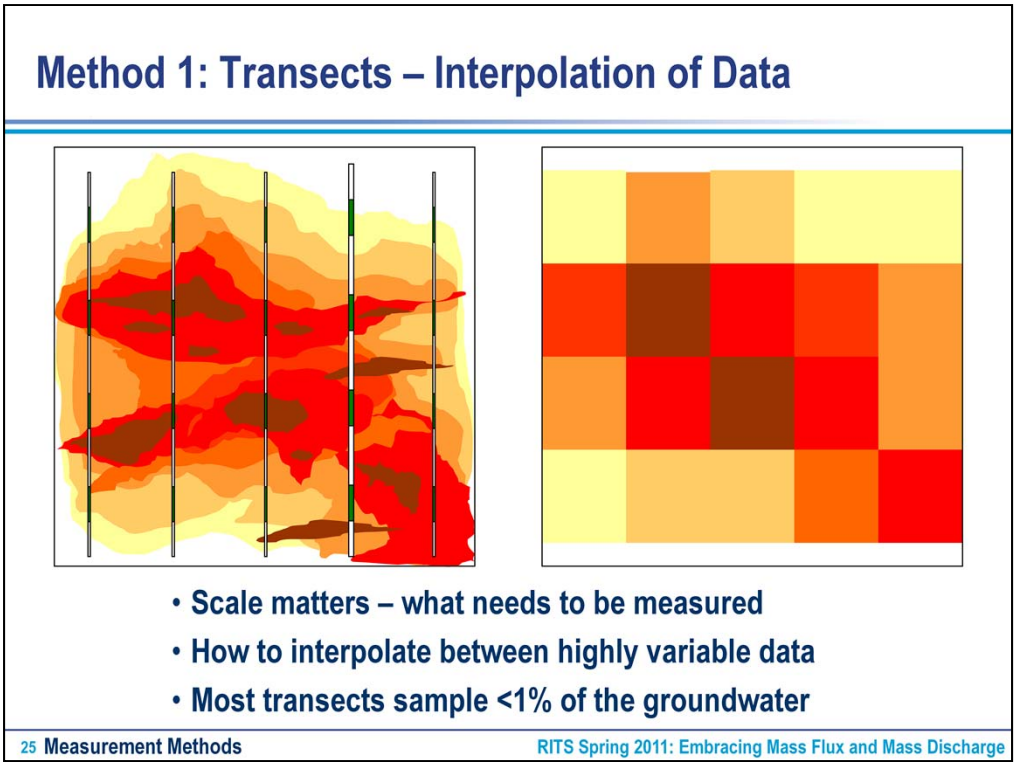
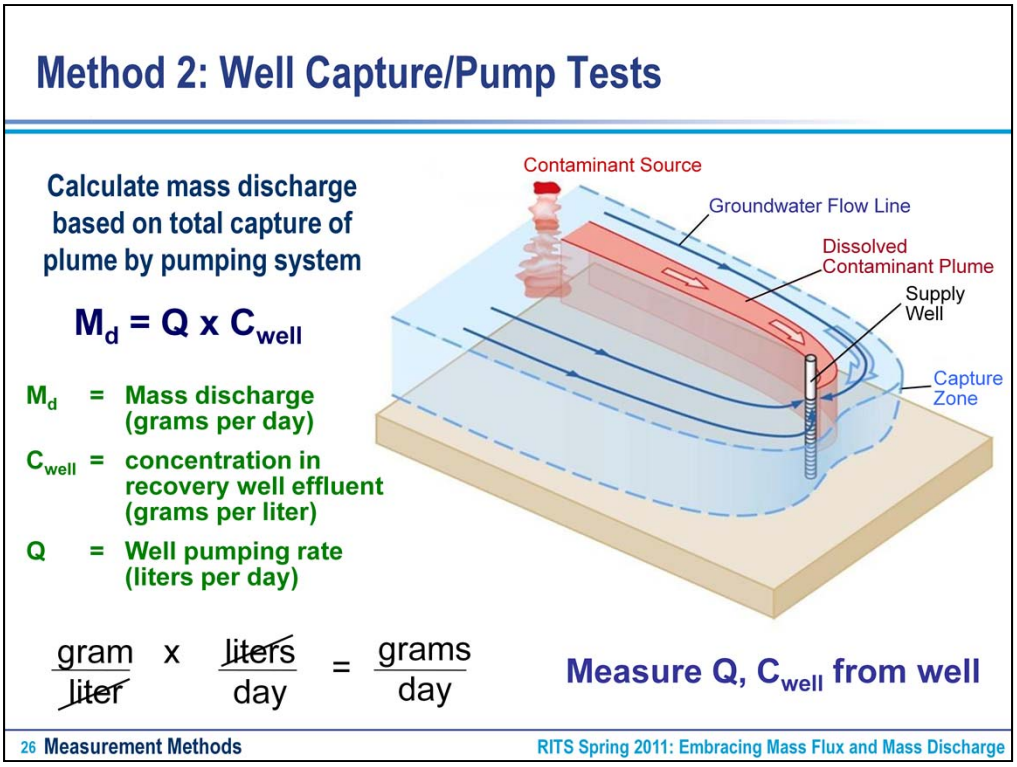
Usually a lot of sites we're looking at there's enough wells to create a few transects and so the uncertainty comes with how much data you have. If you're using existing data you may not have enough to get all that accurate but you can go out and get more data, but of course there are costs associated with that. This is, conceptually, the idea of getting more data and that depends on details of what's going on in a transect—is that important? Do we need to have multilevel data information or are we happy with sort of a grosser scale? It depends what you'd like to do with it. Do you want to use this information to look at the larger scale plume and linkages and such? Then a coarser scale is probably okay, but if you're going to try to target and really go after some of that DNAPL pool areas or high flux zones, you'll probably need some higher resolution.

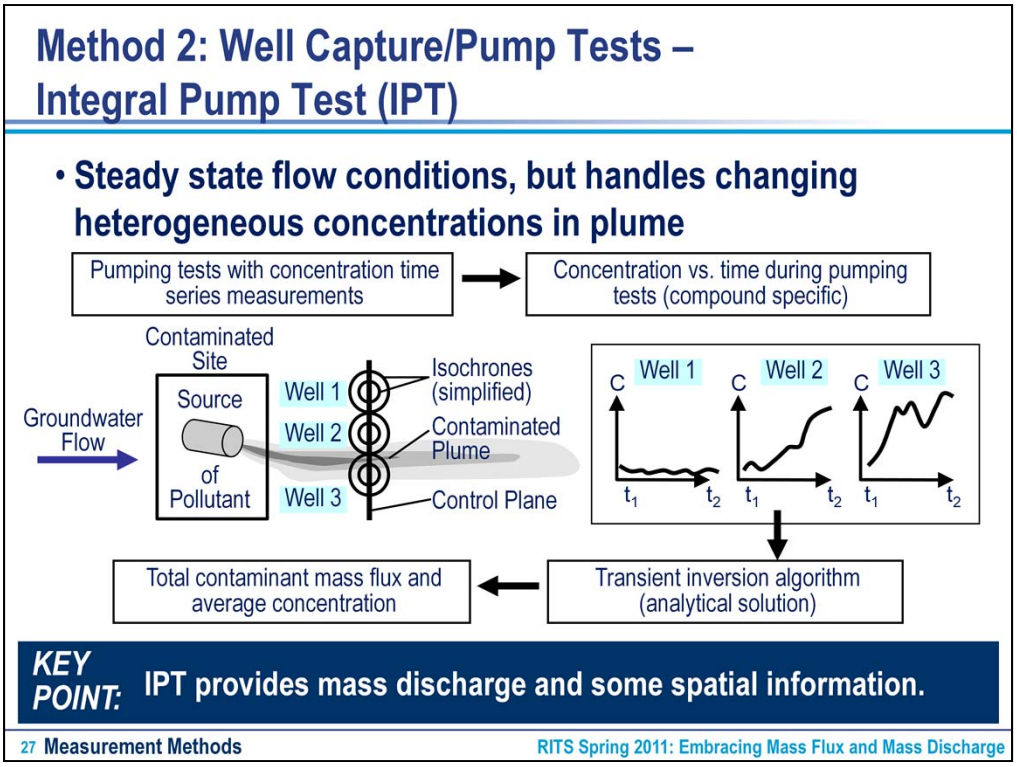
In any case we rarely sample very much of it.



If you do the calculations, it's scary. We sample hardly any of the aquifer. We're doing interpolations across these large scales because you can't afford to go out there and collect 10% of the data--it's just not possible.



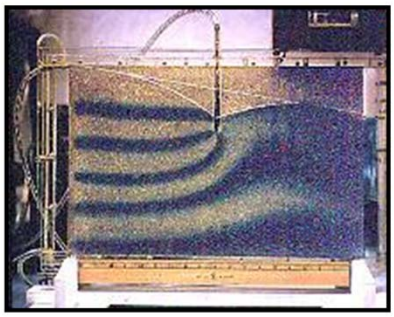
A second method is the well capture method. This is an actively pumping method, where you have a long term pumping well, where you've reached a condition where the contaminant source is delivering mass and you're capturing it. So if you've got a pump and treat that's been going on for a while, then this is an ideal scenario for the mass discharge calculation. You simply take the flow coming out times the concentration and you'll get your load coming out of there, your mass per unit time. A lot of sites don't have this and it's not too practical to put it in and start pumping because it's going to take years to reach capture but this is an option for some sites.



Somewhat more practical is the integral pump test. The integral pump test is where we put in or use existing wells, perhaps we have three or four wells across a plume, and pump the wells over a shorter timeframe maybe 2-3 days over a few weeks and we collect some concentration data, this will tell us what is going on with the plume. This one here started a bit low and came up then this one started a little bit low and came up, that is saying that they're pulling water in from something that's between the wells. You may have missed this if you'd just taken a regular groundwater sample, but by taking a big sample you've actually discovered that that mass is there. And there's some techniques that are out there to estimate mass discharge at sites and you do get some spatial knowledge of what's going on.

Method 2: Well Capture/Pump Tests (cont.)

