Headquarters U.S. Air Force

Integrity - Service - Excellence

Oxygen and Hydrogen Releasing Materials

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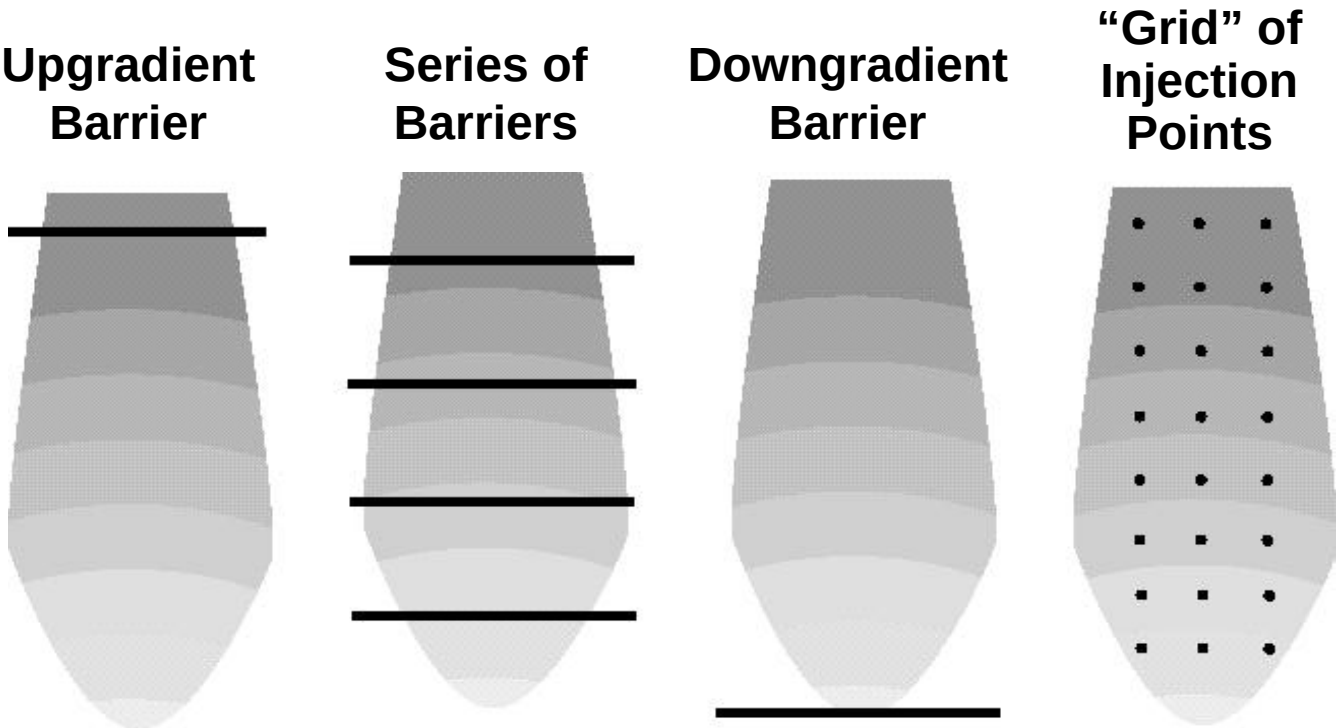
AFCEE/ERT
31 January 2001

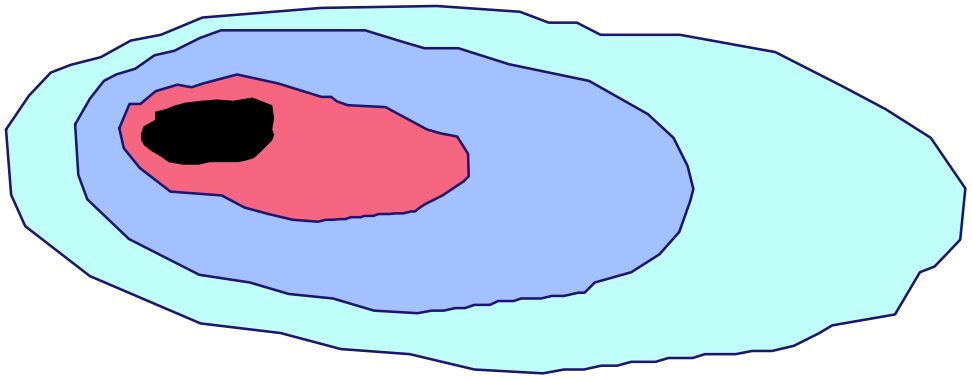
Injectable Bioremediation Products

- **Delivery Systems - bore-hole backfill or injection via direct-push technologies**
- **Designs for Barriers and Source Treatment**



Oxygen Releasing Materials

- **Question:** **If 100 gallons of gasoline were spilled and ground water was contaminated, what would be the method and cost of ground water remediation using oxygen releasing materials?**



Oxygen Releasing Materials

- **Assumptions/Background:**
  - **Oxygen releasing materials are composed of magnesium peroxides or calcium peroxides and contain approximately 10% oxygen by weight**
  - **It takes approximately 3 lbs of oxygen to biodegrade 1 lb of petroleum hydrocarbon (e.g. hexane)**
    - **Oxygen releasing materials cost approximately $10/lb (or $100 per pound of oxygen potentially delivered)**
    - **100 gallons of gasoline weighs approximately 660 lbs**
    - **All of the 100 gallons will solublize**

Oxygen Releasing Materials

- Thus, approximately 2000 lbs. of oxygen would be required to biodegrade 100 gallons of gasoline (660lbs. * 3 lbs/lb hydrocarbon)
- Since oxygen releasing compounds are 10% oxygen by weight, >20,000 lbs. would be required to meet the minimum oxygen demand.
- In order to provide the required oxygen, ~$200,000 worth of oxygen releasing materials would be required.

Emplacement Methods

- Placement of oxygen releasing material canisters or “socks” in site monitoring wells;
- Placement of oxygen releasing materials in closely-spaced borings or in trenches;
- Jetting oxygen releasing material slurry into the saturated soil pore space using direct push (e.g. Geoprobe®) or other injection tools.

Trench or Boring Emplacement

- **$5,000 - $15,000 cost per emplacement every 3- 6 months**
- **$100,000 - $600,000 for 10-year source**
- **200 ft plume may reduce to a 100 ft plume for the 3 - 6 months the oxygen releasing material is active**
- **Contaminant concentrations will likely rebound after the oxygen releasing material is depleted.**

Natural Biodegradation Site Profiles *(mg/L)*

	Observed Change in Concentration (mg/L)					MAX	Expressed Assimilative
Installation	O_2	Nitrate	Iron	Sulfate	Methane	BTEX	Capacity
Hill AFB, UT	6.0	36.2	55.6	96.6	2.0	21.5	35.4
Battle Creek, MI	5.7	5.6	12.0	12.9	8.4	3.6	17.1
Madison, WI	7.2	45.3	15.3	24.2	11.7	28.0	32.5
Elmendorf, AK	0.8	64.7	8.9	25.1	9.0	22.2	30.9
Elmendorf, AK	12.7	60.3	40.5	57.0	1.5	30.6	32.5
King Salmon, AK	9.0	12.5	2.5	6.8	0.2	10.1	7.2
King Salmon, AK	11.7	0	44	0	5.6	5.3	12.9
Plattsburgh, NY	10.0	3.7	10.7	18.9	0.3	6.0	8.9
Eglin AFB, FL	1.2	0	8.9	4.9	11.8	3.7	17.0
Patrick AFB, FL	3.8	0	2.0	0	13.6	7.3	18.7
MacDill AFB, FL	2.4	5.6	5.0	101.2	13.6	29.6	41.5
MacDill AFB, FL	2.1	0.5	20.9	62.4	15.4	0.7	35.0
MacDill AFB, FL	1.3	0	13.1	3.7	9.8	2.8	14.4
Offutt AFB, NE	0.6	0	19.0	32.0	22.4	3.2	36.8
Offutt AFB, NE	8.4	69.7	0	82.9	0	103.0	34.9
Westover, MA	10.0	8.6	599	33.5	0.2	1.7	40.0
Westover, MA	9.9	17.2	279	11.7	4.3	32.6	27.5

