Assessing Source Zone Remediation: Review of Case Studies (ROCS)

Naval Facilities Engineering Service Center
Tel. (805) 982-1616

Definition of Source Zone:

- **EPA defines the DNAPL zone as:**

  "that portion of the subsurface where free-phase or residual NAPL are present either above or below the water table." **(EPA, 1996)**

- **General rule of thumb: Concentrations in groundwater exceeding 1 to 10% of solubility limits for the particular contaminant of concern (COCs)**
  - **PCE: 2.4 mg/L**
  - **TCE: 13.9 mg/L**
- ***"Although DNAPLs are not very soluble in water, both ganglia and pools continue to act as a long-term source for continuing dissolution of contaminants into water."*** **(ITRC draft, 2004)**

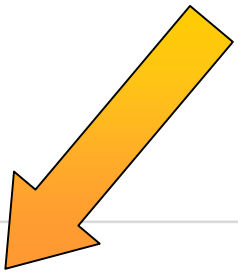
Introduction:

- **Problem Statement: A number of technologies claim to provide source zone remediation. Yet, there's confusion regarding what is attainable with a given technology in terms of:**
  - **mass removal,**
  - **reduction of aqueous phase contaminant flux,**
  - **reduction of aqueous phase concentrations, and**
  - **reduction in source zone lifespan.**
- **Approach: Conduct a Web-based Survey**
  - **Solicit site and technology information from users that have attempted remediation of source zones areas**
  - **Evaluate the results of the technology applications and compare them to:**
    - Site's geology / hydrogeology, and
    - Cost of the application
- **EQ Requirement: Navy EQ Req. No. 1.I.1.g:**
  - **Improved remediation of groundwater contaminated with chlorinated hydrocarbons and other organics**
  - **Priority: High**

Survey

GeoSyntec Consultants

User: Carmen Lebron
Email: lebronca@nfesc.navy.mil
Site: testing



Geology

Enter relative percentage of media type. If your site has both consolidated and unconsolidated media, then enter the relative percentage of both media in the appropriate box. For fractured media, you are asked to provide information on both the degree of fracturing, as well as the permeability of the matrix.

Consolidated Media (i.e. bedrock)

Degree of Fracturing

Discretely Fractured: (< 10 conductive fractures)	0%
Highly Fractured: (fractures are visible throughout zone of interest, many water conductive fractures)	0%
Unfractured:	0%

Matrix Permeability

Low Permeability Matrix: (crystalline, metamorphic rocks, some limestones, etc.)	0%
High Permeability Matrix: (some limestones, sandstone, etc.)	0%
Unknown:	0%

Unconsolidated Media (i.e. sand, clay, etc.)

Low Heterogeneity: (heterogeneity not visible to trained geologist - e.g., beach sands)	0%
High Heterogeneity: (variable soil types, orders of magnitude variation in K, layers, etc.)	0%
Unknown:	0%

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GeoSyntec Consultants

User: a b
Email: zzzzz
Site: zzzzz

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Hydrogeology

Please choose, from the following lists, the hydrogeological parameters that best describe the BULK conditions of the DNAPL source area.

Hydraulic Conductivity:	1.e-14 to <1.e-13	cm/s
Groundwater Velocity:	1.e-08 to <1.e-07	cm/s
Sustainable Well Yield:		gpm Leave blank if unknown.
Depth to Groundwater:	5	ft Leave blank if unknown.
Hydraulic Gradient Horizontal:	0.0001 to 0.001	
Hydraulic Gradient Vertical:	<0.0001	

◁ BACK NEXT ▷

Dissolved Contaminant Profile

Estimate of the **maximum** concentration of each chlorinated solvent that occurs within the defined source. If value is unknown, please leave the field blank.

Select Units:	mg/L

Chlorinated Ethenes:

tetrachloroethene (perchloroethylene):	
trichloroethene (trichloroethylene):	1200
1,1-dichloroethene (1,1-dichloroethylene):	
cis-1,2-dichloroethene (cis-1,2-dichloroethylene):	
trans-1,2-dichloroethene (trans-1,2-dichloroethylene):	
chloroethene (vinyl chloride):	

Chlorinated Ethanes:

hexachloroethane:	
pentachloroethane:	
1,1,1,2-tetrachloroethane:	
1,1,2,2-tetrachloroethane:	
1,1,1-trichloroethane:	
1,1,2-trichloroethane:	

Other Groundwater Geochemistry

Choose applicable concentration ranges from the following list of chemicals that may be relevan in terms of technology effectiveness:

Nitrate:	>1 and <10 mg/L
Nitrite:	Unknown
Sulfate:	>10 and <100 mg/L
Sulfide:	Unknown
Phosphate:	Unknown
Calcium:	>100 and <1000 mg/L
Magnesium:	>10 and <100 mg/L
Carbonate:	Unknown
Mercury:	<1 mg/L
Arsenic:	<1 mg/L
Hexavalent Chromium:	Unknown
Hydrogen:	Unknown
Dissolved Iron:	>10 and <100 mg/L
Total Iron:	>10 and <100 mg/L
Dissolved Manganese:	Unknown
Total Manganese:	Unknown

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User: Carmen Lebron
Email: lebronca@nfesc.navy.mil
Site: testing

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Dense Non-Aqueous Phase Liquid (DNAPL) Description

Please provide the following information on the DNAPL distribution and mass prior to the onset of remedial activities. For sites with multiple DNAPL source zones, please provide the TOTAL value for all source zones (e.g., areal extent, volume, mass etc.) as appropriate.

What is the total areal extent of DNAPL distribution?	Unknown	m2
What is the total volume of impacted soil (pre-remediation) containing DNAPL?	Unknown	m3
What is the maximum depth of the DNAPL?	Unknown	cm

How is the DNAPL distributed in the subsurface:
(choose all that apply)

- ☐ In pools
- ☐ Residual
- ☐ Sorbed
- ☐ Diffused into low k layers (rock matrix or clay)
- ☐ Dead-end fractures

What was the estimated shape of the DNAPL distribution in the subsurface used in determining treatment geometry:

○ Unknown ○ Cylindrical ○ Inverted triangle ○ Triangular ○ Rectangular ○ Irregular

Enter the total number of sampling locations used to locate the DNAPL source area(s) for each of the following techniques:

Fully-Screened Monitoring Wells:	0
Nested Monitoring Wells:	0

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Email: lebronca@nfesc.navy.mil
Site: testing

Technology

Please choose all the technologies you would like to contribute information about:

Excavation

- [ ]

Bioremediation

- [ ]

Chemical Oxidation

- [ ] Persulfate
- [ ] Permanganate
- [ ] Fenton's Reagent
- [ ] Ozone
- [ ] Other

Thermal

- [ ] ChemOxTechnology
- [ ] Steam
- [ ] Six phase heating
- [ ] Three phase heating
- [ ] Resistive heating
- [ ] Other

Surfactant Flushing

- [ ]

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User: Carme m
Email: lebr ifesc.navy.mil
Site: te
Technology mediation -

Effectiveness of Technology

In general, how would you rate the effectiveness of this technology in remediating DNAPL source zones (check all that apply)?