- Pros
  - Fewer wells
  - Better integration of flow and concentration data
  - Can use existing pumping system

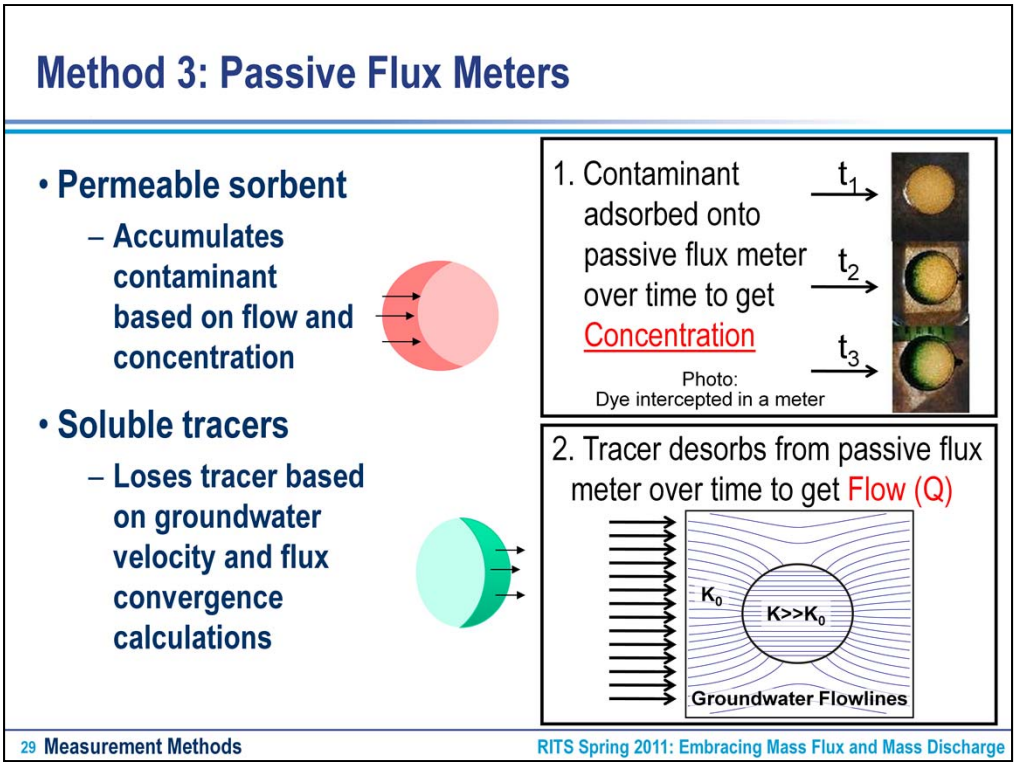


- Cons
  - No mass flux data HVR42
  - Large volumes of water that need disposal/treatment
  - Possible to change plume characteristics
  - Difficult to assure full plume capture

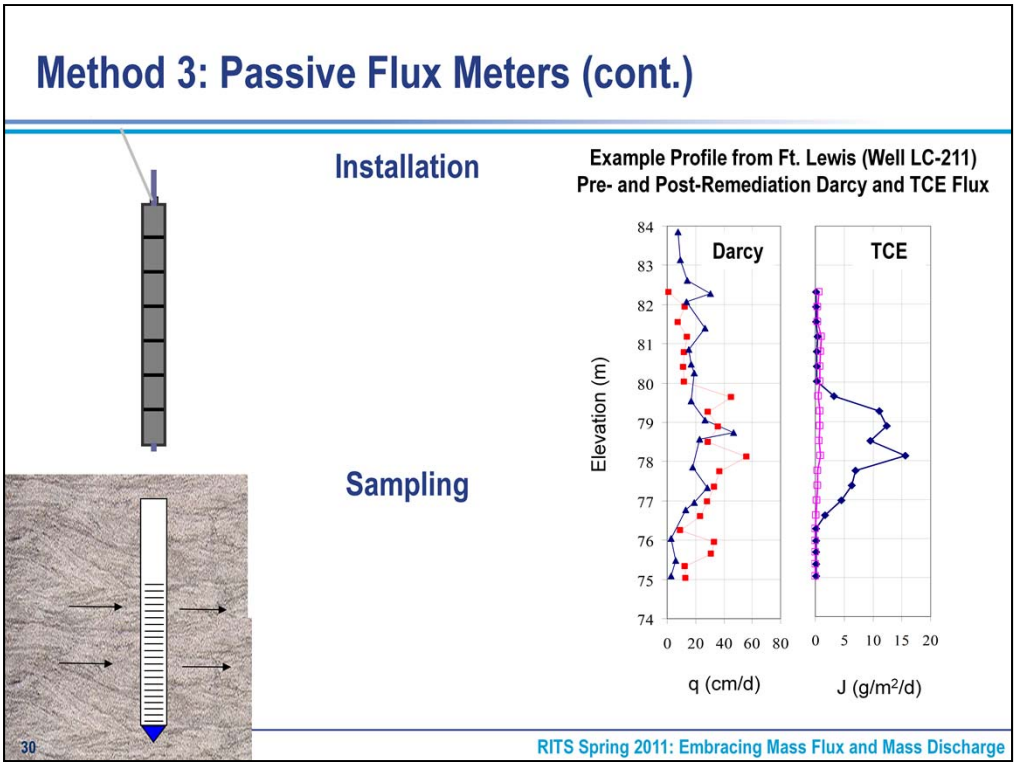
The big pro is you don't need as many wells, it integrates, you don't miss hotspots, the biggest con is disposing of that water, and it may or may not be that big of an issue it depends on the sites.

Slide 28

HVR42 Make sure to explain this con.
HVR, 4/5/2011



The third method is one developed at the University of Florida, it's called the passive flux meter, a sorbent, typically activated carbon, is put into a well screen and as its in the well screen it traps contaminants on the resin and we also put tracers on there we took a suite of alcohol tracers with different characteristics so if we lost 50% of that tracer we can tell how much groundwater flowed through there.

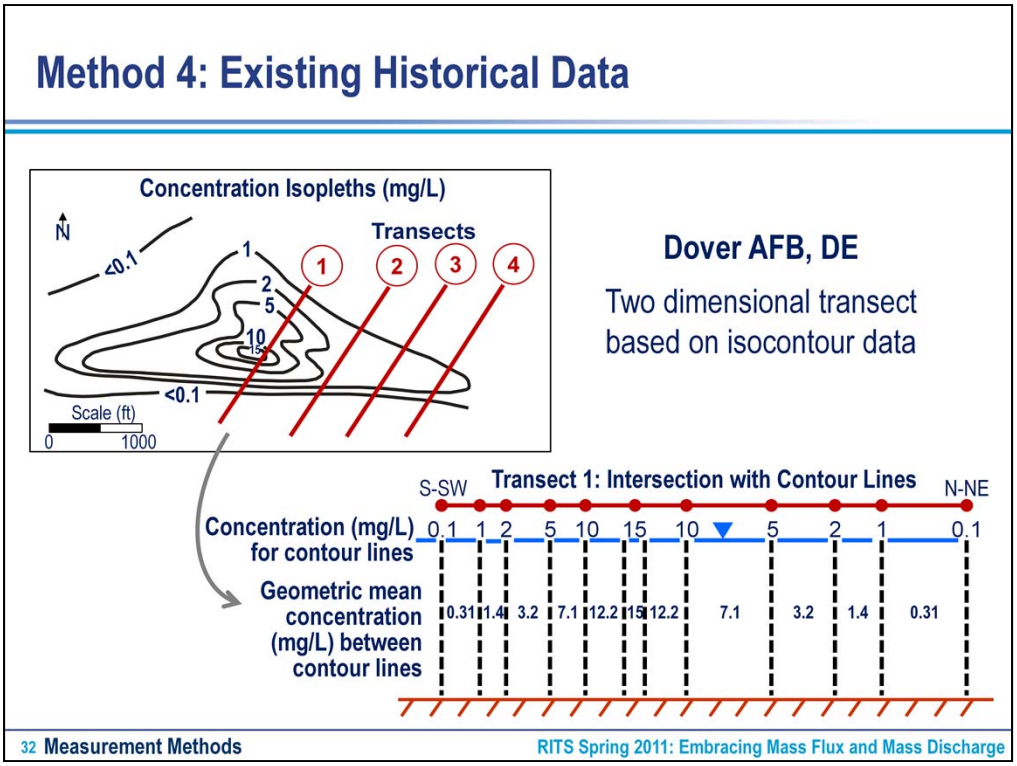


It's calibrated to determine that piece of information. I brought a prop, I brought a mini version of this. This is one foot long--these are typically 5 feet long and we would go up to a well put it on top and push it in down into the screen interval you're interested in, leave it there for about two weeks, and then pull it out and take a measurement of how much of the tracer is there and how much TCE is on the carbon. That allows you to calculate groundwater flow and mass flux. So we get profiles from that. It has a retriever cable. So you can sample that at any interval you want and you get individual profiles that go through the well screen and you can see some type of a finite high flux zone so that kind of gives you a vertical resolution of where you'd like to target and often they're associated with areas where the DNAPL sits and resides.

Method 3: Passive Flux Meters (cont.)

- Pros
  - "One stop shop" for both flow and concentration
  - Provides vertical profiles
  - Easy to install in the field
  - Minimal waste generated
  - Vendor available to implement this method
- Cons
  - Some method-specific issues (lower measurement in pushed wells, slight biodegradation of tracer at one site, competitive sorption under some conditions)
  - Relies on well convergence calculations

We do get Darcy velocity as well and its nice because you're getting flow and flux. some issues with degradation tracing is where you have low flow rates and want to leave it in for longer you have issues with degradation but the typical time is 2 days to 2 weeks, a pretty robust timeframe

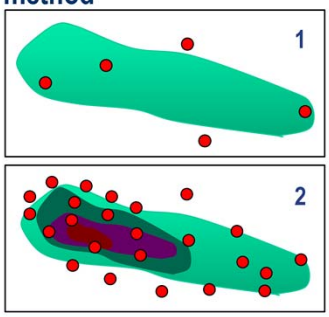


You can use historical data similar to what we talked about in the first transect method but you're going to use the contoured data set.

Method 4: Existing Historical Data (cont.)

- **Pros**
  - **Does not need special field study**
    - Can use existing, historical data from existing monitoring system
  - **Limited additional expense**
- **Cons**
  - **Wide range of opinion about usefulness of this method**
  - **Can be inaccurate if plume map is built with only a few wells. For example consider:**
    1. Gas station site with 5 wells throughout entire plume
       - Not likely to provide high quality mass flux/mass discharge data

       versus
    2. Well-characterized site with 40 wells in source zone
       - Likely to provide higher quality data



Now this is fraught with problems and we all know how poor some of these contour packages can be but it's a useful approach to get estimates to see how a mass discharge is changing—whether we're getting attenuation through a plume but it's really the same approach so I won't go through in detail, but it's the same where you look at the concentration through the range and each window represented by each data point across there and again you're going to take this and you're going to add all them up and the sum total is the total mass discharge. There are tool kits, one developed by EPI as well. Historical data, one of the problems is you may not have much and you can't really do much about that but there are some where you have quite a bit and you can really do a good job with estimating mass discharge according to this approach.

Method 5: Solute Transport Models

Using computer models:

1. Calibrate model
2. Get flow and concentration data across transect

DISSOLVED HYDROCARBON CONCENTRATIONS IN PLUME (mg/L at Z=0)

Transverse Distance (ft) ↓ / Distance from Source (ft)	0	32	64	96	128	160	192	224	256	288	320
100	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
50	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0	12.021	7.387	5.927	5.206	4.742	4.392	4.101	3.841	3.595	3.352	3.099
-50	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
-100	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
MASS FLUX (mg/day)	9.1E+3	9.8E+3	7.8E+3	6.9E+3	6.3E+3	5.8E+3	5.4E+3	5.1E+3	4.8E+3	4.4E+3	4.1E+3

Time: 6 Years Target Level: 0.005 mg/L Displayed Model: Inst. Reaction

Model to Display:
- No Degradation Model
- 1st Order Decay Model
- Instantaneous Reaction Model

KEY POINT: Models integrate flow and concentration.