Natural Biodegradation Profiles (cont) (mg/L)

Installation	Observed Change in Concentration (mg/L) O_2	Nitrate	Iron	Sulfate	Methane	BTEX	Expressed MAX Assimilative Capacity
Myrtle Beach, SC	0.4	0	34.9	20.7	17.2	18.3	28.2
Langley AFB, VA	6.4	23.5	10.9	81.3	8.0	0.1	35.3
Griffiss AFB, NY	4.4	52.5	24.7	82.2	7.1	12.8	40.2
Rickenbacker, OH	1.5	35.9	17.9	93.2	7.7	1.0	38.7
Wurtsmith, MI	8.5	25.4	19.9	10.6	1.4	3.1	12.9
Travis AFB, CA	3.8	9.5	14.9	4,200	5.4	103	900
Pope AFB, NC	7.5	6.9	56.2	9.7	48.4	8.2	70.5
Seymour Johnson	6.0	1.7	32	40	17	18.2	28.2
Grissom AFB, IN	9.1	1.0	2.2	59.8	1.0	0.3	17.4
Tyndall AFB, FL	1.4	0.1	1.3	5.9	4.6	1.0	7.7
Keesler AFB, MS	1.7	0.7	36.2	22.4	7.4	14.1	16.7
Average	5.5	17.4	49.6	186	9.1	17.6	56.3
Median	5.9	6.3	16.6	24.7	7.6	7.8	28.2

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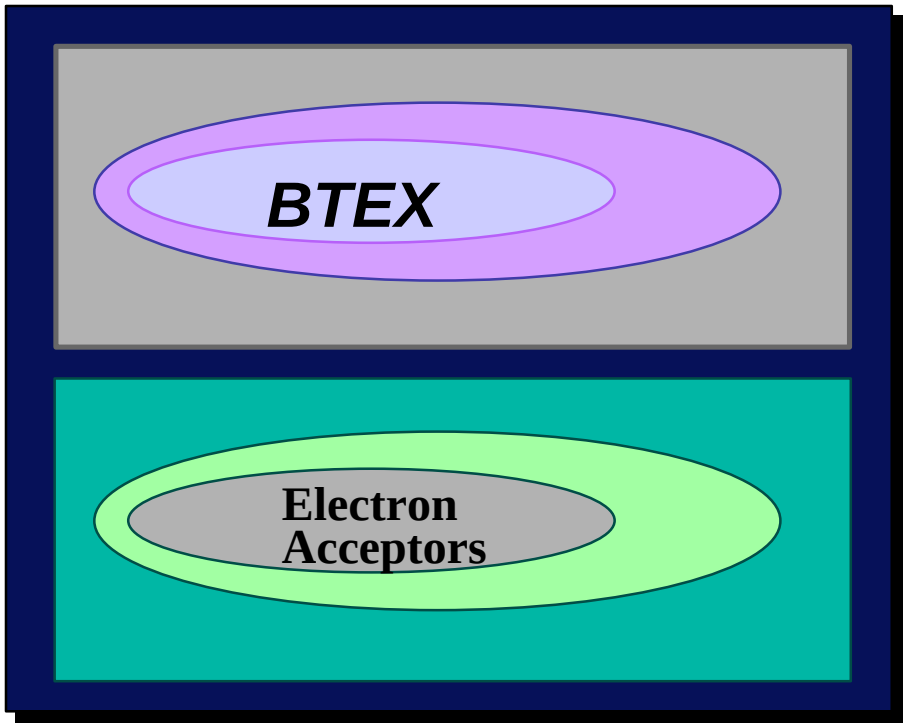
Conclusions

- **Do not add electron acceptors/donors unless you have to!**



Hydrogen Releasing Materials

- Any organic carbon source that can be fermented resulting in the production of hydrogen
- Hydrogen can utilized by methanogens or reductive dechlorinators
- Hydrogen Releasing™ (HRC™) is a lactate-based polymer designed to be a "slow-release" source of hydrogen and redox potential
  - ~50% water by weight
  - ~$6/lb
  - Injected as a viscous slurry

HRC Field Demonstration in USA

PCE Degradation Rates

Days	Total Mass (grams)	Half Life (d) Total Mass	Half Life (d) Well TW01	Half Life (d) Well TW08	Ratio TW01/Total	Ratio TW01/TW08
70	158	66	**338**	**29**	5.11	11.50
120	75.9	79	**211**	**43**	2.66	4.94
149	55.4	85	**256**	**53**	3.00	4.84
191	47.0	128	**309**	**45**	2.41	6.80
253	56.2	109	**205**	**38**	1.87	5.41

HRC Field Demonstration in USA

TCE Test Tube Experiments Data Summary

Days	TCE	DCE	VC	TCE	DCE	VC
0	10	0	0	25	0	0
9	5.27	2.19	0	8.06	1.98	0
15	2.32	0.29	0	3.6	0.22	0
21	2.13	0.32	0.49	2.24	0.25	0.17
29	0.9	0	0	1.5	0.08	0.06

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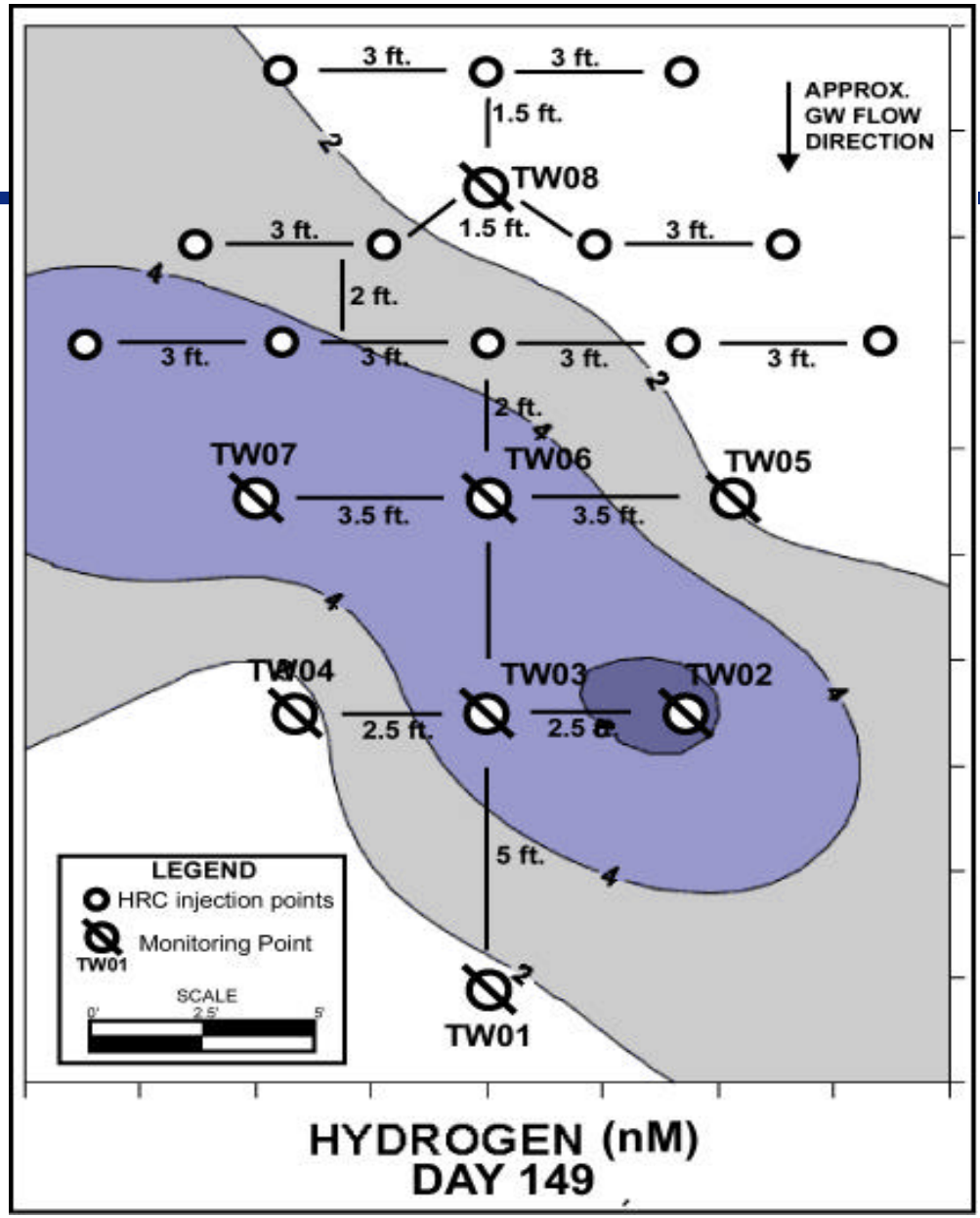
HRC Field Demonstration in USA