- [ ] Able to achieve treatment goals at a reasonable cost
- [ ] Technology is limited to certain site conditions (i.e. depth of contaminant, geology)
  Specify:
- [ ] Technology requires further development before it can be routinely applied
- [ ] Reasonable ease of implementation
- [ ] Reasonable ease of use
- [ ] Reasonable ease of design
- [ ] Adequate number of trained vendors to implement technology
- [ ] Other factors that might affect technology usefulness
  Specify:

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User: Carmen Lebron
Email: lebronca@nfesc.navy.mil
Site: testing
Technology: Bioremediation -

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Methods of Assessing Performance and Monitoring

How are you planning to assess the interim technology performance (check all that apply)?

- [ ] Concentration reduction in specific monitoring wells
- [ ] Reduction in soil concentrations
- [ ] Achieve maximum contamination levels (MLCs) in monitoring wells
- [ ] Reduction in plume mass flux (or mass discharge)
- [ ] Reduction in plume size
- [ ] Production of degradation by-products
- [ ] Total Mass removed
- [ ] Mass remaining
- [ ] Will not measure

What is the estimated duration of the field treatment activities and how long have they been on-going to date?

Estimated: [ ] days To Date: [ ] days

How much decrease in mass flux has been observed to date (if applicable)?

81-100%

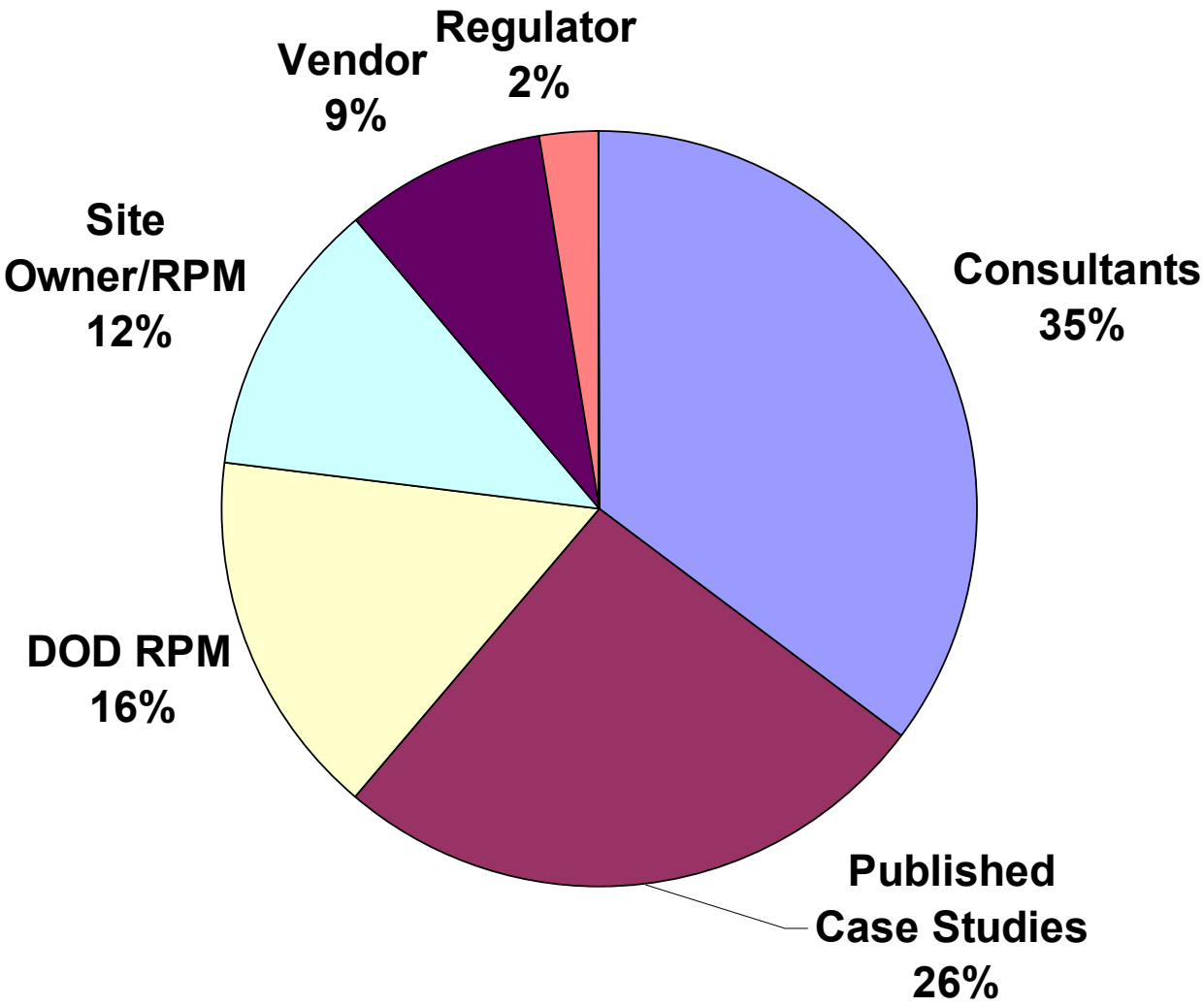
Over what duration is post-treatment monitoring expected to be conducted?

Results

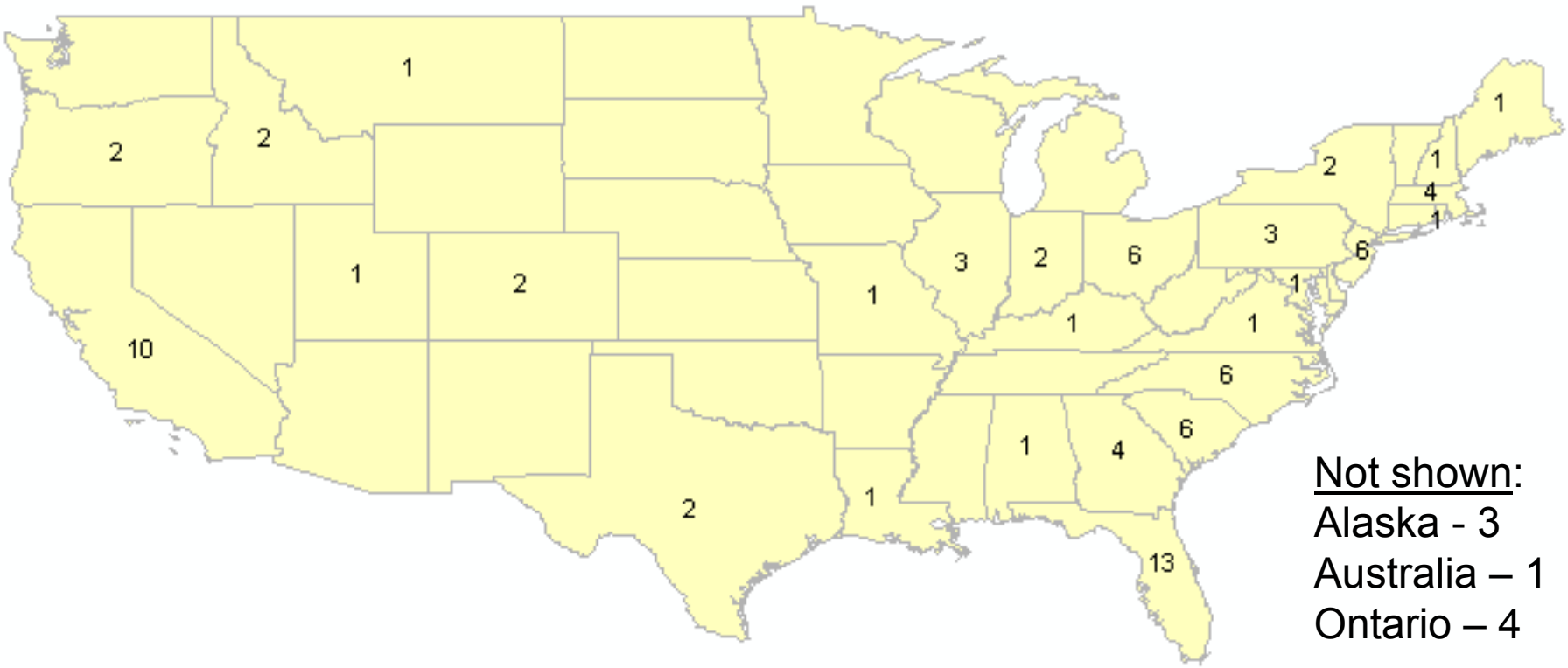
Survey Respondents:

- Number of respondents: 213
  - No. of people who put some information in the survey but didn't necessarily complete both the site and technology surveys
- Number of technology application locations: 118
  - These are locations within sites, as some users had multiple applications within one site
  - This number also includes 21 Published sites, (INEEL, Pinellas, Savannah River, Hill AFB, Santa Clara, Launch Complex 34, AF Plant 4, Portsmouth, etc.)
- Number of users: 82
  - Number of people who completed surveys for 1 or more sites
  - If 1 person entered information on 3 sites, it still counts as 1 user, that's why it adds up to 118 locations
- A User can have multiple sites and a site can have multiple technologies
- Most questions were NOT mandatory, resulting on different "total numbers"

82 Completed-Survey Users:



Geographical Distribution of Sites:

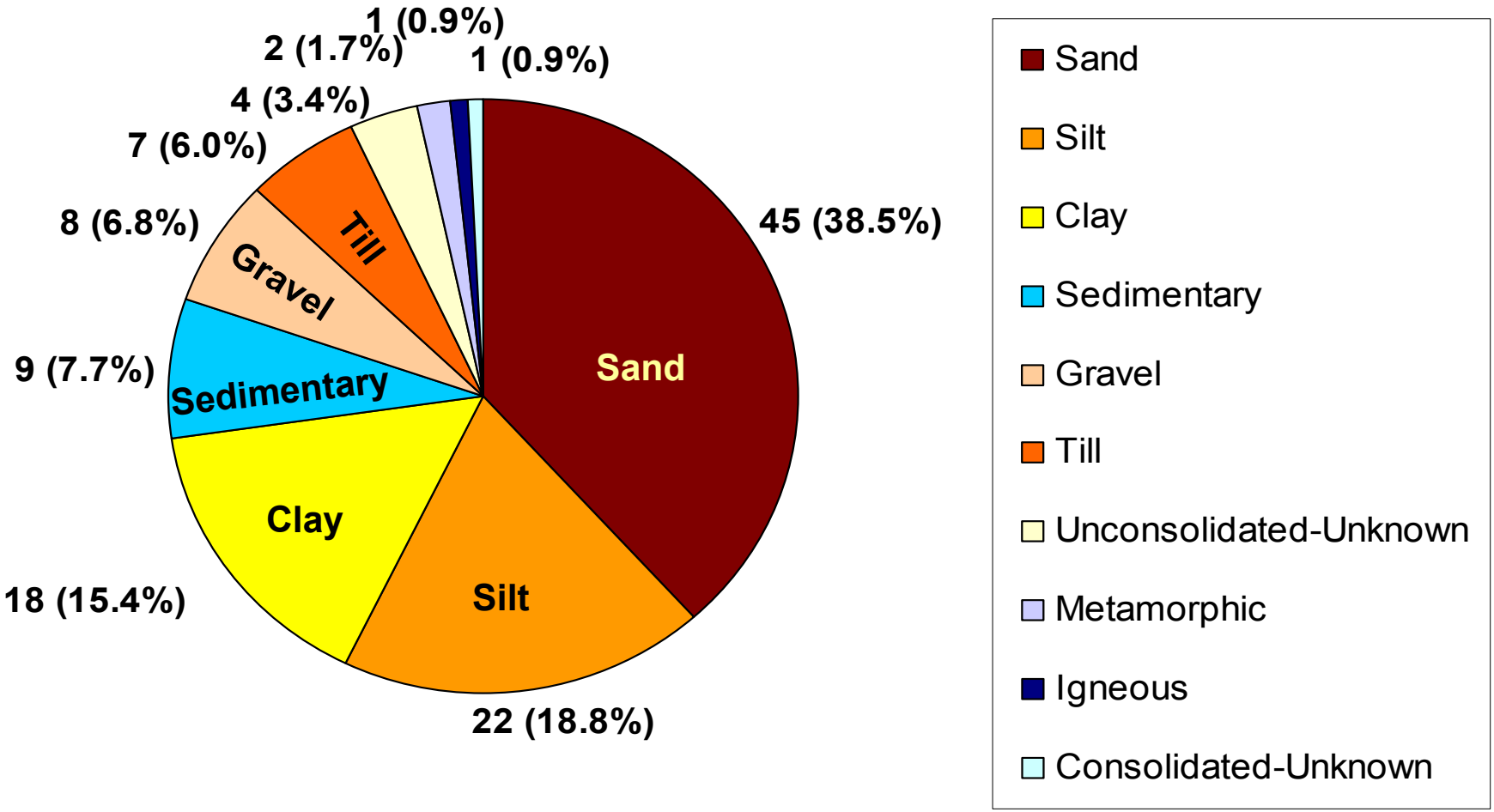


Not shown:
Alaska - 3
Australia – 1
Ontario – 4

Areal Extent / Volume Impacted:

- **Sites ranged greatly in size and volume**
  - **Areal extent**
    - From <100 ft^2 (generally the technology demonstrations)
    - To over 100,000 ft^2
  - **Volume**
    - Was unknown in 47% of the cases
    - In the known cases, it ranged from <10 ft^3 to >1,000,000 ft^3
- **Majority**
  - **Areal extent of 10,000 ft^2 to 100,000 ft^2**
  - **Volume greater than 100,000 ft^3**

Lithology



Total Number of Sites with Specified Technology and Lithology = 117
Unconsolidated = 104 (89%) Consolidated = 13 (11%)

COCs Concentrations:

- **Survey users were asked to provide maximum groundwater concentrations of the chlorinated compounds at the site**