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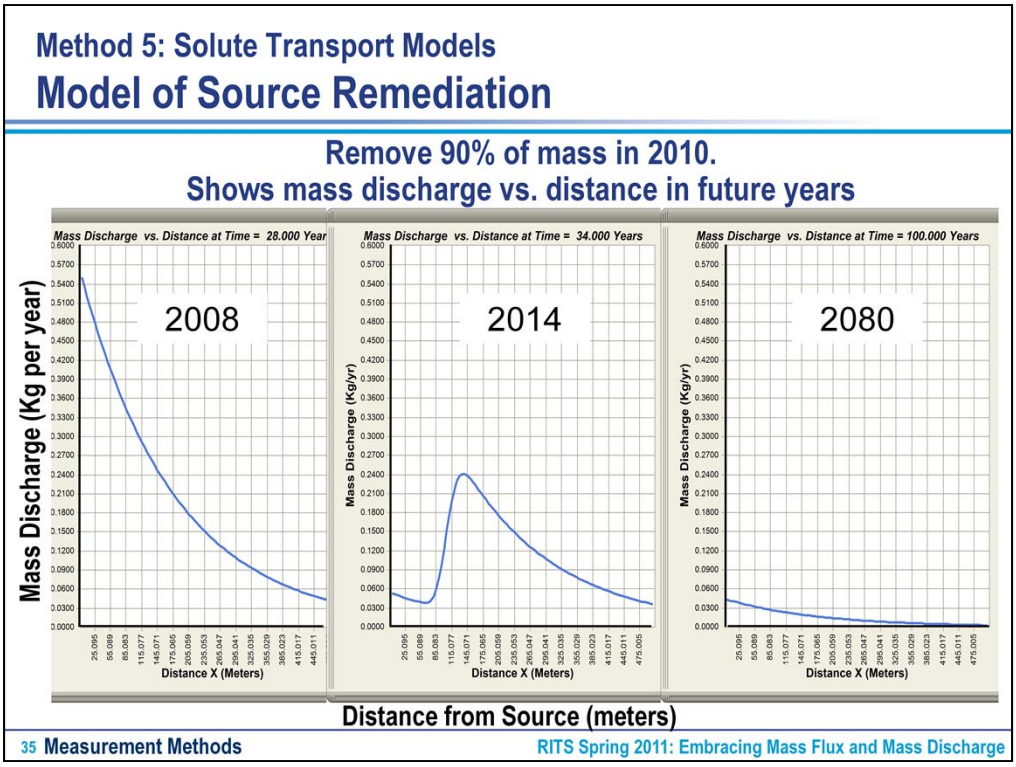
The fifth and final method is to use groundwater flow models—bio screening is an example-- if you have applied models to the site to try to match data then you're really doing the same kind of thing and really doing the same as the previous, you're taking a model and backing out the mass discharge. This is something out of that mass flux toolkit: it's just a spreadsheet where you add up the windows of discharge. This says mass flux but it's really mass discharge because those terms are used interchangeably all the time.



Another program that's out there is REMChlor and if you look at this especially if you deal with DNAPL sites, its more of a screening model, that can predict the mass discharge as a function of the plume axis down the center of the plume.

Method 5: Solute Transport Models (cont.)

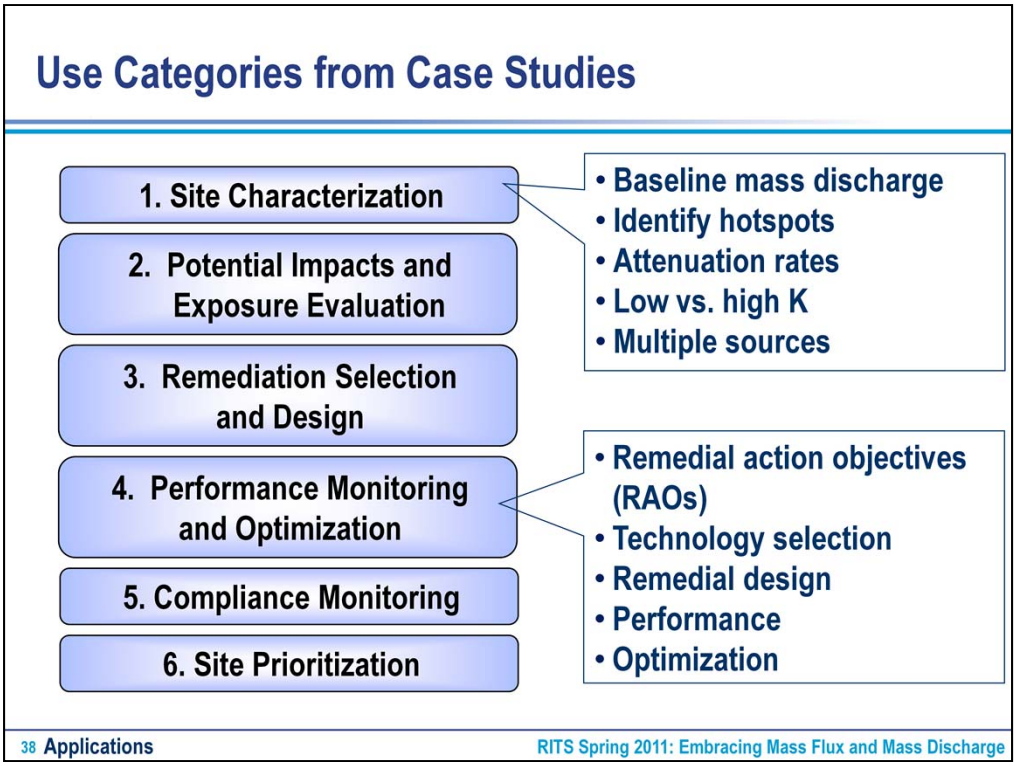
- Pros
  - Does not need special field study. Can use existing, historical data from existing monitoring system
  - Models are designed to combine flow, concentration data
- Cons
  - Helpful to have experience/training in using models
  - Need good data – both flow and concentration data
  - Amount of data depends on what information is being used for

And one of the best things it does a really good job of is if you go through remedial effort is you can understand the plume progression in response of removing 90% of the mass and use it to predict forward.

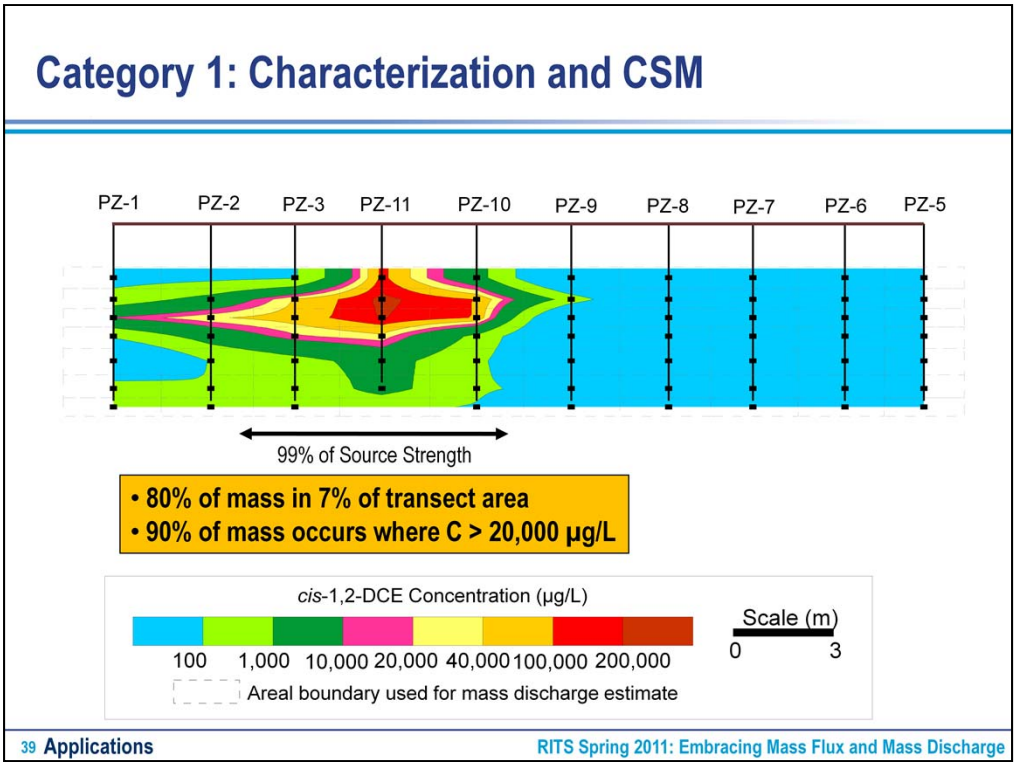
Again, this is geared toward the removal of source mass and oriented for mass discharge in DNAPL contaminated sites. Another thing it has in it—the power law that I mentioned with a gamma power term, not too many models have that but this is forward thinking in that sense.

Presentation Overview

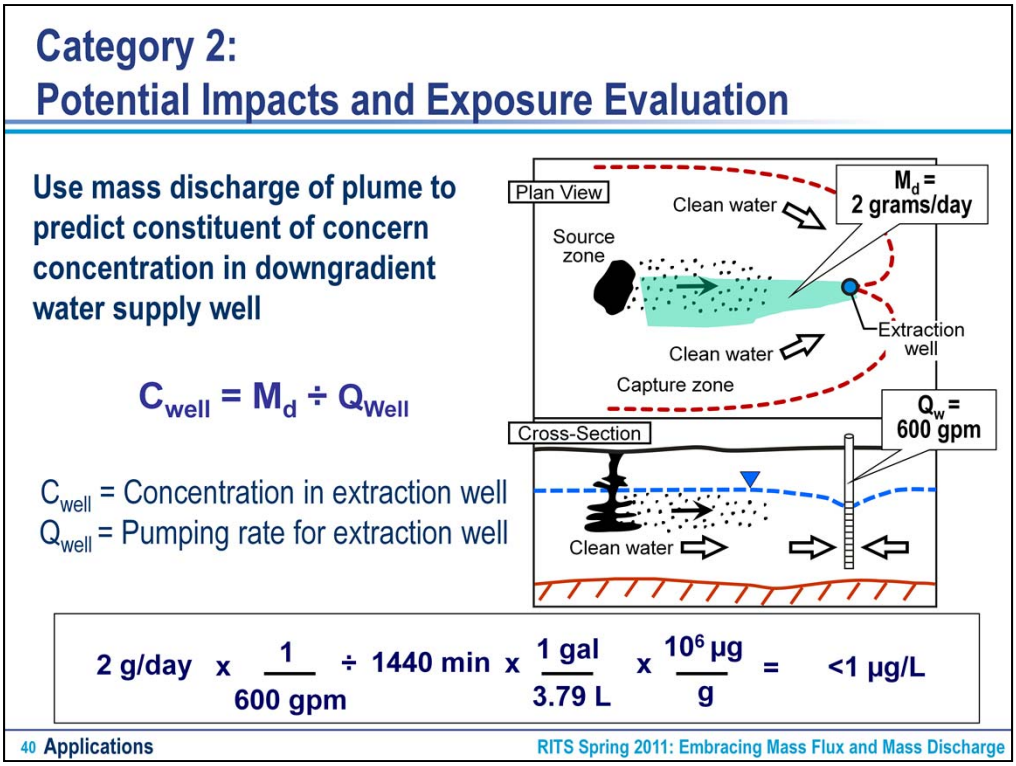
- Mass Concepts
- Measurement Methods
- ► Applications
  - Site Characterization/Conceptual Site Model
  - Potential Impacts and Exposure Evaluation
  - Remediation Selection and Design
  - Performance Monitoring and Optimization
  - Compliance Monitoring
  - Site Prioritization
- Advantages/Disadvantages
- Regulatory Considerations
- Case Studies
- Summary