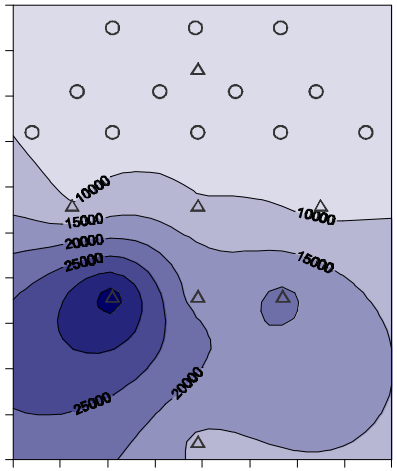
HRC Injection Diagram Overlaying Hydrogen Concentration Map at Day 149



PCE Mass Reduction Upon HRC Application

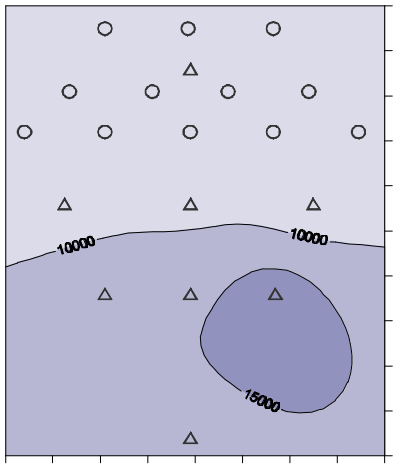
HRC Field Demonstration in WI
Change in PCE