Chloroethenes

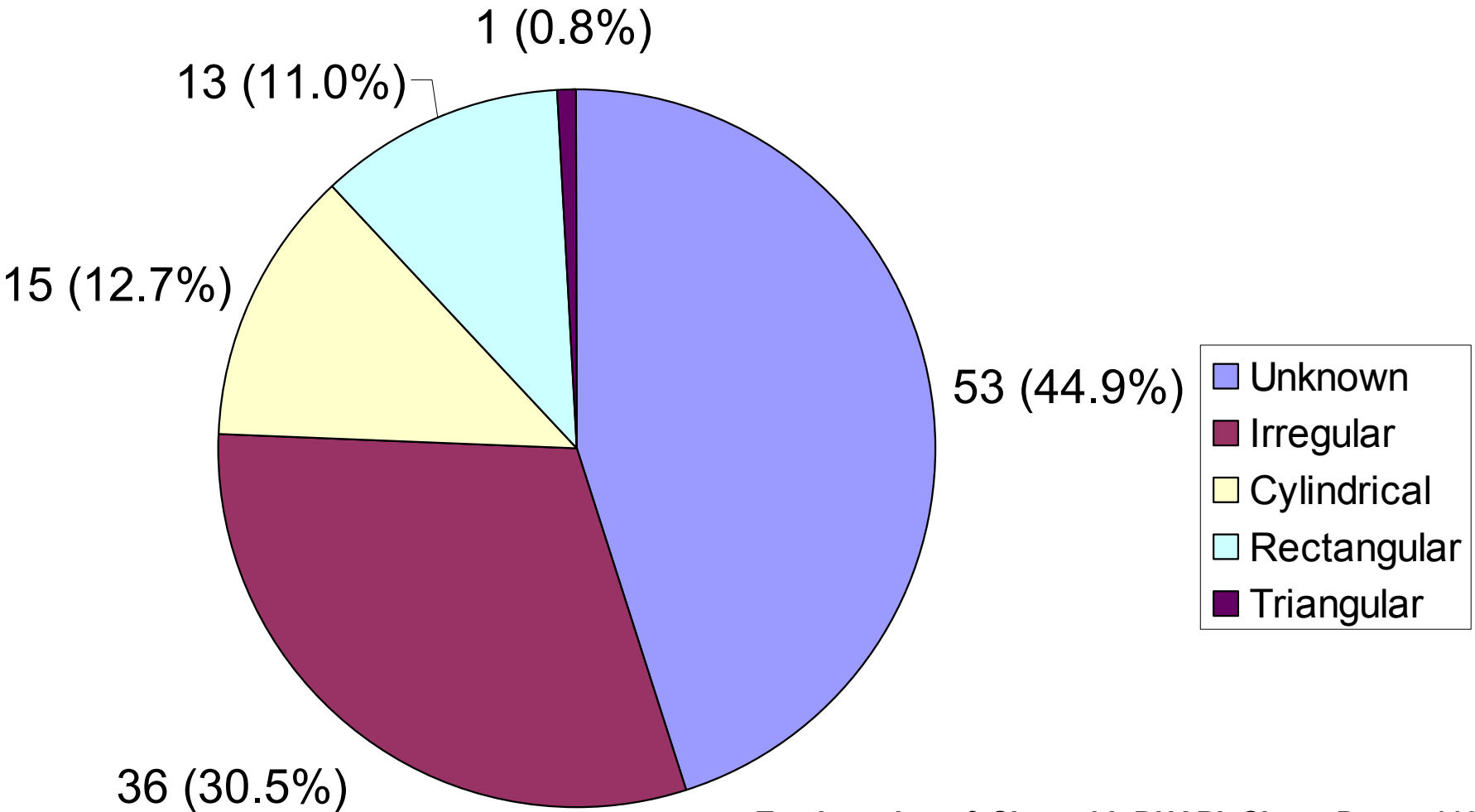
	PCE	TCE	1,1-DCE	c-1,2-DCE
Min (mg/L)	0.1	1.0	0.03	0.10
Max (mg/L)	220	1400	50	940
Median (mg/L)	44	100	25	9
Average (mg/L)	63	268	25	126
1% of Solubility (mg/L)	2.4	13.9	2.3	70.0
Solubility Limit (mg/L)	237	1385	2250	6996

DNAPL Distribution:

- 75 sites/locations responded to this question
  - 83% residual DNAPL
  - 61% sorbed DNAPL
  - 44% pooled DNAPL
  - 40% diffused into low K layers
  - 11% trapped in dead-end fractures

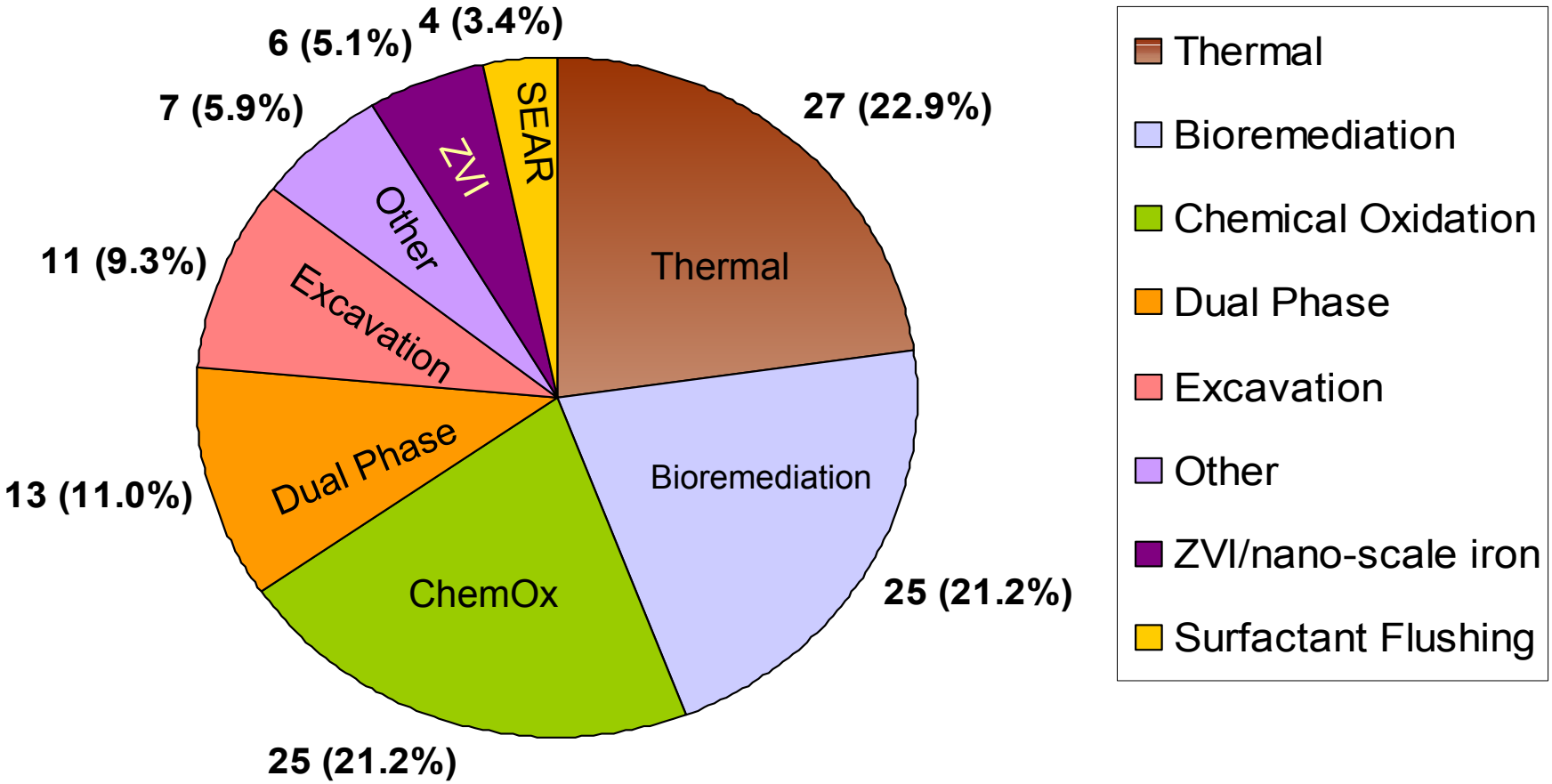
Percentages add to >100% as respondents were asked to choose all that applied to their site.