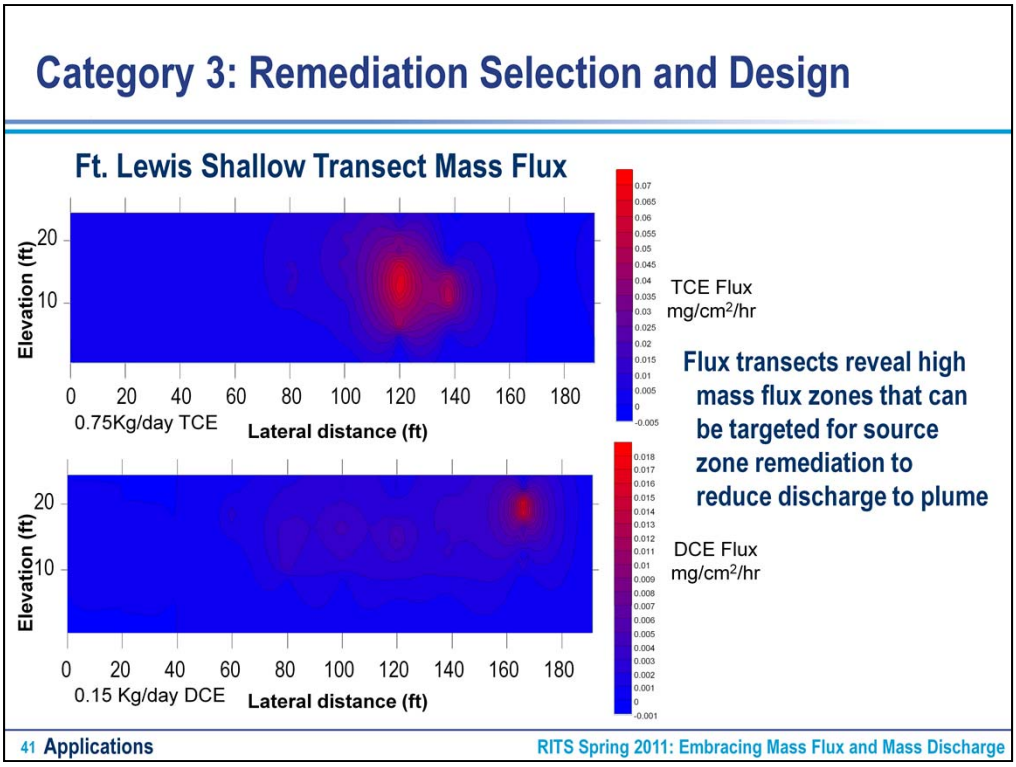
Applications, I'm going to skip through most of that because we already talked about those site conceptual model, remodeling, site characterization, prioritization, conceptual site model: refining conceptual site model, the thing that almost always happens when you collect additional information especially higher resolution.



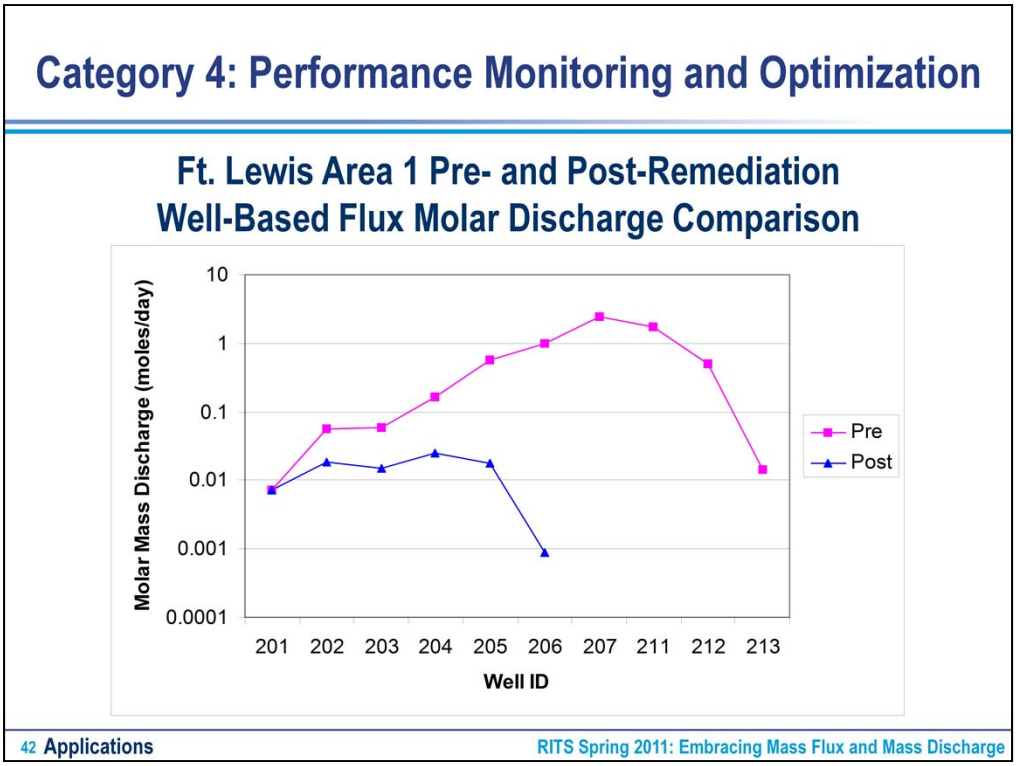
Here's a case where you go higher resolution samplers put in along a transect and this is one of the sites at Alameda and they, this initial thought was that this entire transect was the transect downgradient from the source area and the wall concept that you have here. You go into that collect high resolution data and discover that 80% of the mass is going through 7% of the transect. There've been a lot of sites where we have this kind of a realization where the high fraction of the mass flux associated with the site goes through a very small window. And so high resolution data are these tier chains of data conceptual models and we took it from something that looked pretty big and we took it down to manageable portions.



Potential for exposure, if you have a well capturing flow downgradient--the method for getting mass discharge—and kind of turning that around and saying my source is delivering some mass, in this case 2 grams/day, if I want to estimate the net concentration coming out of that pumping well downgradient I really want to know how fast the flow rate is, and then you can go and cancel out all your units make sure they cancel out properly, you'll get the correct number and its lower than the ppb number. What's happening is dilution by high flow but at least it kind of links the strength of the source area in mass discharge to an impact—and that can be done for a surface water feature as well.



Here's another transect at Fort Lewis where they had identified a source area treatment that they were going to target with thermoremediation. We came in and put in a transect of wells and collected the data and again most of the mass discharge was in a small window of the area. They wound up treating all this area here because we came in late and overdesigned it.

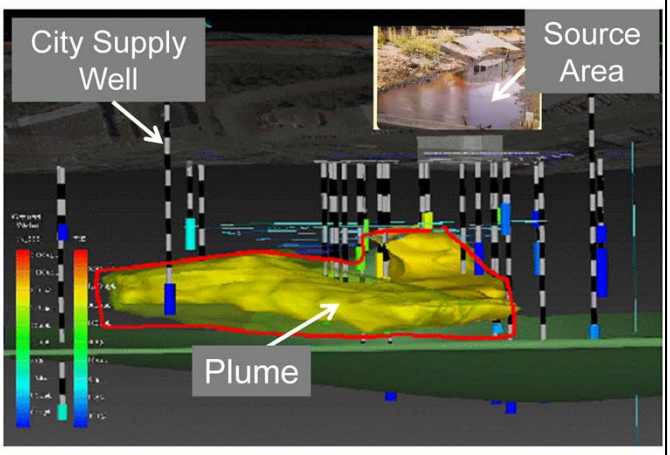


It was still successful and when you look across that transect this is mass discharge now on the molar basis, it's also on a log scale, but the initial looks something like this and the final looks like something like that and there's a substantial reduction in mass discharge.

Category 5: Compliance Monitoring

- **Focused Feasibility Study Evaluation:**
  - Reduce source strength (M_d) by 90%, MNA sufficient to achieve compliance
- **ROD Amendment:**
  - Multi-component remedy – reduce source discharge (M_d) by 90% & transition technology (if necessary)

Performance metric → remedy
Operational and Functional



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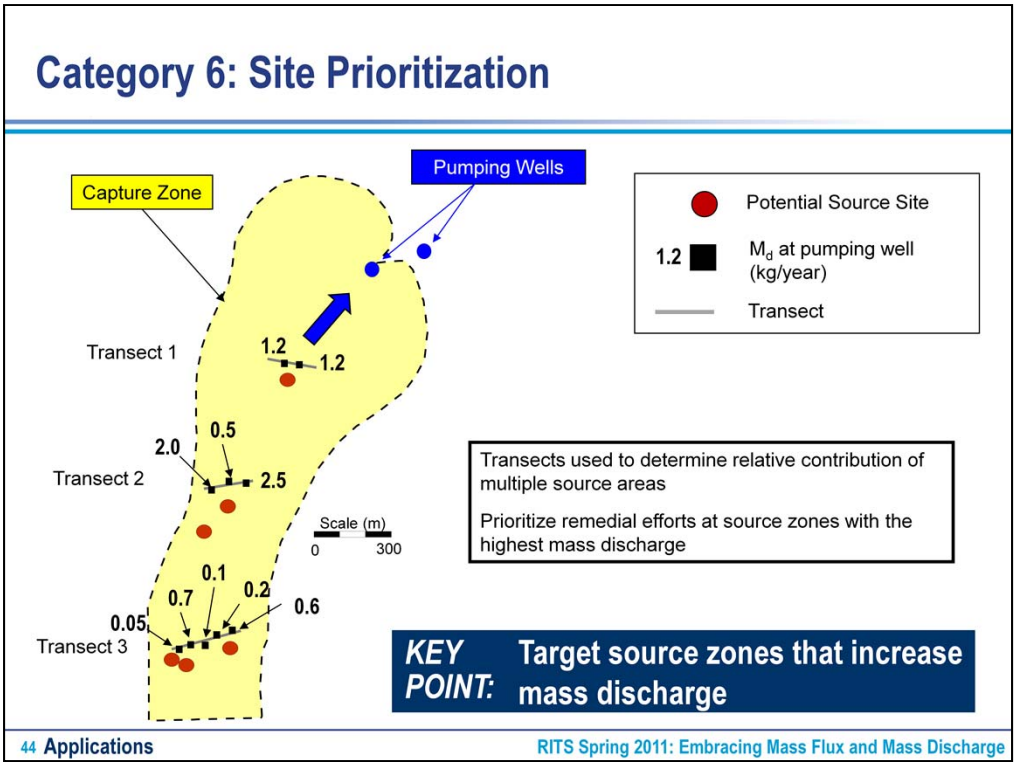
Now this is compliance monitoring and just note that there's the Tacoma 12-A site that is a pretty big TCE contaminated site where they're going to go in and target the source area for remediation but the important thing here is that they have set as part of their ROD a 90% reduction in source strength so that's not the end clean up target for the site-more of an interim goal where there goal is to substantially reduce the plume footprint and risk associated with that by going into the source and reducing the mass discharge by an order of magnitude. This is an interesting site that we'll keep an eye on as it moves forward. Site prioritization where you compare one side of the river to the other, we could also do that within a site.