GW Flow



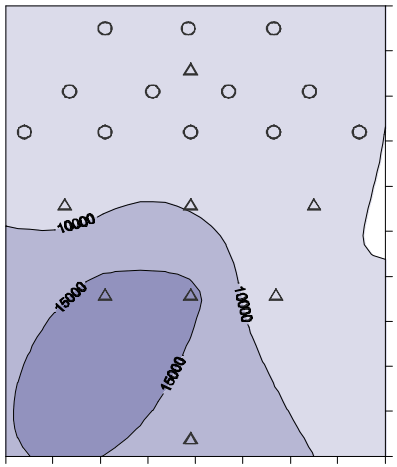
PCE CONCENTRATIONS (ppb)
DAY 0

Mass = 158,000 mg



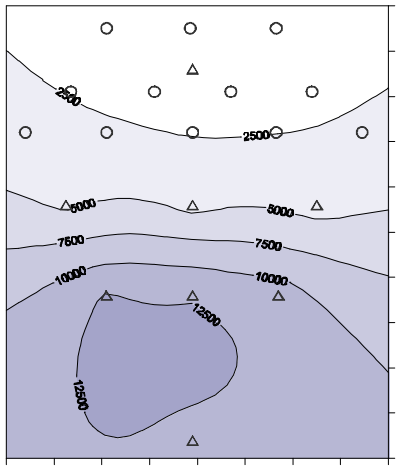
PCE CONCENTRATIONS (ppb)
DAY 14

Mass = 109,000 mg



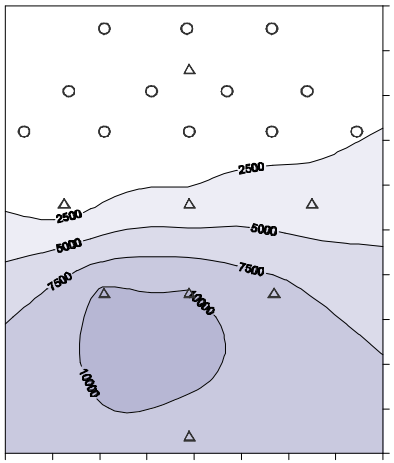
PCE CONCENTRATIONS (ppb)
DAY 28

Mass = 102,150 mg



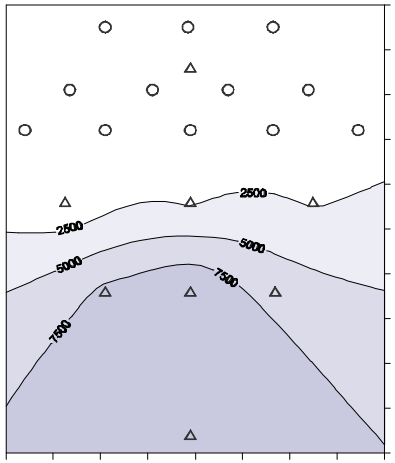
PCE CONCENTRATIONS (ppb)
DAY 71

Mass = 75,930 mg



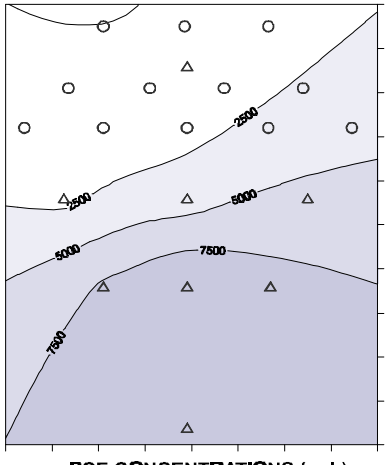
PCE CONCENTRATIONS (ppb)
DAY 120

Mass = 55,420 mg



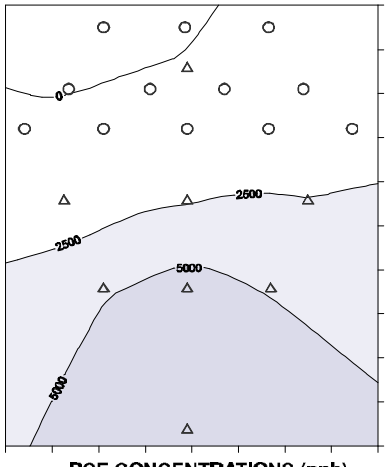
PCE CONCENTRATIONS (ppb)