DNAPL Shape:



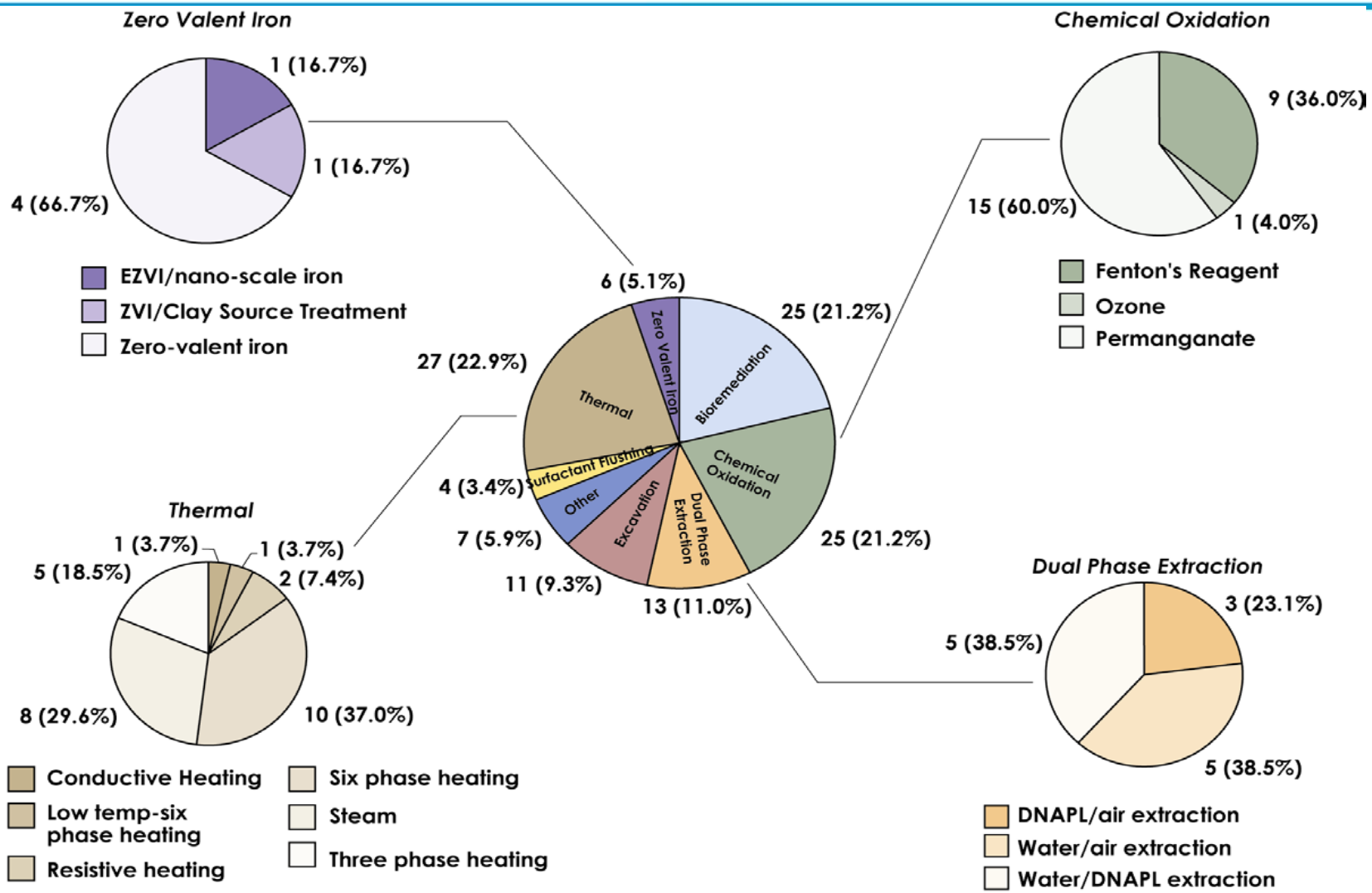
Total number of Sites with DNAPL Shape Data = 118

Sites Sorted by Technology:



Number of Sites with Specified Technology Data = 118

Sites Sorted by Specific Technologies:



11 (9.0%) = Number of Sites (% of total sites with technology)

Treatment Cost:

(Treatment costs do not include site characterization costs)

- **16 responses for completed & on-going Full-Scale Applications**
  - **Largest cost was $15M**
    - water/DNAPL dual-phase treatment
    - site with areal extent between 100,000 to 1,000,000 ft^2
  - **Thermal treatment, pump and treat, and dual-phase extraction applications appeared to be significantly more expensive than chemical oxidation cases on large sites**
  - **Average full-scale application is $2.8M**
  - **Lower cost full scale application was $75K for:**
    - Bioremediation (small site)
    - ZVI (site <1000 ft^2, <10,000 to 100,000 ft^3)
- **31 responses for Pilot-Scale Applications**
  - **Majority of cases costs were < $500K for sites <1,000 ft^2**
  - **None of the pilot tests had costs greater than $2M.**

Treatment Duration:

- **Estimated treatment durations:**
  - **Cases considered are full scale applications**
    - Dual Phase Extraction: 60 years
    - Pump & Treat: 158 years
    - Chemical Oxidation: ~4 years
    - Thermal Technologies: ~4 years
    - ZVI Technologies: ~4 years
    - Bioremediation: ~4 years

Total Count: 16 full scale completed and on-going applications

Benefits / Payback: Sites Applicability

PCE

Concentration Range			Units	Site Count
> 5	to	<1,499	ppb	194
> 1,500	to	<14,999	ppb	13
> 15,000	to	<149,999	ppb	4
> 150,000	to	<1,500,000	ppb	2

TCE

Concentration Range			Units	Site Count
> 5	to	<9,999	ppb	352
> 10,000	to	<109,999	ppb	36
> 110,000	to	<1,099,999	ppb	8
> 1,100,000	to	<10,999,999	ppb	3

Solubility: PCE=150,000 ppb TCE=1,100,000 ppb

MCL: PCE 5ppb, TCE=5ppb

Benefits / Payback:

- **Highest cost: $15M and 60 years treatment duration**
- **Average cost: $2.8M**
- **Lowest cost: $75K and 4 years treatment duration**
- **Assumption:**
  - **That as a result of this survey, half of the 66 site owners are persuaded to pursue:**
    - Chemical Oxidation: ~4 years
    - Thermal Technologies: ~4 years
    - ZVI Technologies: ~4 years
    - Bioremediation: ~4 years
- **Savings**
  - **[33 * (Highest cost – average cost) + O&M costs for 56 years]**
  - **Savings are ~$402M + O&M costs**