Here's a large plume at a site that has multiple sources within a single plume and you're trying to sort out which are most important. Well if you look at mass discharge, there are some numbers here that kind of range in the low, .5, .6, .7, through here and then we get to the second source and there are higher numbers of 2, 2.5 kg/year. And then farther down gradient you see 1.2 as mass discharge. This should tell you that this source [the second source] is delivering most of the mass as the plume passes there. So in terms of prioritization, if you're going to attack these one at a time, this is really the one you really want to target, this is the one that's most contributing to the ultimate plume behavior.

Category 6: Site Prioritization (cont.)

Site	Contaminant	Mass Discharge (g/d)	Reference
Sampson County, NC	MTBE	0.6 - 2	Borden et al., 1997
Vandenberg AFB, CA	MTBE	4 - 7	Unpublished
Unnamed Site	MTBE	4	Unpublished
Elizabeth City, NC	MTBE	7.6	Wilson, 2000
St. Joseph, MI	TCE	167	Semprini et al., 1995
Dover AFB, DE	CVOCs	630	RTDF, 1998

KEY POINT: **Sites with higher mass discharge may pose more concern.**

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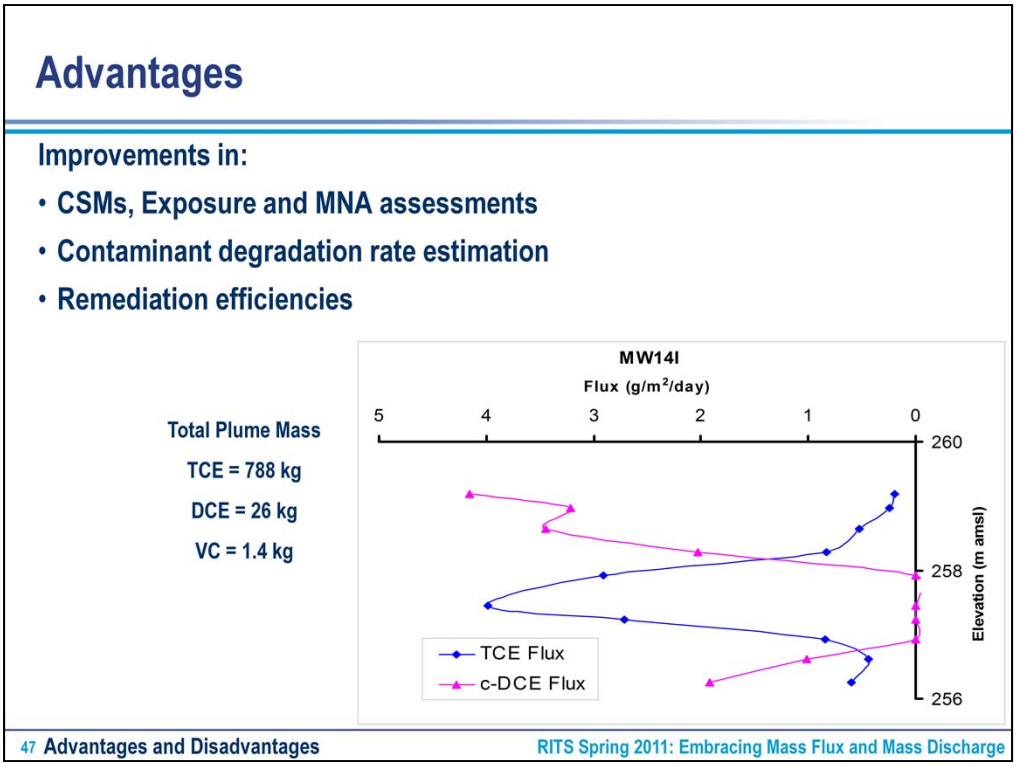
Also you can look at different sites there's a huge range out there of mass discharge values, all in grams/day I like this number grams/day, Fort Lewis is 105, Hill Air Force Base is around 100 and those are kind of big sites. There are some of these smaller sites, one of the smaller sites we worked on was a drycleaners in Jacksonville, they had somewhere around 2 grams a day so it puts it into perspective.

Presentation Overview

- Mass Concepts
- Measurement Methods
- Applications
- ► Advantages/Disadvantages
- Regulatory Considerations
- Case Studies
- Summary



We talked a bit about conceptual site models, I've mentioned a couple times measuring site attenuation, trying to tell if mass is actually being attenuated in the plume. Here's a case where not only looking at attenuation going through the plume, downgradient but also through a vertical profile within a chlorinated solid with TCE. Flux—this was measured with a flux meter approach—the TCE is low to very high at this mid depth and drops back off. The DCE is doing just the opposite, so we're getting some transitions—some conversions from TCE to DCE and it follows an opposite signal. This is the idea of a fringe process on the margins of a plume where you see some conversion or degradation, whereas the center of the plume you're not seeing it so much.

Disadvantages

- How to manage uncertainty?
- Cost – How much time and resources should be put into using/analyzing for Mass Flux and Mass Discharge?
- Uncertainty inevitable, but manageable
  - Similar uncertainty with concentration data
- Spatial heterogeneity and sample volumes
  - May need >>1%
  - Source/Plume Boundary?
  - Hard to find and hard to define
- Solutions – Work Smart
  - Consider source architecture, plume evolution, hydrogeology, etc.
  - Consider iterative investigation
  - Vertical variability is usually >>Lateral

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So one of the big questions that comes up is uncertainty, so you measure some mass flux and mass discharge put some uncertainty on that number for us and there's been some work to try to ask how much data you'll need to get a reasonable estimate. How many wells across a transect are adequate and what kind of uncertainty are you talking about there. In general you're going to need about six to ten wells to get an error within a range of twenty to thirty percent error estimate. We sample a very, very small area of that cross section.

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Precedence

- Federal Superfund…signed Record of Decision (ROD) identifying a mass discharge interim goal in October 2009
- Surface water regulation (e.g., TMDLs), National Pollutant Discharge Elimination System (NPDES) is based on mass discharge
- Groundwater extraction gives estimate of mass discharge over capture zone
- Natural attenuation relies on mass discharge reduction

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So one of the big questions is: is this useful in a regulatory framework where a lot of the regulatory framework is completely oriented toward MCLs. I think its compatible in a sense that if you're trying to meet a target MCL at some downgradient region of interest, then the way to do that is to reduce the amount coming out of your source to achieve that target. So that builds the link from the source area to some targeted location downgradient or in terms of a load to surface water. What's an acceptable load and what is the target concentration in the river and that establishes an objective to meet in terms of mass discharge and you can turn that around and convert it back to concentration if you want to but the key is that it is mass flow and mass movement that are controlling the ultimate concentration endpoints.

Regulatory Concerns

- Complexity and uncertainty of mass flux and mass discharge measurements
- How best to relate mass flux or mass discharge to risk and exposure
- Unclear how mass flux relates to standard regulatory metrics
  - e.g., Maximum Contaminant Levels (MCLs)

This will keep coming up—uncertainty, complexity, how good are these measurements-- if we're gonna start talking regulatory that's going to be a huge issue, but if we're talking about managing a site to determine the best strategy toward reducing mass flux and mass discharge, the uncertainty is perhaps not as significant but what is, is to be able to identify, in a relative sense, the hotspots and then also in a relative sense to be able to say "the hotspot was this high, 100 g/day/square meter and we're going to knock it down to 1" so that's a relative sense of a measure.

Looking Ahead

- **How should RPMs best incorporate these concepts into the ever changing regulatory landscape (both federal and state)?**
  - **Gain more familiarity with mass flux and mass discharge concepts, methods, and uncertainties**
  - **Use ITRC MASSFLUX-1 guidance document (August 2010)**
  - **Apply Mass Flux and Mass Discharge**
    - Cleanup Strategies
    - Goals and Objectives
    - Performance Metrics
    - Monitoring

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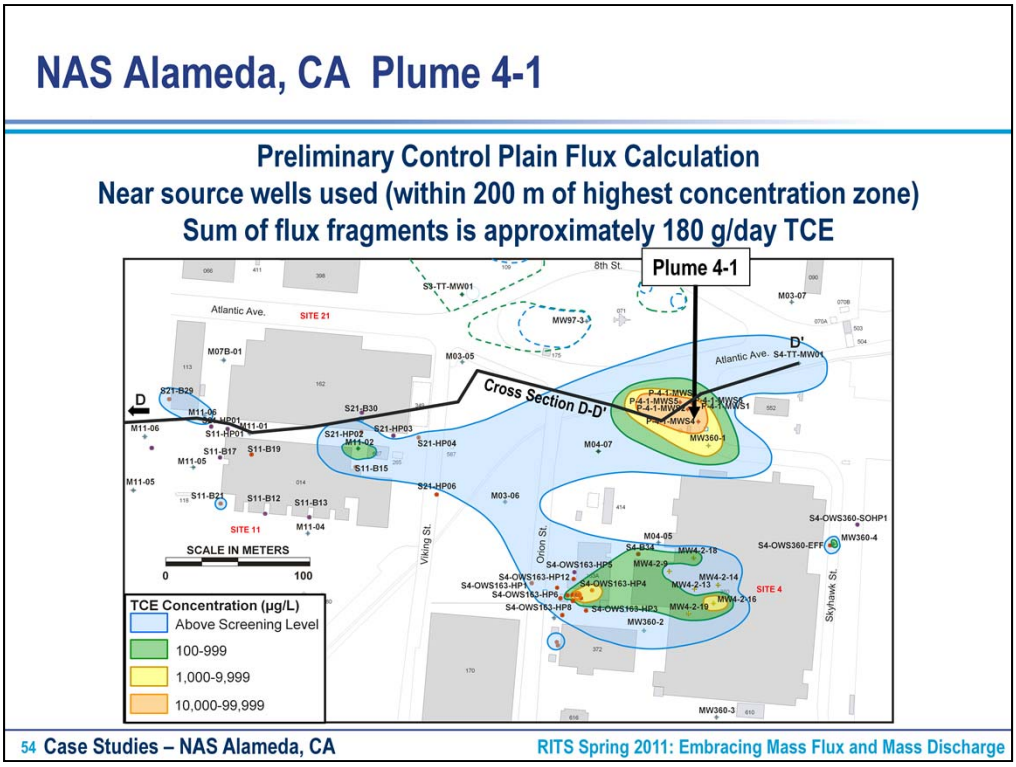
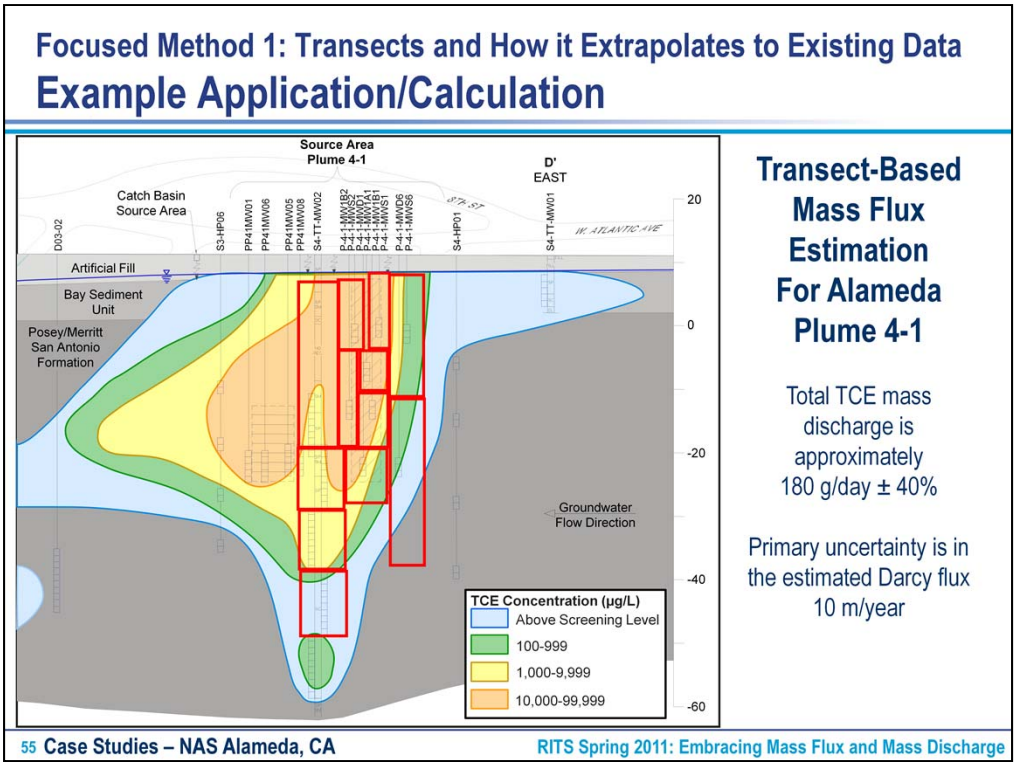
How to incorporate these into your thinking or strategy for a site, I think there're some examples out there that involve remedial performance assessment, pre and post remediation and then I think that setting interim target objectives but what we haven't done as much of is ask the question what is an acceptable mass discharge from the source are, is 1 gram/day acceptable? Is 0.1 g/day acceptable? .01? And to answer those questions we need to ask what the aquifer can assimilate, how much mass it can handle. It's not zero, but it can handle some. Maybe turn it around and say well its currently handling 100g/d and this is what the plume looks like but how would that change the plume if I knocked it down two orders of magnitude? Just to be clear, if I clean up the source zone it doesn't change the amount that is there it just changes the back side of that.