DAY 149

Mass = 46,990 mg



PCE CONCENTRATIONS (ppb)
DAY 191

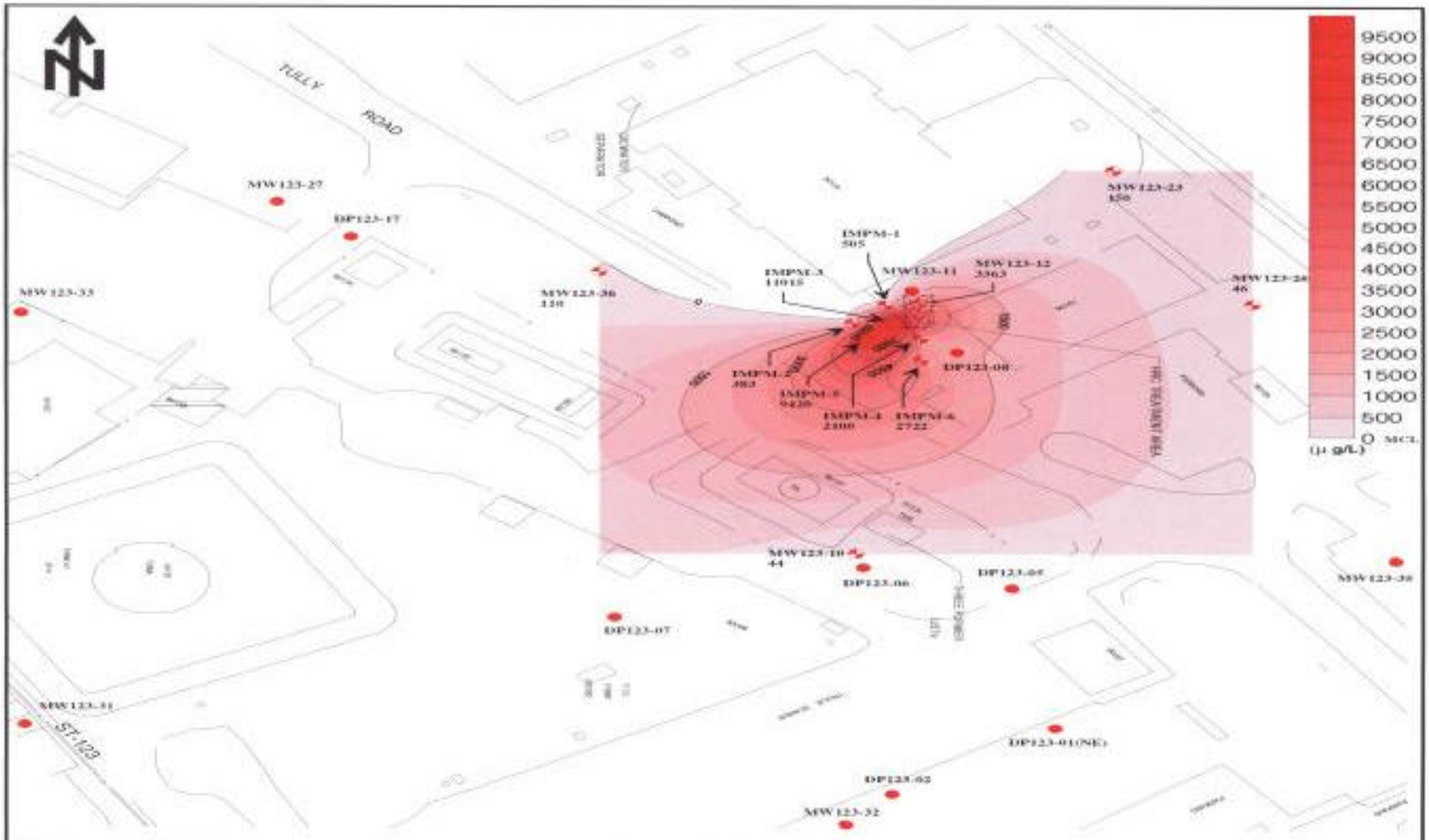
Mass = 56,222 mg



PCE CONCENTRATIONS (ppb)
DAY 253

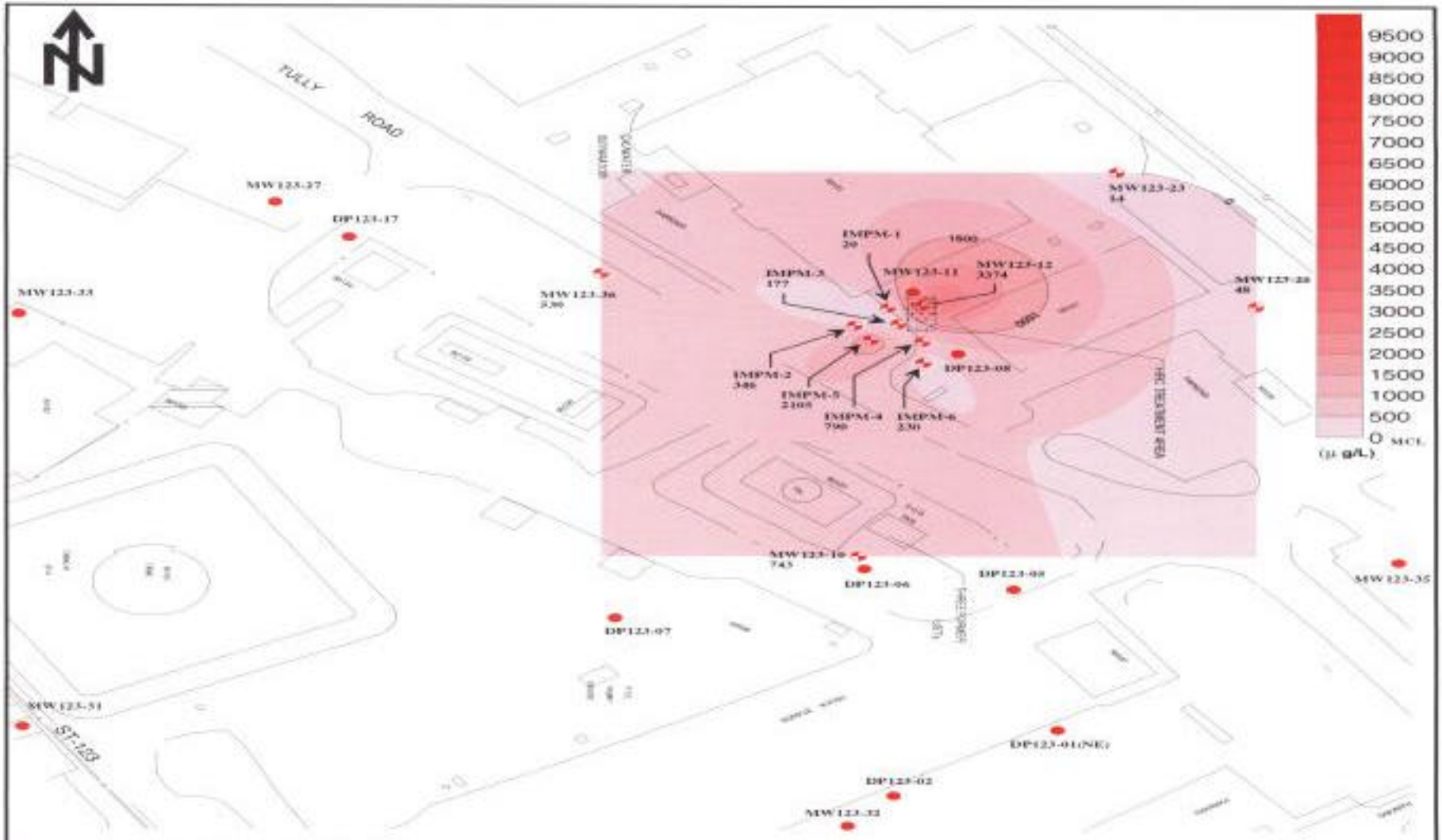
Mass = 31,777 mg

○ **HRC injection point** △ **Monitoring well**

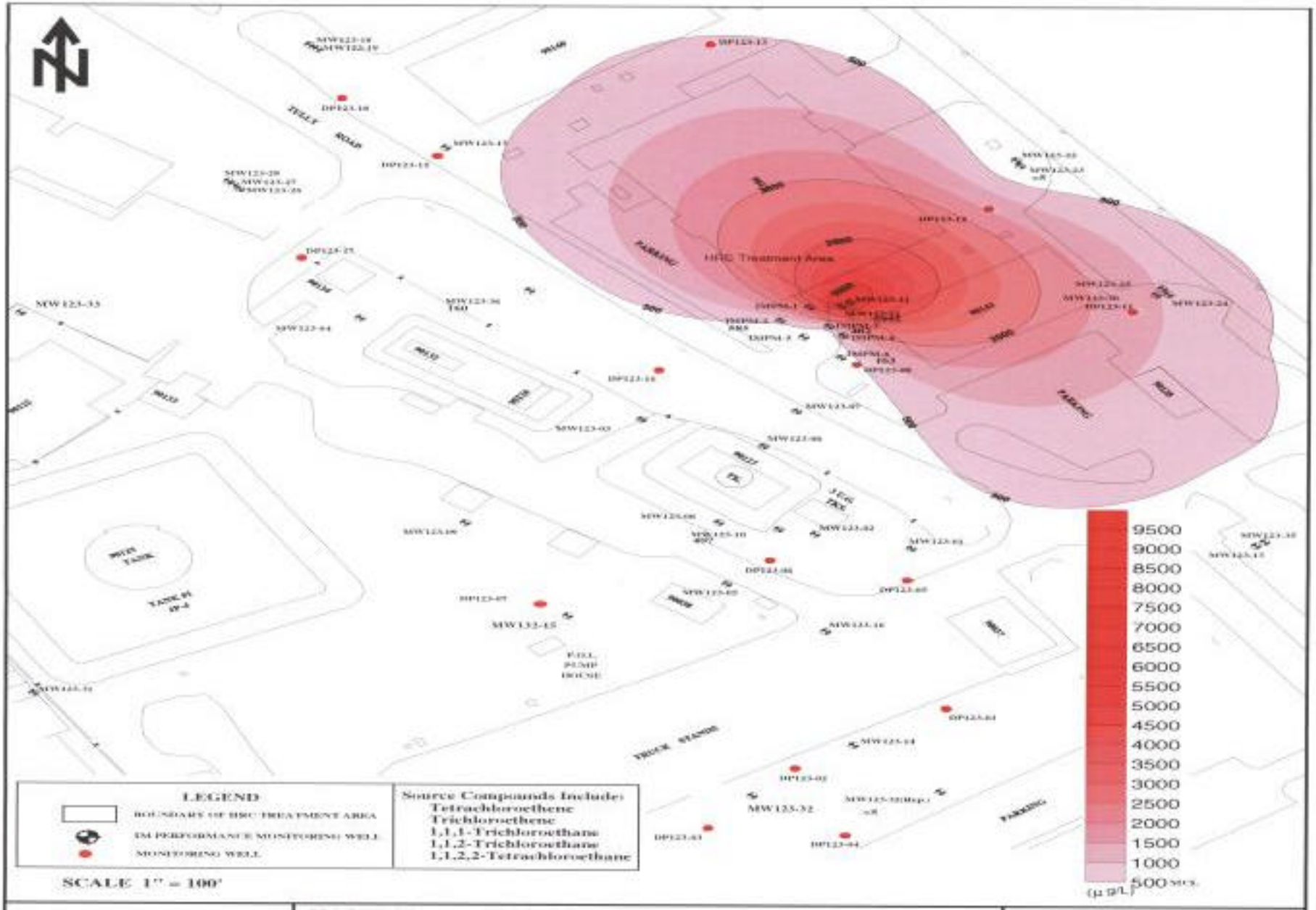


SCALE 1" = 100'

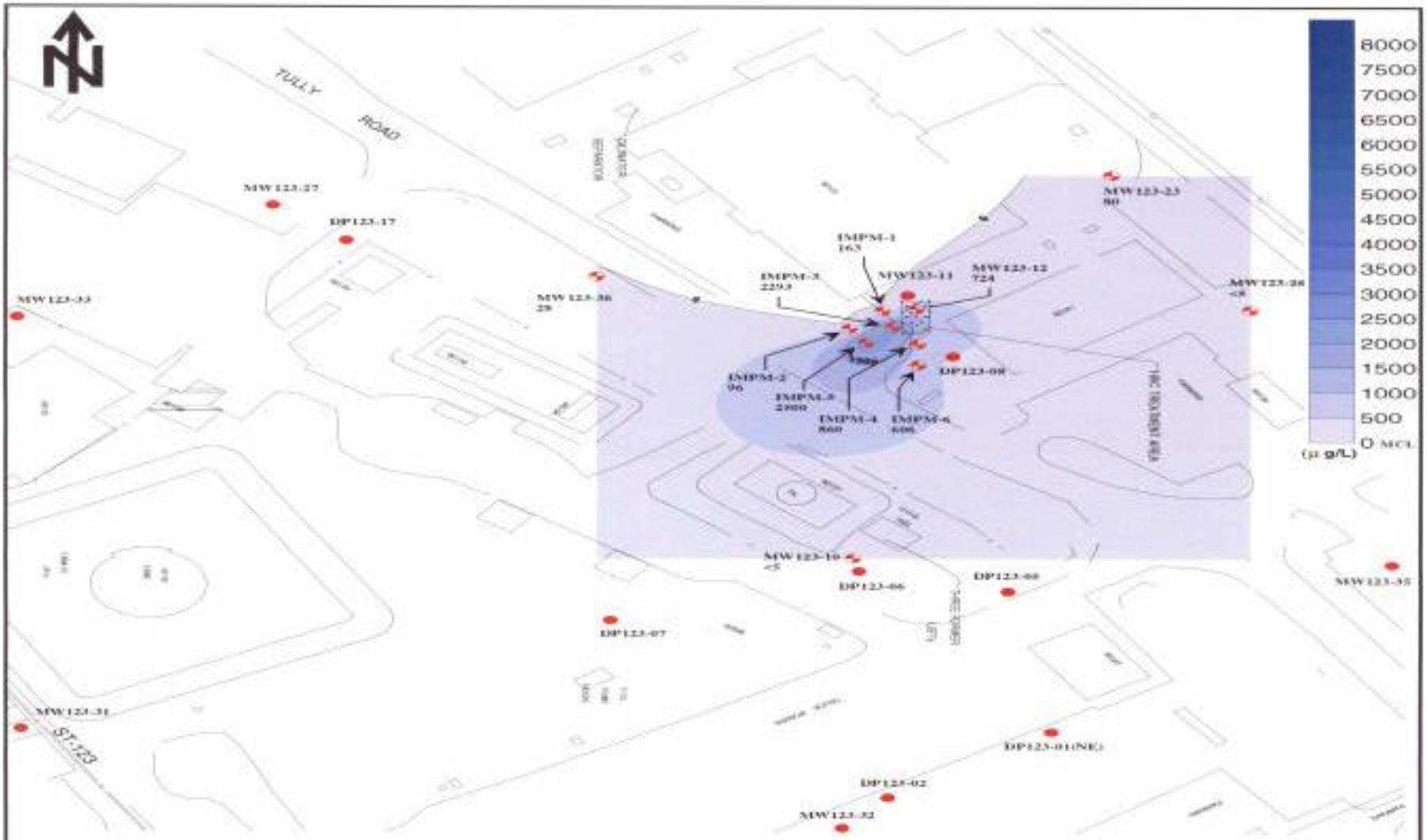
DATE: 10-8-99	PROJECT NAME ST-123 HURLBURT FIELD INTERIM MEASURES PROGRESS REPORT	PROJECT NO. 138696
	DRAWING TITLE CONCENTRATIONS OF SOURCE COMPOUNDS 0 DAYS AFTER HRC® INJECTION	FIGURE 1A