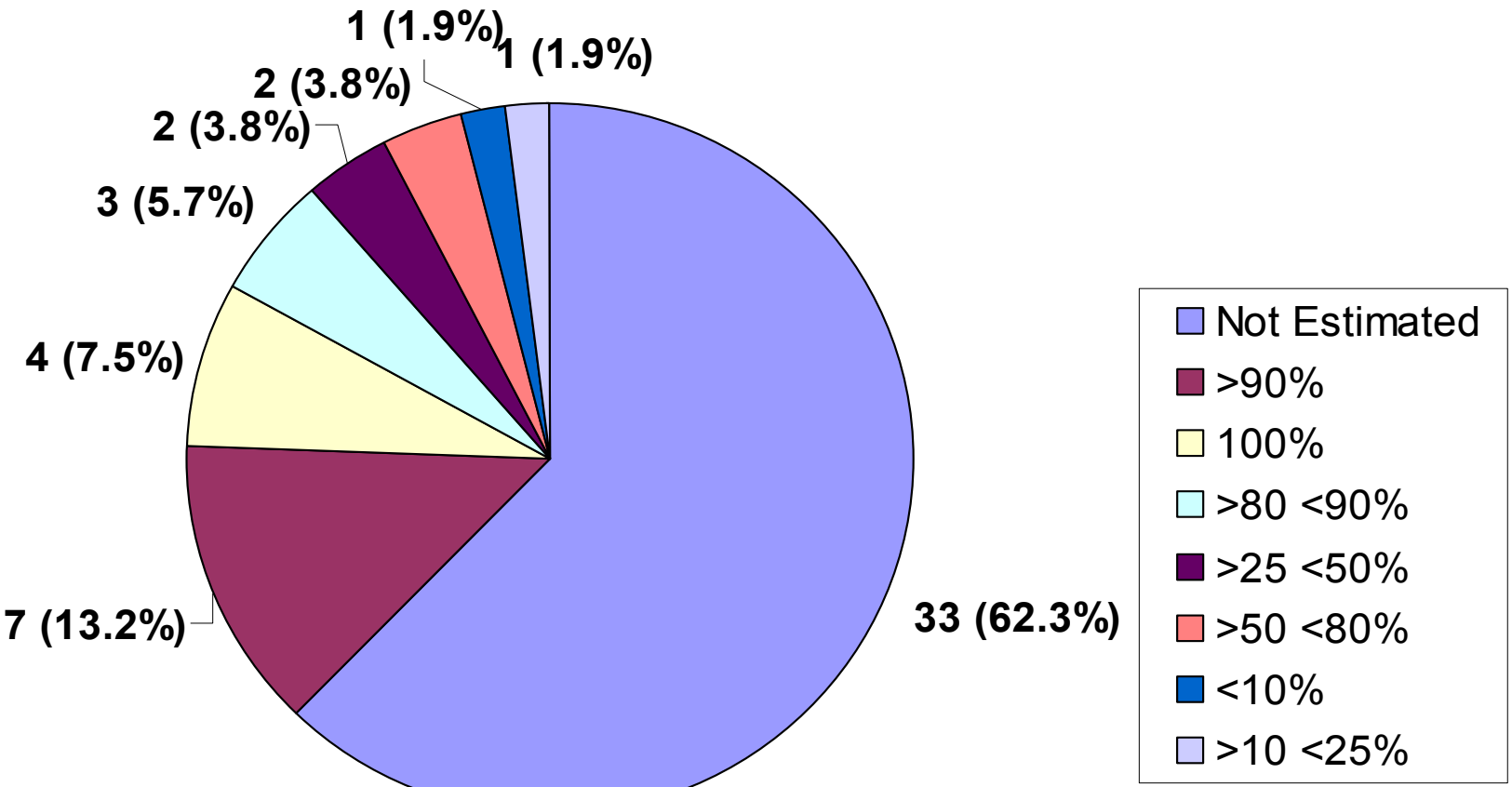
Evaluating Success:

- **Of the 118 locations, 80 had data that allowed us to evaluate technology performance**
- **Of the 80 technology evaluations:**
  - **28 technology applications are on-going**
    - 10 Pilot-Scale Demonstrations
    - 18 Full-Scale Applications
  - **53 technology applications are completed**
    - 39 Pilot-Scale Demonstrations
    - 14 Full-Scale Applications
- **In order to evaluate success, only data from the completed technology applications (53) was considered**

Success Parameters:

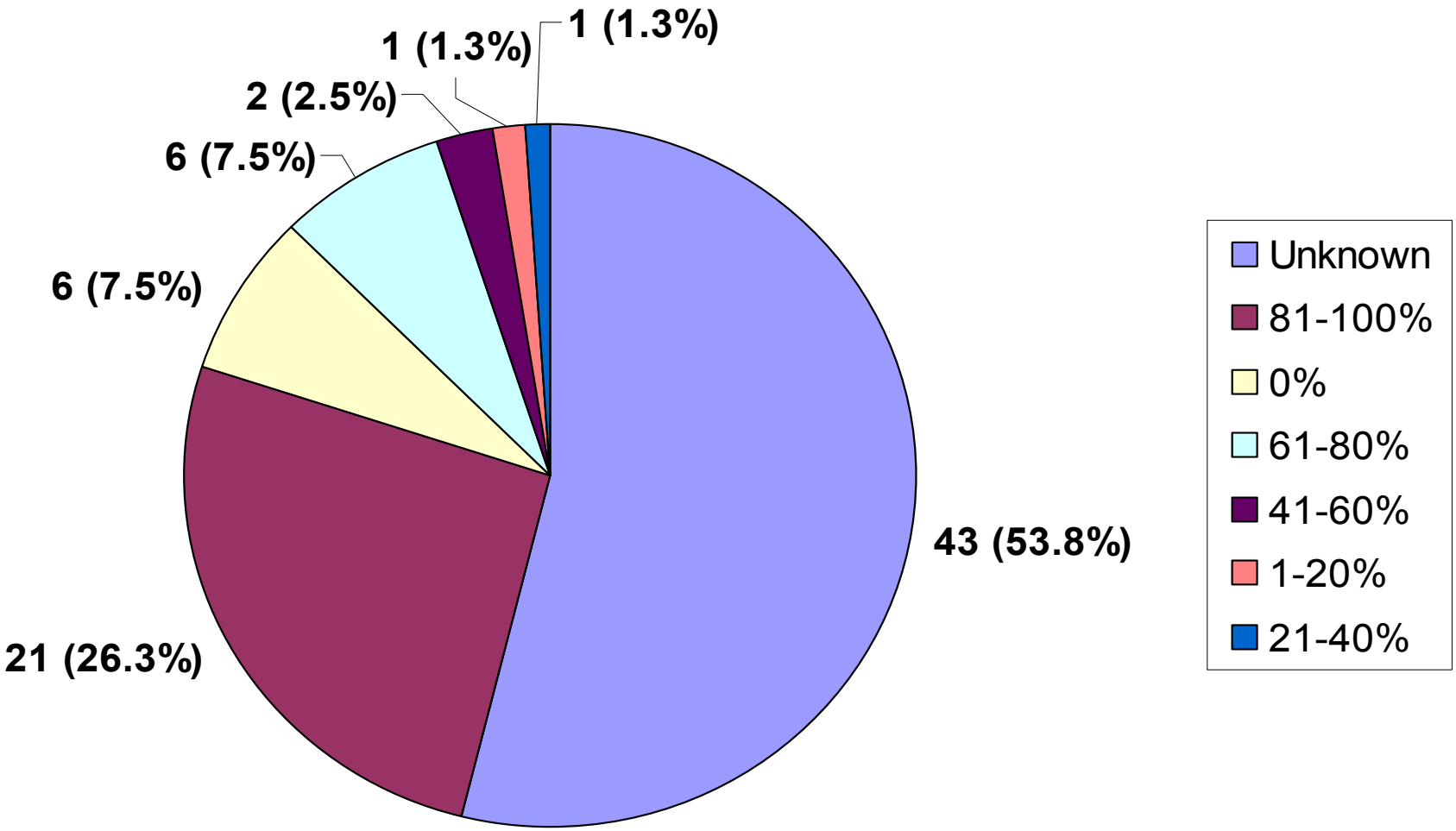
- **Relative success criteria is based on 4 parameters:**
  1. **Reduction in DNAPL mass**
  2. **Decrease in mass flux**
  3. **Rebound of dissolved chlorinated solvents**
  4. **The user must qualify the application as successful**