Presentation Overview

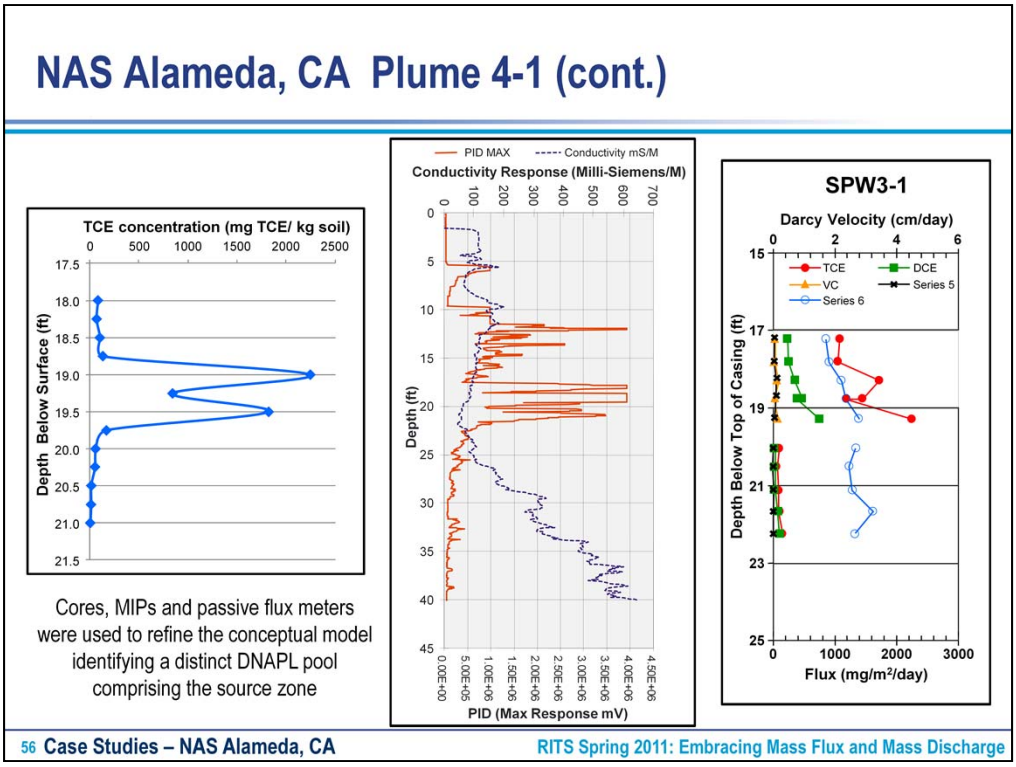
- Mass Concepts
- Measurement Methods
- Applications
- Advantages/Disadvantages
- Regulatory Considerations
- ► Case Studies
  - NAS Alameda, CA
  - Hill AFB, UT
  - Fort Lewis, WA
- Summary



Alameda: this is like most bases, there's lots of different plumes to look at, this one we're looking at called plume 4-1 has two identified source areas--release of 'TCE specific-- they seem to mingle into a plume but there's enough information here to know with certainty that there's a DNAPL source area there. And so we chose to focus in and look at this specific plume. We did a quick estimate of mass discharge and I'll show how this was done. this is the transect method, there are a number of wells and multi level vertical resolution we highlight each one of these monitoring locations and identify a contributing area to that.

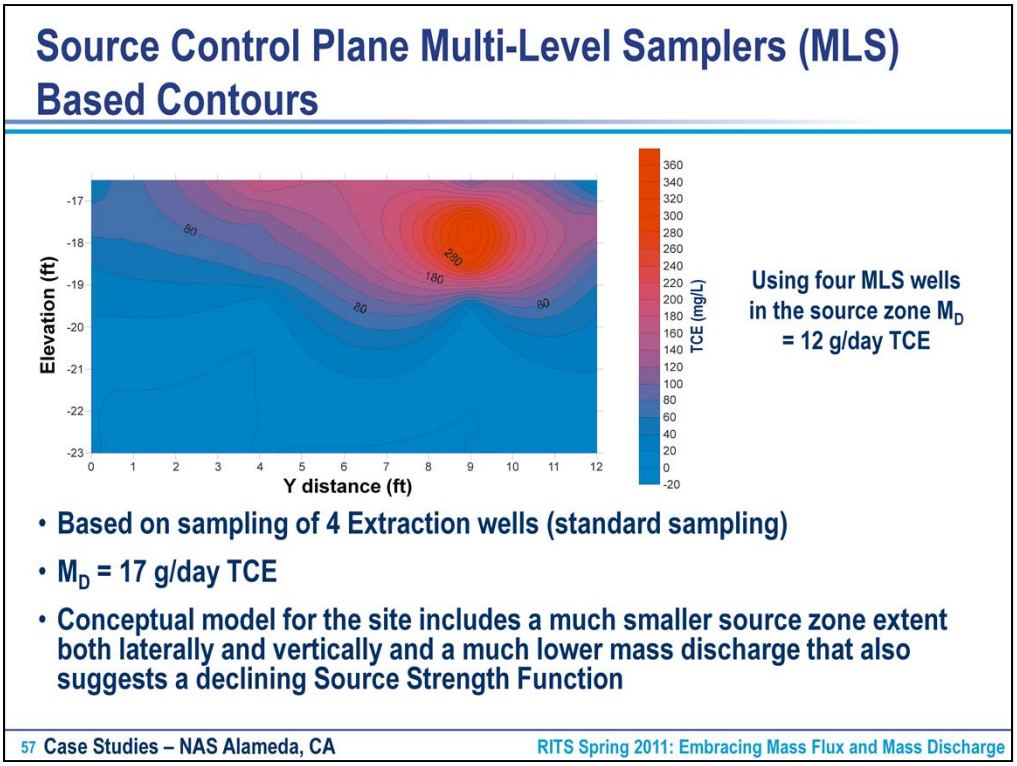


They add those up to a number that turned out to be180 g/day and I put a fairly high error associated with that and a lot of that uncertainty is in the Darcy flux value, we're using a single value throughout the site and there's some knowledge about that but it's a crude number but it immediately puts it into perspective but it's a high number mass discharge of TCEs in this case.



Now we went out and collected some additional data at the site and I'm showing a bit of it. Here's coring and we took some core samples, and measured some TCE in the core samples and we did it at a fairly high resolution. And you can argue that we have three data points that clearly indicate NAPL presence and it's good to do that because then you actually know that we can collect and quantify samples that clearly have NAPL presence and at a location nearby we had a membrane interface probe and we're looking at the PID signalers, and there's also PCD, but the PID record was the best indicator of the NAPL presence ECE was completely overwhelmed, but here in this same depth window 18/19 feet to 20-21 there is a strong indication that you're pushing through something that looks like a contaminated NAPL area we've had a fair number of those—a lot of those were clean and we used that to delineate the footprint and we also did some passive flux meter.

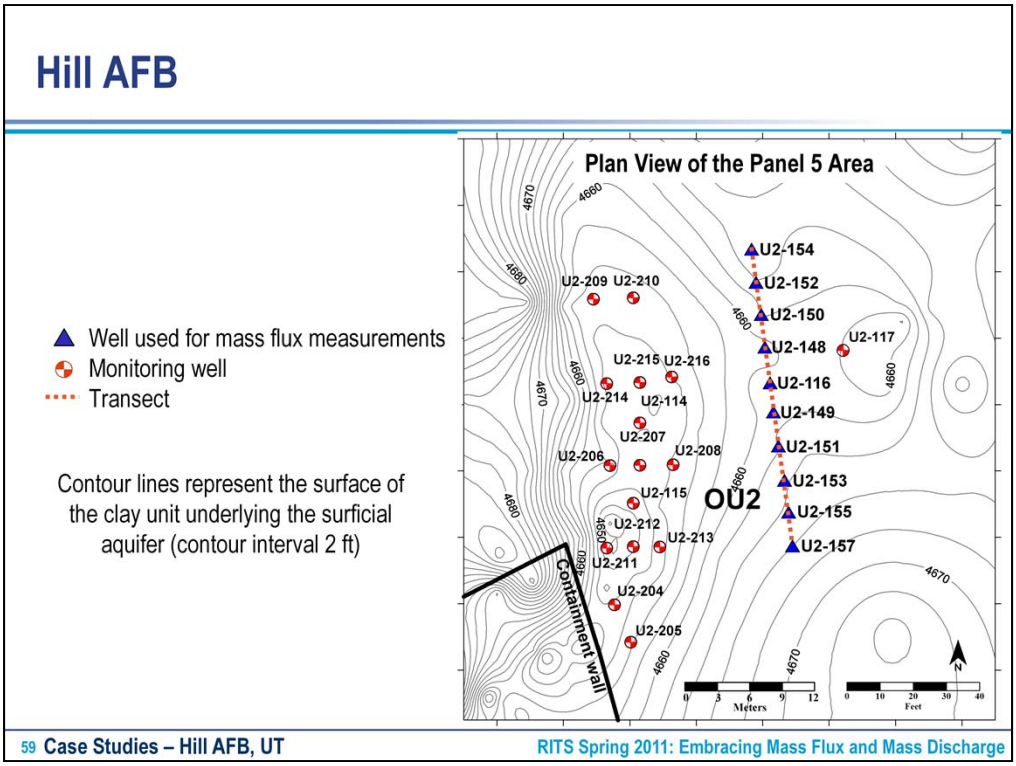
The main thing here is there was a very high TCE flux and so we screened them like that and so we know we have a pool and its sitting on that twenty to twenty one foot area and that's where all the mass discharge is sitting at so we took something that looked like a pretty big site and we focused it down to a remaining source, the source could've been bigger historically—it was—but the remaining source is focused on that individual layer through there. So we're really changing our conceptual model that's much smaller footprint than originally determined.