DATE: 10-8-99	PROJECT NAME **ST-123 HURLBURT FIELD** **INTERIM MEASURES PROGRESS REPORT**	PROJECT NO. 138696
	DRAWING TITLE CONCENTRATIONS OF SOURCE COMPOUNDS 106 DAYS AFTER HRC® INJECTION	**FIGURE 1B**



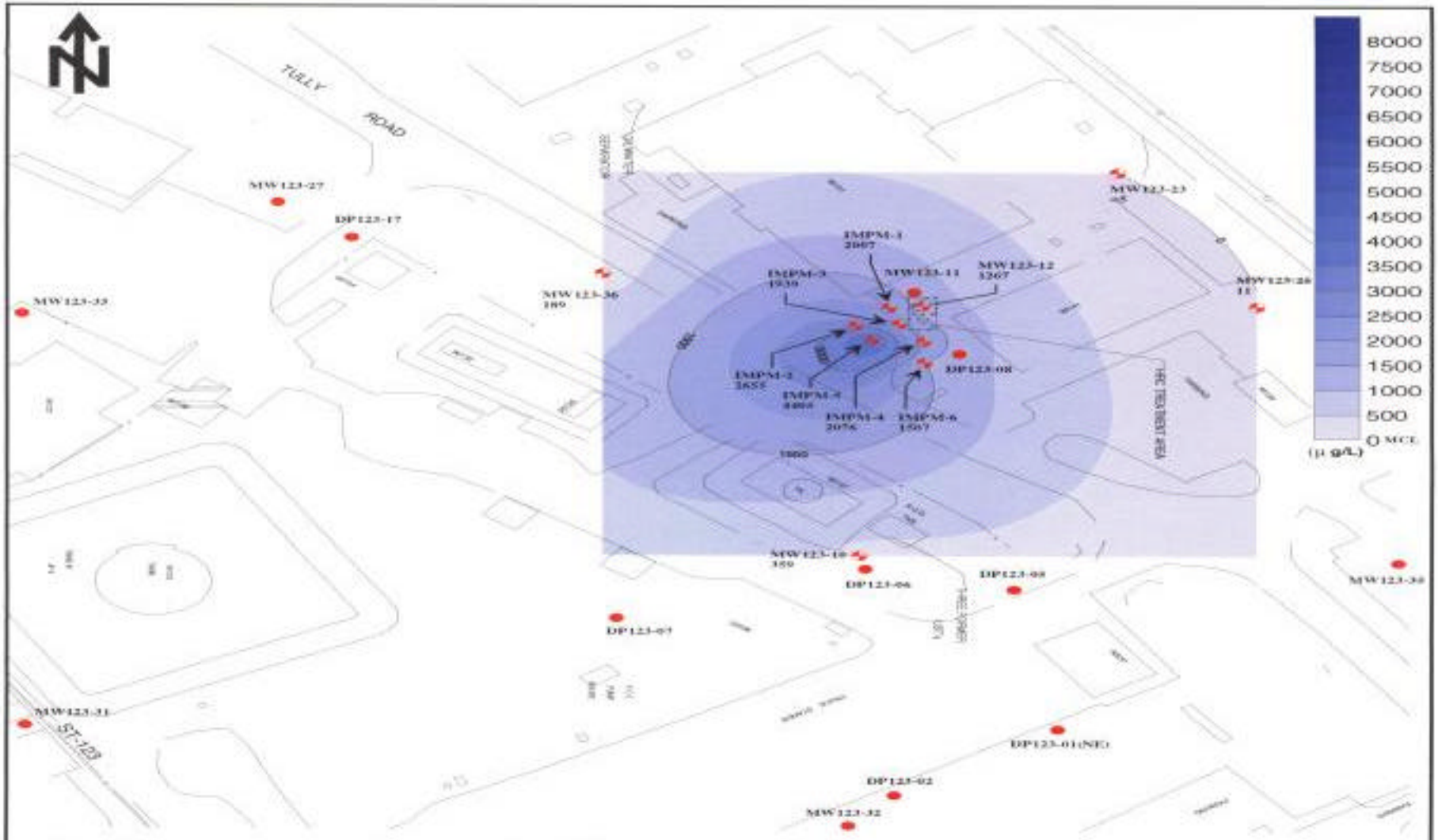
DATE: 10-8-99	PROJECT NAME: ST-123 HURLBURT FIELD INTERIM MEASURES PROGRESS REPORT	PROJECT NO. 138696
	DRAWING TITLE: CONCENTRATIONS OF SOURCE COMPOUNDS 243 DAYS AFTER HRC® INJECTION	FIGURE 1C



LEGEND	First Generation Daughter Compounds Include:
BOUNDARY OF HRC TREATMENT AREA	1,1-Dichloroethene
IM PERFORMANCE MONITORING WELL	cis-1,2-Dichloroethene
MONITORING WELL	trans-1,2-Dichloroethene
	1,1-Dichloroethane
	1,2-Dichloroethane

SCALE 1" = 100'

DATE: 10-8-99	PROJECT NAME: ST-123 HURLBURT FIELD INTERIM MEASURES PROGRESS REPORT	PROJECT NO. 138696
	DRAWING TITLE: CONCENTRATIONS OF FIRST GENERATION DAUGHTER PRODUCTS 0 DAYS AFTER HRC® INJECTION	FIGURE 2A



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	1,1-Dichloroethane
	1,2-Dichloroethane

SCALE 1" = 100'

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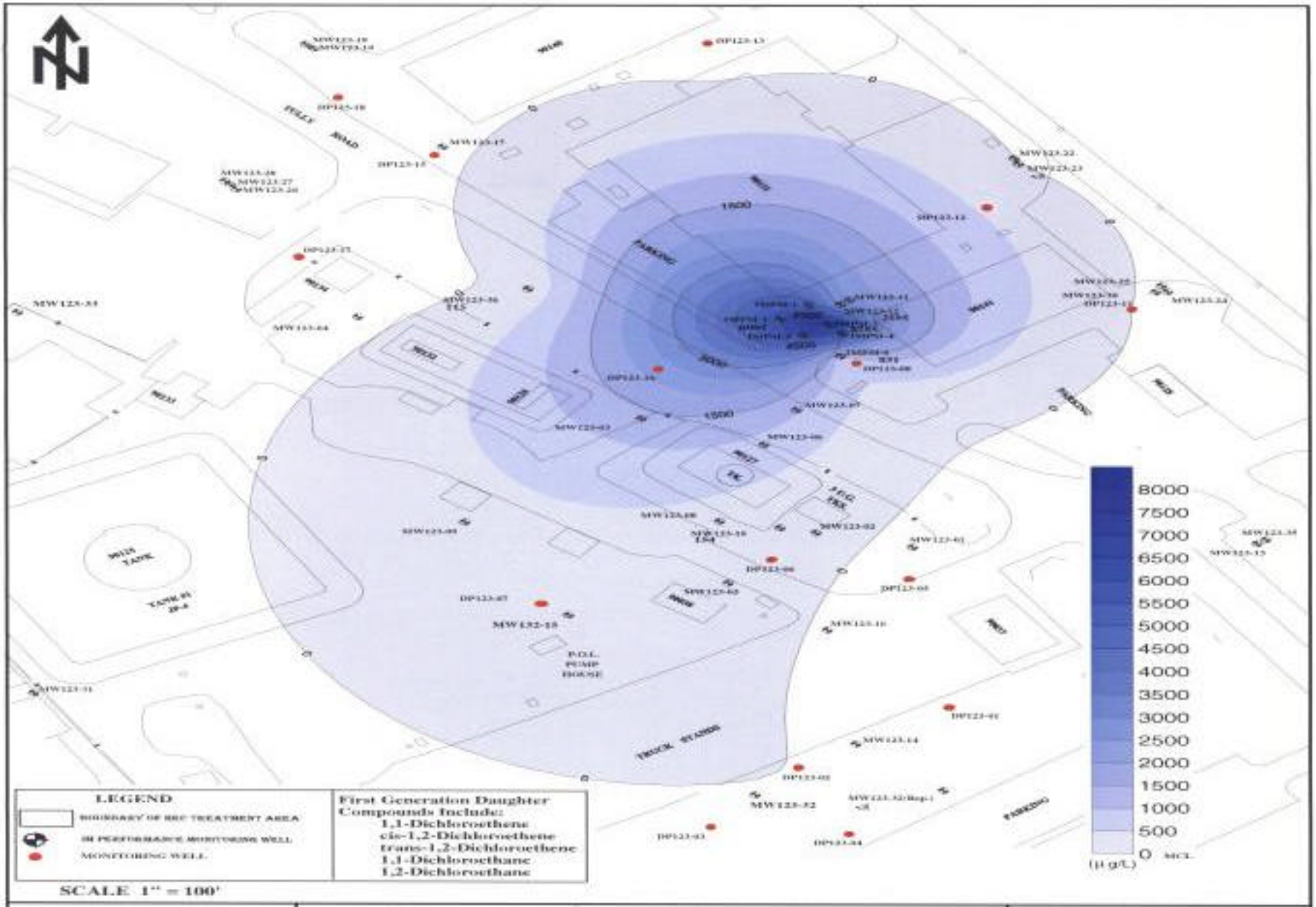