Level of Source Mass Removal



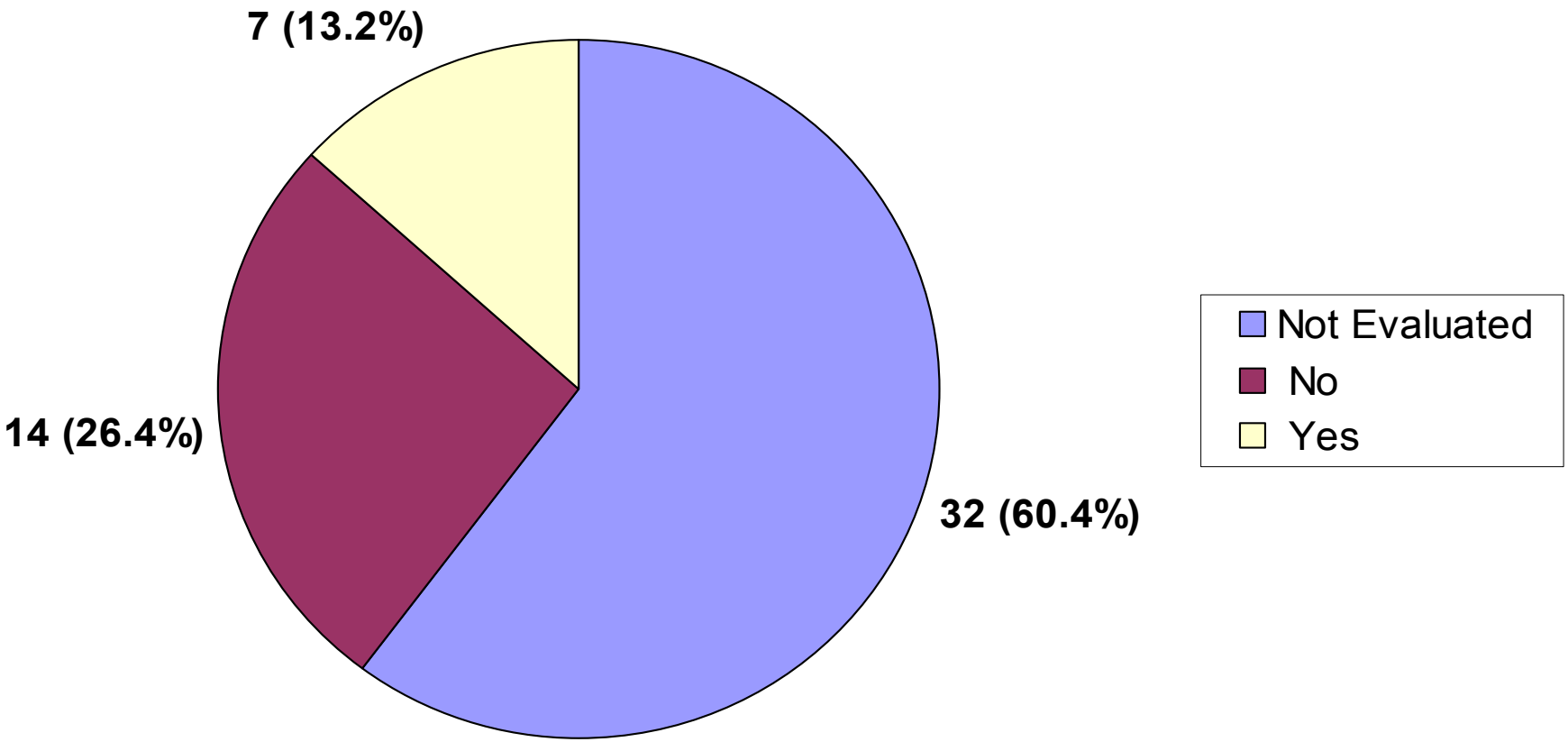
Total number of Sites with Source Mass Removal Data = 53

Decrease in Mass Flux:



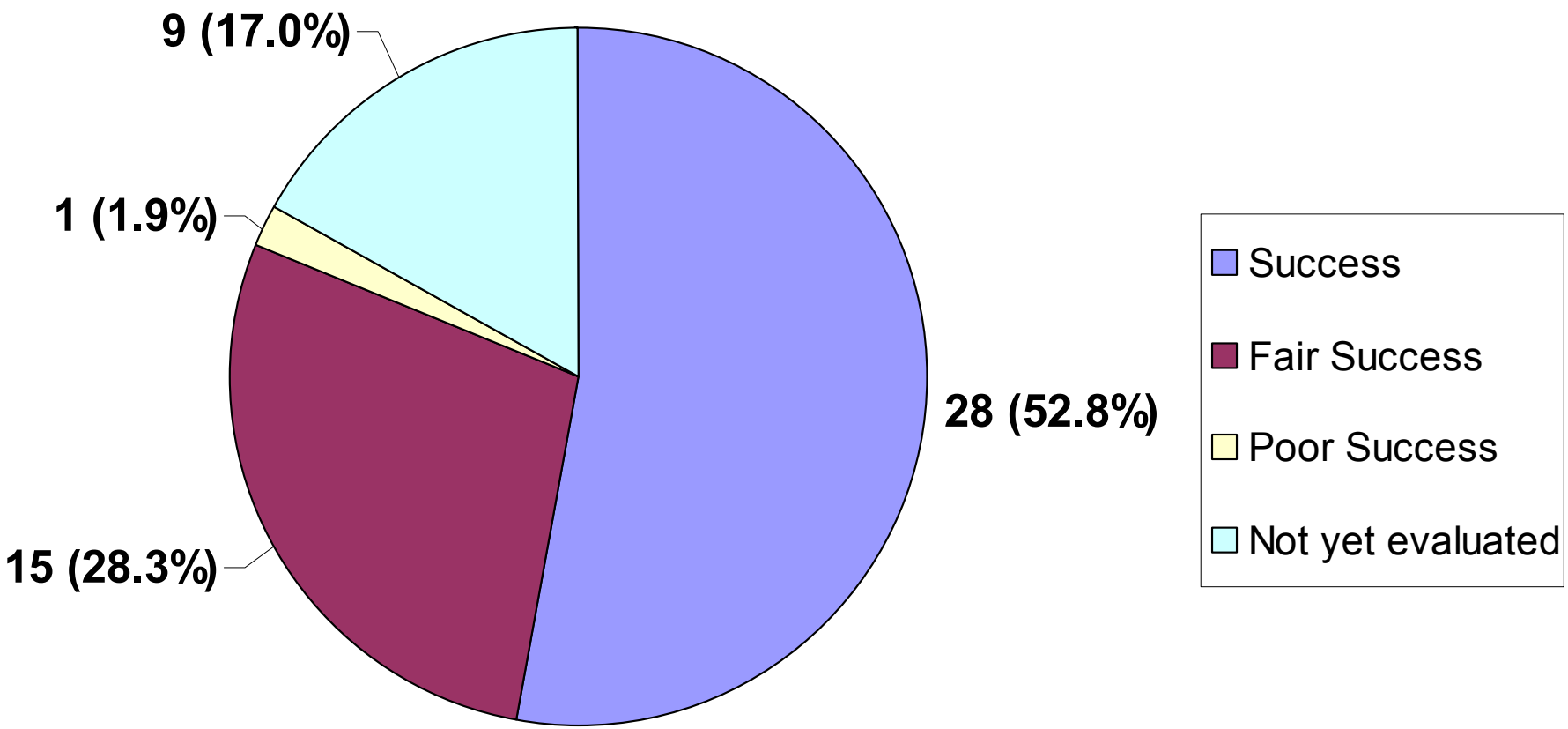
Total number of Sites with Mass Flux Data = 80