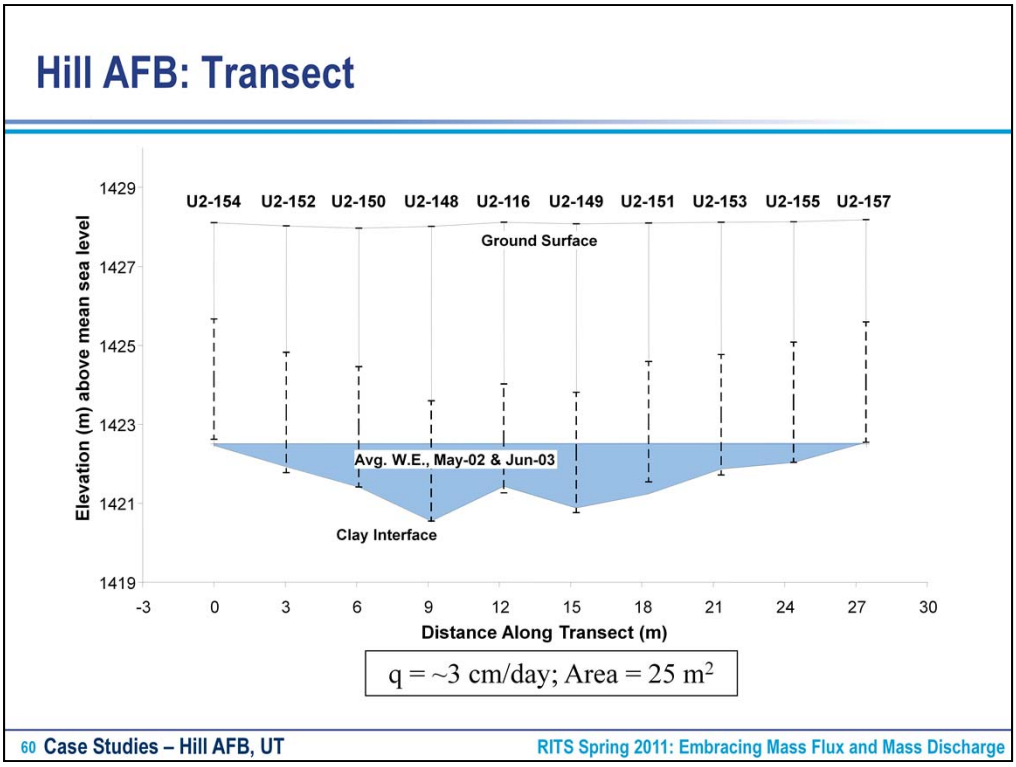
We also had some multileveled samplers in there and again: collect some higher resolution data and you find that there's this local hotspot in terms of vertical and horizontal resolution. And I don't know what kind of number this would be but probably again 80% of the mass is going through 20% of the domain and it really changes your thinking around and it's about these targeted hotspots. And so now with that site we redid some multilevel calculations that indicated around 12g/day we also had some extraction wells that we did standard sampling on and we did integral pump test too and that indicated about 17g/day and the flux meter data was in that ballpark range. So we took a site that we thought had 180 or so g/day and it we realize it's much lower and more focused and now we're looking at something that's in the 10-20 range. 180 was based on historical data from 8-9 years ago so it's reasonable that it could've declined to some degree, but probably not to this level. So we're reassessing the site-wide mass balance and now we're going to design and target the remedial strategy and probably enhance biotreatment of this smaller footprint source area.

Presentation Overview

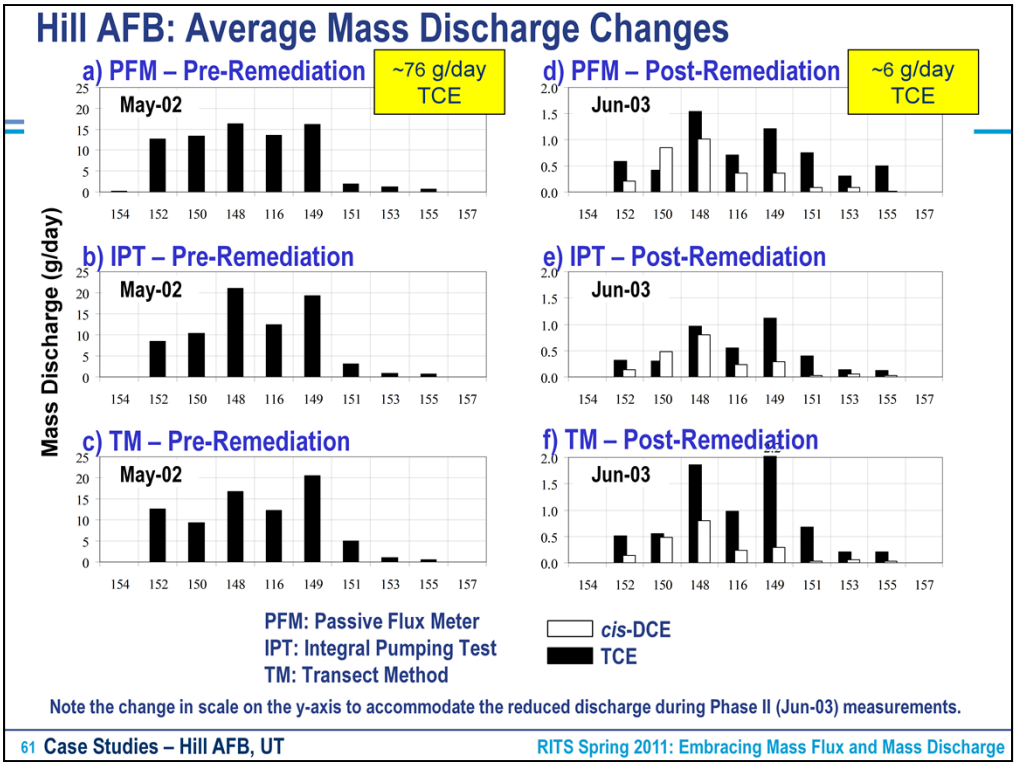
- Mass Concepts
- Measurement Methods
- Applications
- Advantages/Disadvantages
- Regulatory Considerations
- ► Case Studies
  - NAS Alameda, CA
  - Hill AFB, UT
  - Fort Lewis, WA
- Summary



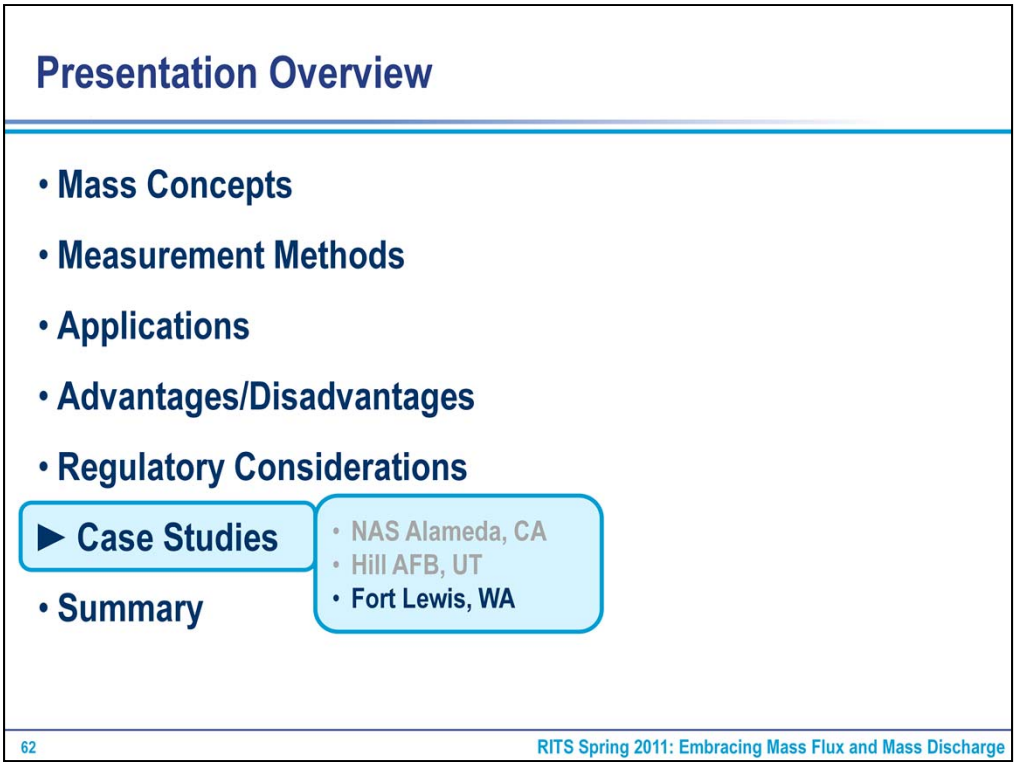
We had 10 wells along a transect



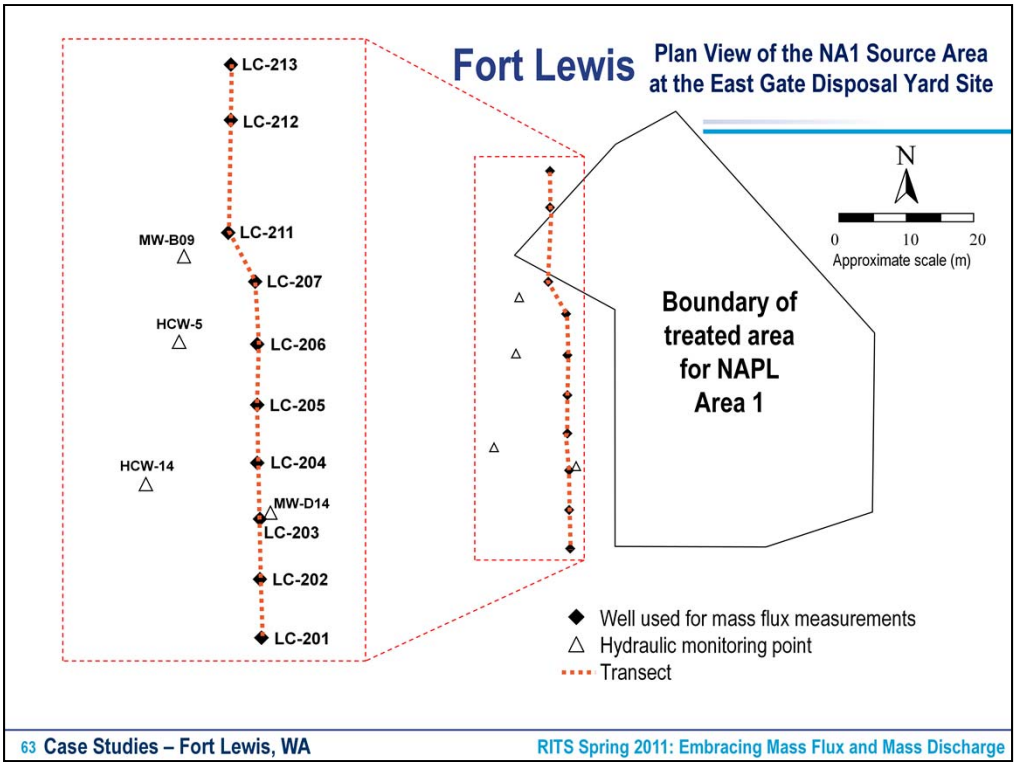
These transects were put in specifically for flux monitoring and remedial assessment pre and post remedial effort if you're not familiar with Hill it's simply a case of "put in a containment wall and you discover that there's DNAPL outside the containment wall" so you did have to treat this and they did a surfactant flood on that area, so we're focusing on that pre and post surfactant flow and this was a paleo channel that everything was flowing through and that was quite nice because it was contained to the finite area, Darcy flux around 3cm/day through that cross sectional area.