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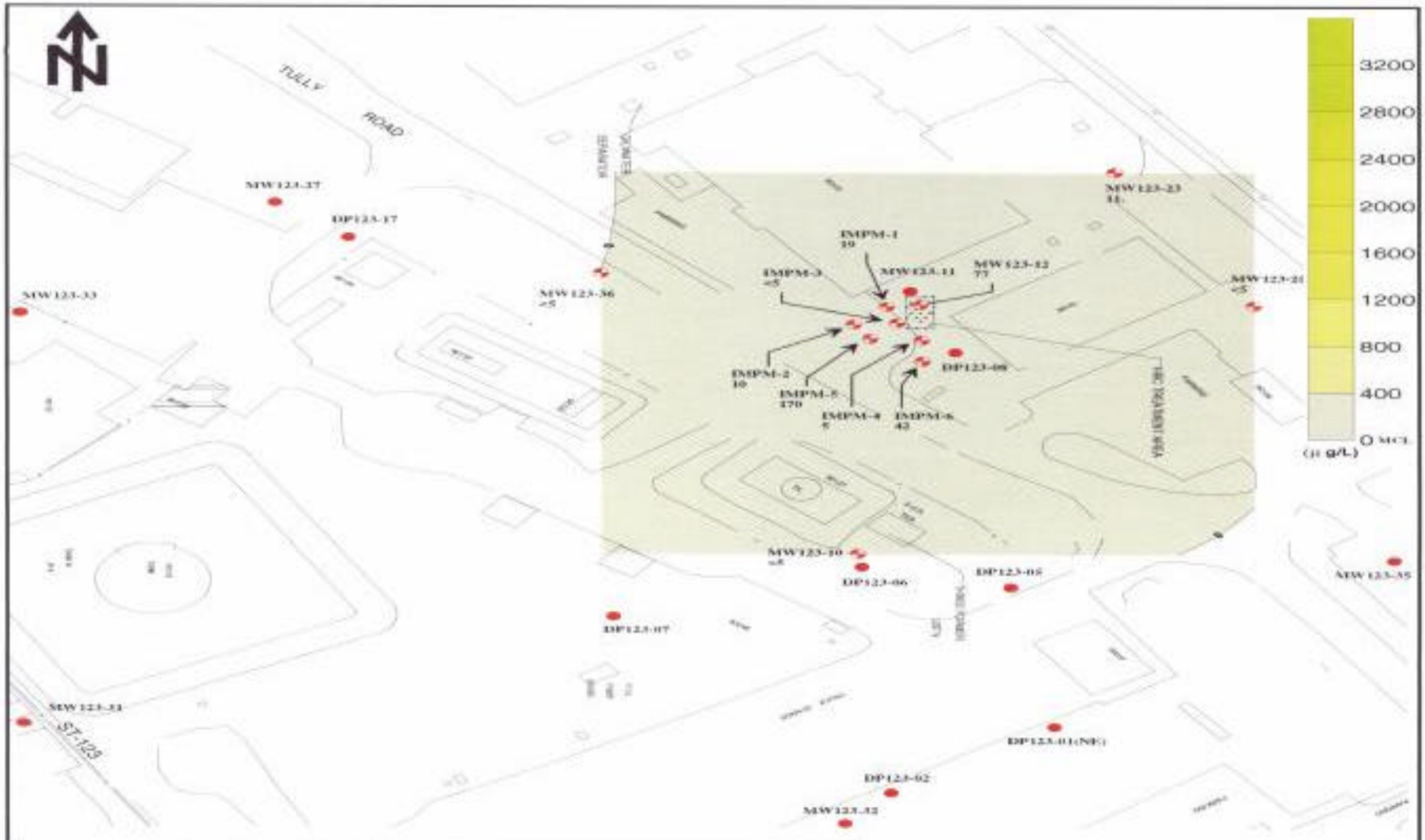

SCALE 1" = 100'

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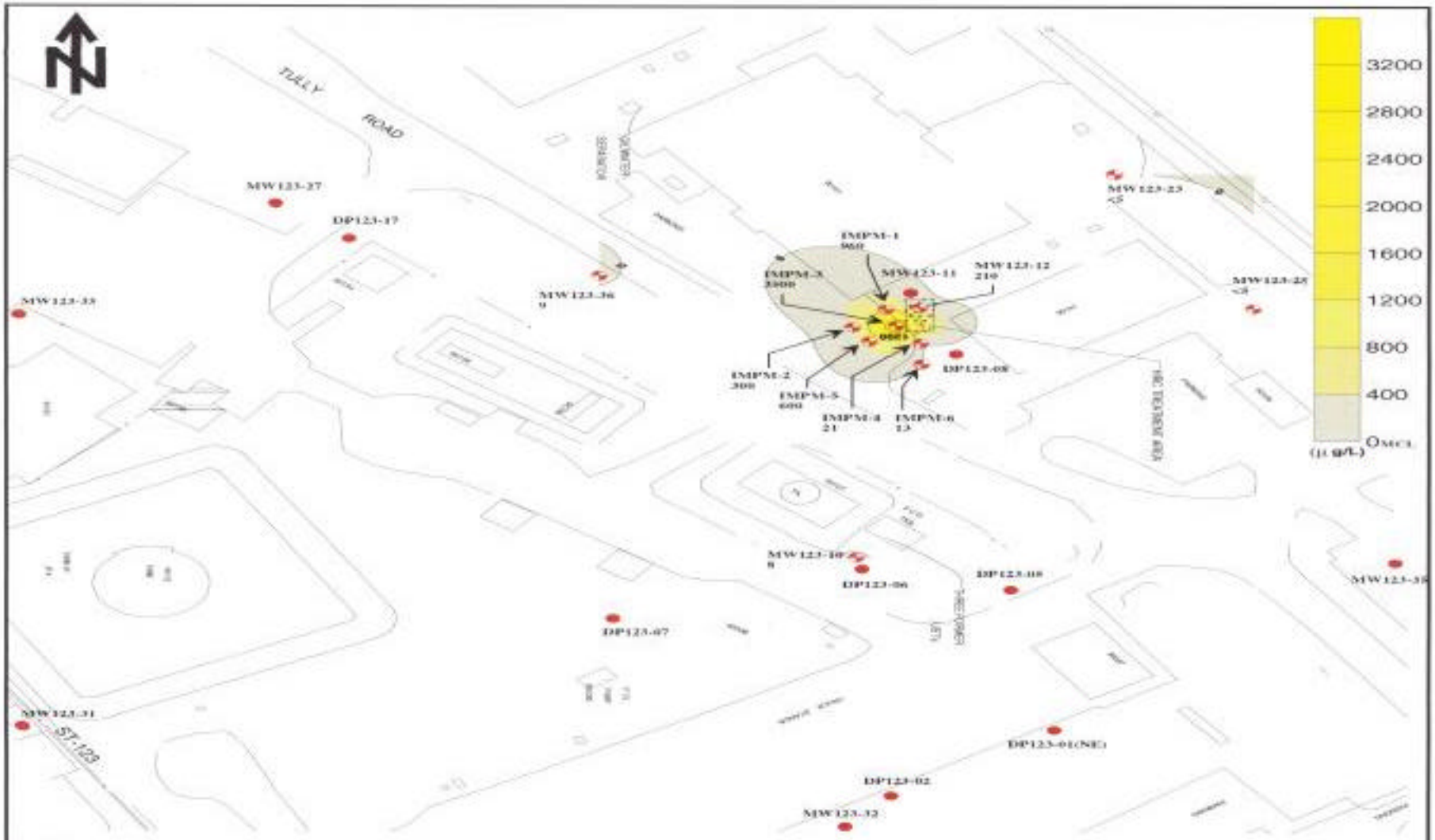
	DRAWING TITLE CONCENTRATIONS OF SECOND GENERATION DAUGHTER PRODUCTS 0 DAYS AFTER HRC® INJECTION	FIGURE 3A