Observed Rebound:



Total number of Sites with Rebound Data = 53

Perceived Success:



Total number of Sites with Perceived Success Data = 53

Qualified Success:

- **Of 53 completed technology applications (full and pilot scale) only 2 met all of the most stringent criteria:**
  - **–Higher than 80% Source Mass Removed**
  - **–Higher than 61% Mass Flux Reduction**
  - **–No Rebound**
  - **–Perceived to be Successful by the user**

Technology	Lithology	Count
Bioremediation (pilot scale)	Sand	1
Chem Ox/Permanganate (pilot scale)	Sand	1

Qualified Success:

- If criteria is relaxed slightly (rebound removed) then out of the 53 locations, 3 met the following criteria:
  - –> 80% Source Mass Removed
  - –> 61% Mass Flux Reduction
  - –Perceived to be Successful

Technology	Lithology	Count
Bioremediation	Sand	1
Chemical Oxidation-Permanganate	Sand	1
Excavation	Sand	1

Qualified Success:

- **If the criteria is relaxed even more (to simply higher than 50% source mass removed), then of the 53 locations, 16 met the criteria.**

Technology	Lithology	Count
Thermal - Conductive Heating	clay	1
Thermal - Steam	sand	1
	clay	1
Thermal - Six Phase Heating	sand	1
Chemical Oxidation - Permanganate	sand	3
Chemical Oxidation - Fenton's Reagent	sand	1
	silt	2
	clay	1
Excavation	sand	2
	silt	1
Surfactant Flushing	clay	1
Bioremediation	sand	1

Qualified Success:

- **None of the completed remediation attempts achieved MCLs or regulatory site closure.**
  - **–Meeting MCLs was not always the reason source reduction was attempted.**
- **Although site closure was not achieved, significant mass removal and mass flux was achieved in the majority of the cases that estimated mass removal and mass flux.**
  - **–14 sites had >80% source removal**
  - **–4 of these 14 claimed to have 100% removal**
    - 1 excavation pilot test application
    - 1 six-phase heating full-scale application
    - 1 conductive heating full-scale application
    - 1 chemical oxidation/permanganate pilot test application
  - **–the majority of the cases that estimated mass flux achieved an 80 to 100% decrease in mass flux.**

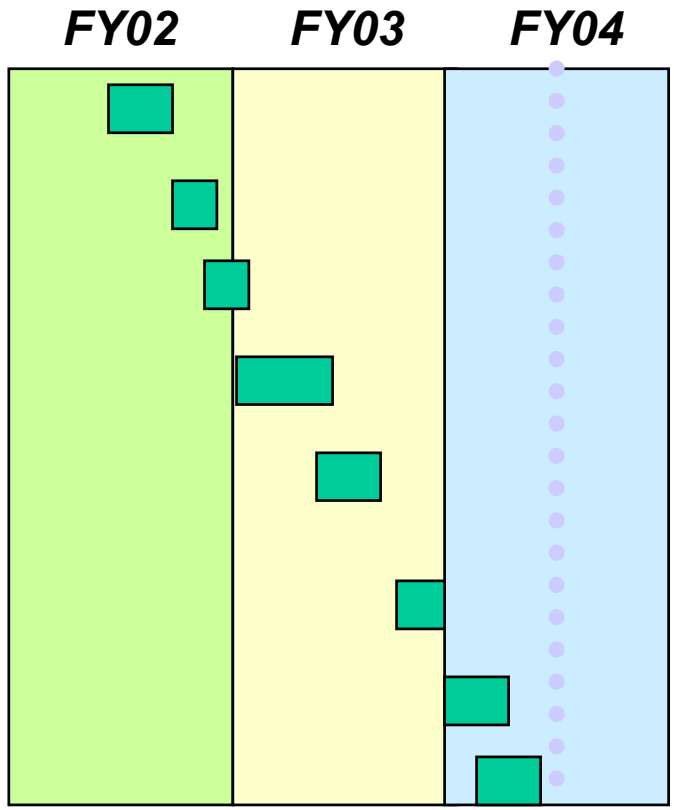
Success v. Media:

- All of the 28 sites where remediation was perceived to be a success were in unconsolidated media
  - 48% were in sand
  - 26% were in clay
  - 15% were in silt
  - 4% each were in till, gravel or unknown
- Of the 16 sites with > 50% mass removal
  - 56% were in sand
  - 25% were in clay
  - 19% were in silt
- None of the technology applications in consolidated material were deemed to be successful
  - May be due to the fact that of the 118 locations, only 13 had consolidated media

Milestones:

Milestone

- ☑ Establish Contract
- ☑ Establish requirements & plan of action
- ☑ Develop and advertise survey
- ☑ Post and maintain survey website
- ☑ Interview Experts
- ☑ Detailed review of limited case studies for each technology
- ☑ Data Analysis and Evaluation
- ☑ Reporting



Tech Transfer

- Final Report is available for downloading from the NFESC Website http://enviro.nfesc.navy.mil/erb/
  - Go to Index
  - Then Documents
- Presentations at SERDP Symposium, ITRC meetings, Battelle Conference
- ROCS Survey featured in NRC (2004), DOE (2003) and ITRC (2004) reports
- Follow-on project approved for funding under ESTCP
  - Goal is to develop a screening tool that can be applied to reduce the uncertainty of estimating and predicting remedial outcomes at DNAPL source zone sites.

    Phase 1 - Assess results from existing efforts

    Phase 2 - Develop template sites

    Phase 3 – Computer Simulations

    Phase 4 – Protocol Validation

    Phase 5 – Develop User-Friendly Screening Tool

Questions?