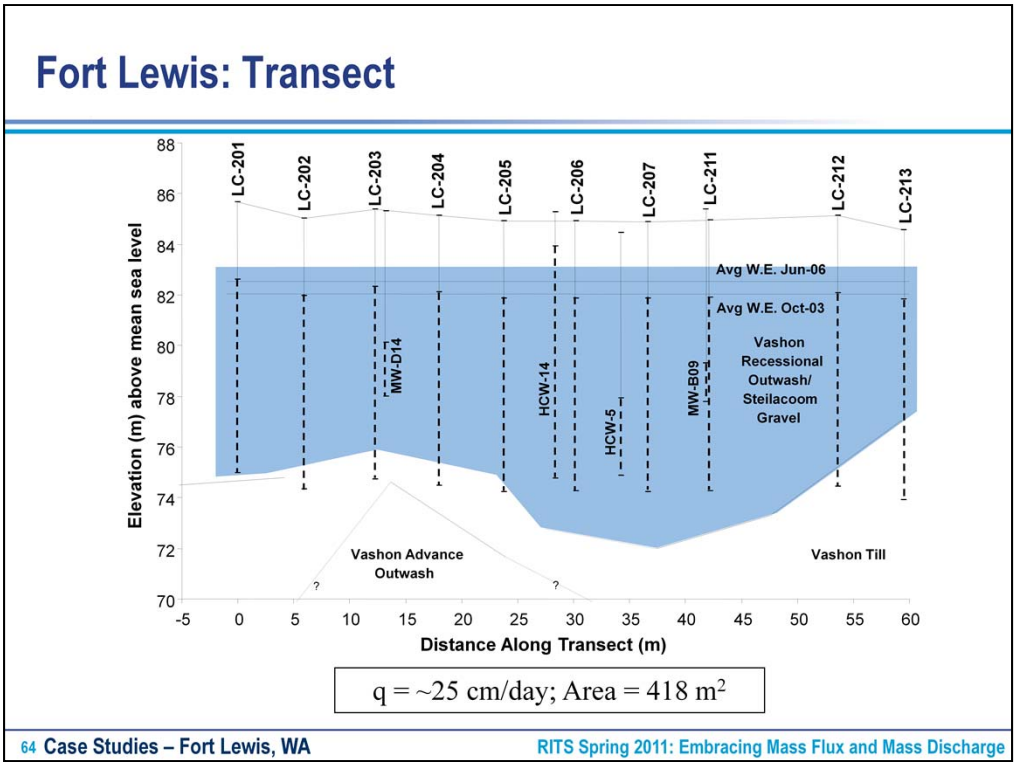
A fair bit of data here pre remediation on this side and post remediation on the right and the scales are different 25g/day and this is 2g/d and this is really to highlight the similarities we're interested in. We did passive flux meters and integral pump tests and the transect method the pre remediation are in agreement in terms of order of magnitude and there were reasonably good agreement. One thing I'd point out: the cis after remediation there was more cis showing up than pre. TCE is mostly TCE and 76g/day to start with and 6 g/day after, that's a pretty significant reduction due to the surfactant flood but when we were doing our post sampling they were also sampling in that source area and there was still some wells that had free product in it. I think the surfactant flood did a great job of cleaning up the residual contributing to flux but there are just pools that are hard to get.



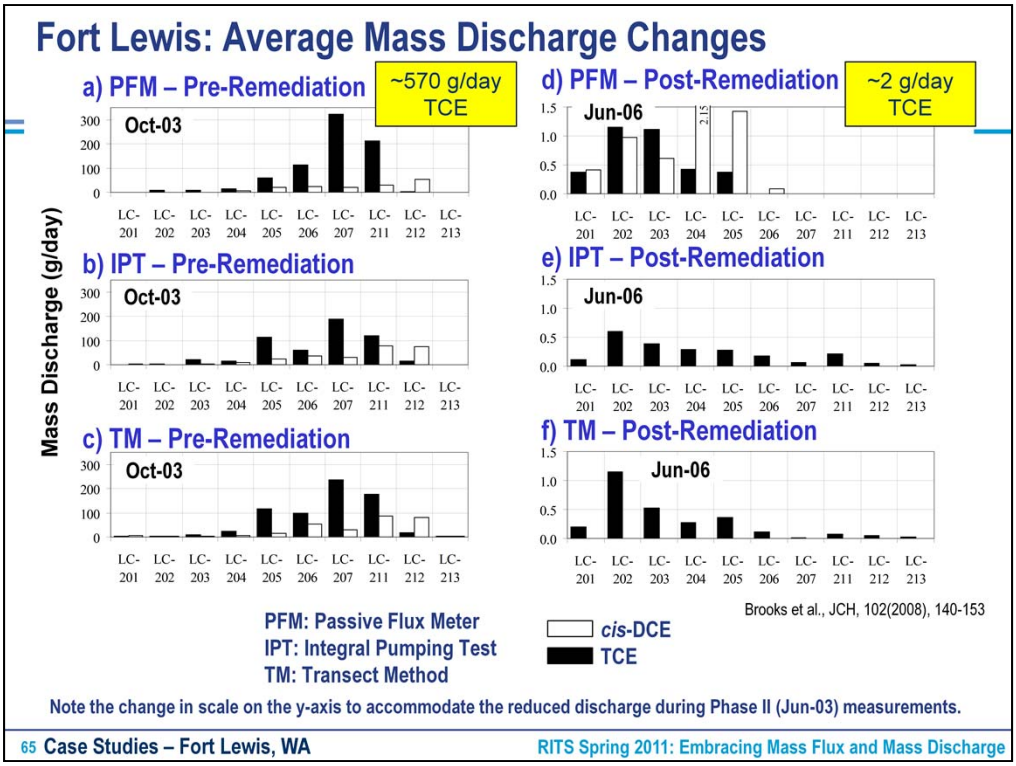
The last case study, Fort Lewis Washington was a large TCE disposal area.



This is called area 1: the entire site had three large areas for targeted thermal remediation and so we just focused on the first one, there's second and the third—the second one is down gradient from this and I actually think this is one of those cases where prioritizing the site based on mass discharge would've make them rethink this second one, most of the mass discharge from the second one was really due to that first site they wound up treating all of these areas. The boundary you see here is actually an asphalt cover to do thermal resistive heating.



So we had our ten well transect, a much thicker zone about 30ft thick through glacial outwash sitting atop a glacial till so it was good because it kept the DNAPL in that outwash window fairly well and there's a much higher velocity 25 cm/day and it was challenging for thermal radiation .



Again there's the same thing as the previous we have our pre remediation, the magnitudes are comparable…again 300 on this axis 1.5 on the other and they're different scales but all three methods are comparable pre and post to our 570 g/day, this is 3-6 times larger than Hill Air Force Base, this is a pretty big mass discharge site. Drop that to 2 grams per day, that's 98.5% reduction in the mass discharge coming off the site but this is from thermal resistance heat, it's fairly expensive and involved but the success was pretty dramatic I thought. One of the things I didn't really discuss was that both techniques, the surfactant and thermal discharge removed a fairly high fraction of the mass that was there, conceptually Fort Lewis removed around 90% and Hill saw 98% so substantial mass removal led to substantial mass reduction at both sites.

Case Studies: Key Points

- Flux measurements at both sites indicate that TCE source mass depletion (>60%) through aggressive treatment resulted in substantial (>90%) reduction in TCE mass discharge at the Source Zone control plane
- Data from both sites suggest that a significant fraction of the mass discharge occurs over a small portion of the SZ control plane, consistent with other field observations
- Flux-based site management should be used as a collaborative process with other traditional characterization and remedial assessment approaches

66 Case Studies – Hill AFB, UT and Fort Lewis, WA RITS Spring 2011: Embracing Mass Flux and Mass Discharge

One of the things I didn't really discuss was that both techniques, the surfactant and thermal discharge removed a fairly high fraction of the mass that was there, conceptually Fort Lewis removed around 90% and Hill saw 98% so substantial mass removal led to substantial mass reduction at both sites.

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Take-Home Points

- More effective site management
- Improve conceptual site models
- Enhance remedial efficiency
- Refinement of exposure assessment
- Can use historical data (20+ yrs.) and existing monitoring networks in some cases
- Can enhance compliance measurements

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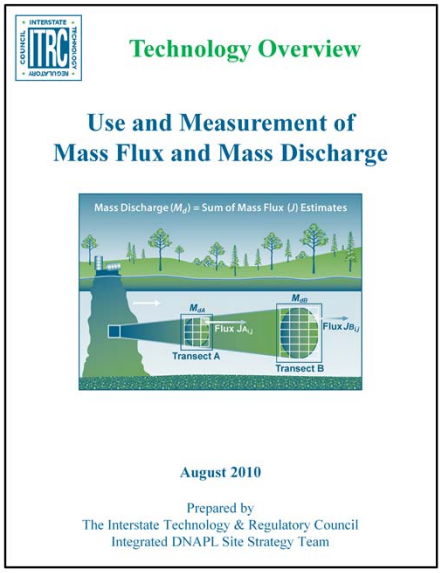
Some of these points I made: its about better managing your site, rethinking target remediation the objective being mass discharge reduction appropriate for some sites. I started off talking about how we got involved in remediation and what the benefits of mass discharge are and this group has been moving it along for 20 years or so.

ITRC – Shaping the Future of Regulatory Acceptance

- Technology overview released August 2010
- Excellent resource
  - Available as a PDF
  - http://www.itrcweb.org/Documents/MASSFLUX1.pdf
- Short Course Training



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There are short courses coming up so if you're interested in learning more about this topic [you should take some]. Thank you.

References

- ITRC (Interstate Technology & Regulatory Council). 2010. Use and Measurement of Mass Flux and Mass Discharge. MASSFLUX-1. Washington, D.C.: Interstate Technology & Regulatory Council, Integrated DNAPL Site Strategy Team.