SCALE 1" = 100'

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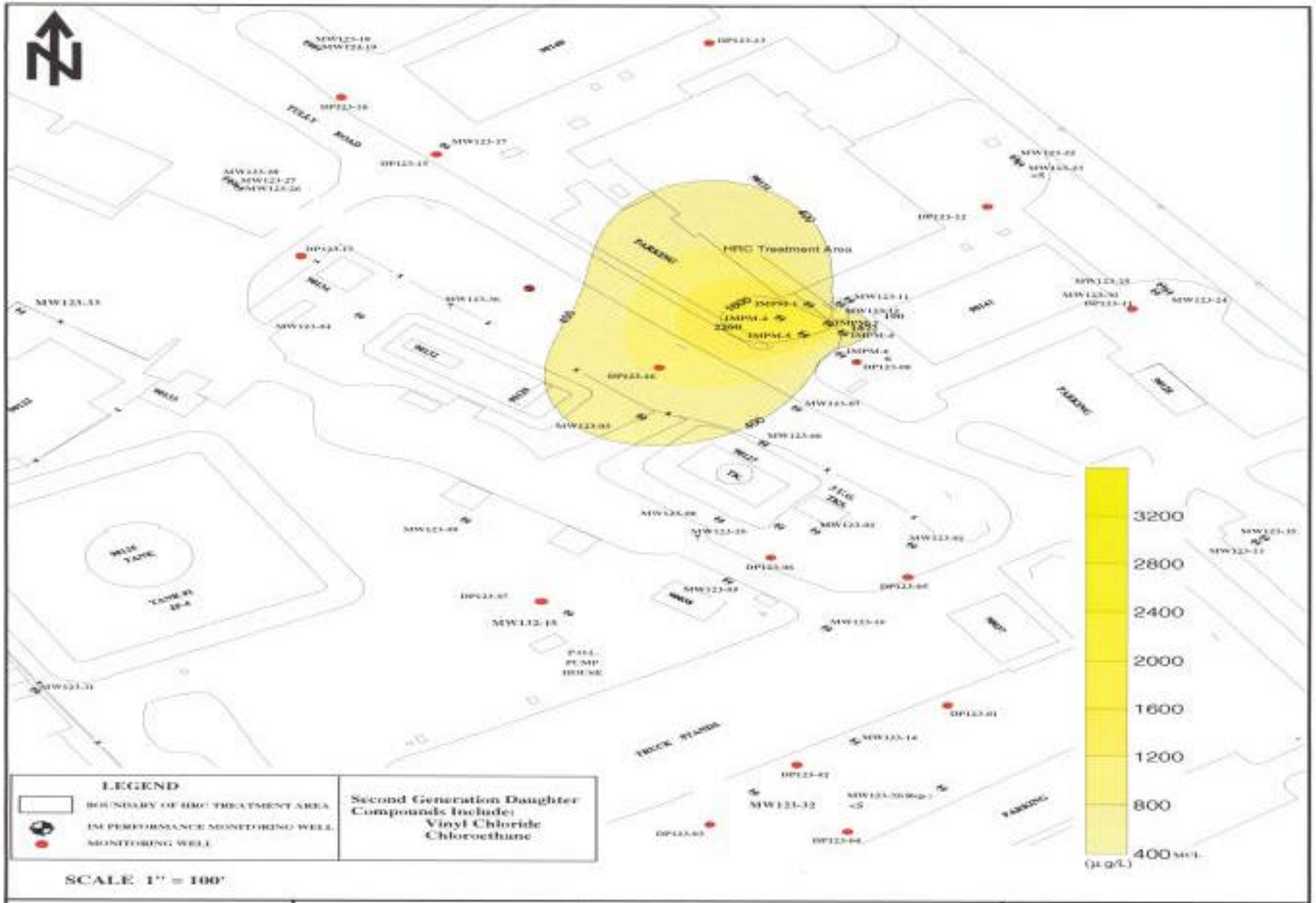
	DRAWING TITLE CONCENTRATIONS OF SECOND GENERATION DAUGHTER PRODUCTS106 DAYS AFTER HRC® INJECTION	FIGURE 3B



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	DRAWING TITLE CONCENTRATIONS OF SECOND GENERATION DAUGHTER PRODUCTS 243 DAYS AFTER HRC® INJECTION	FIGURE 3C

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Summary

- Strategy to address the source is the most crucial aspect
- Biodegradation of petroleum hydrocarbons driven by electron acceptor supply
  - ~3 - 4 lbs Oxygen per 1 lb hydrocarbon
- Biodegradation of chlorinated solvents driven by electron donor supply
  - Stoichiometry and efficiency unknown
    - >20 parts carbon to chlorinated solvent may be a starting point

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Summary cont

- Oxygen releasing materials (ORM):
  - Feasibility based on site electron acceptor demand and duration of demand
  - (Pounds of contaminant) x 30 = minimum amount of ORM required
  - Source lifetime (years) ¸ 1 - 2 injections/year
- Hydrogen releasing materials (HRM)
  - Feasibility based on the ability of the HRM support reductive dechlorination
  - Must overcome site electron acceptor demand
    - lbs O_2 4 3lbs O_2/lb HRM
    - lbs NO_3+SO_4 4 5lbs NO_3+SO_4/lb HRM
    - lbs Fe^{2+} 4 30lbs Fe^{2+}/lb HRM

Summary cont

- Hydrogen releasing materials (HRM)
  - Most crucial parameter is source longevity
    - Mass transfer limitations
  - Lifespan of HRM may be <1 year
    - Frequent reinjections
- Ground water flow
  - Aquifer clogging - Conduct slug or tracer testing
- Rebound testing
  - Mass transfer rates may result in 1 - 3 years to rebound

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Summary cont

- Hydrogen releasing materials (HRM)
  - Appear promising to stimulate reductive dechlorination
  - Underground injection control restrictions are difficult but not impossible to overcome
  - Other carbon substrates exist
  - Economic competitiveness remains to be determined