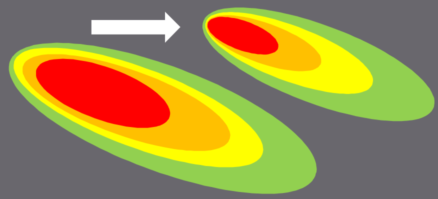
NATURAL LOSSES: Remediation Strategies in Texas

H2A

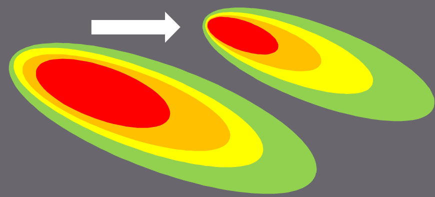
IPEC - October 14, 2014



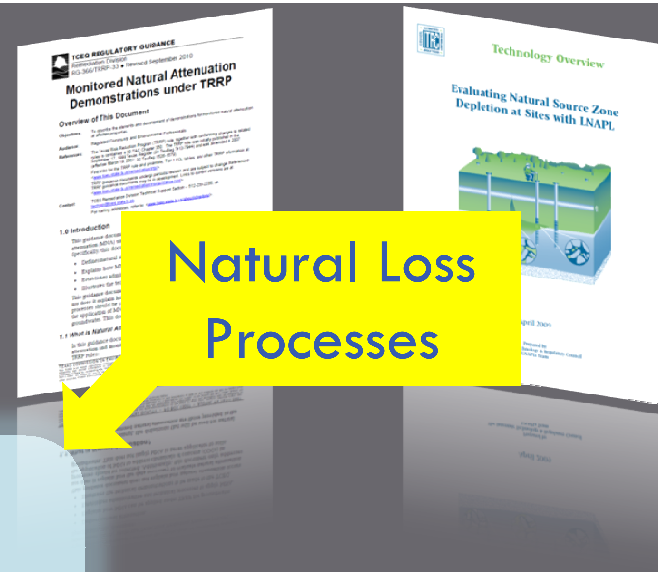
LNAPL Body Life Cycle

NATURAL LOSSES: Remediation Strategies in Texas

Summary



LNAPL Body Life Cycle

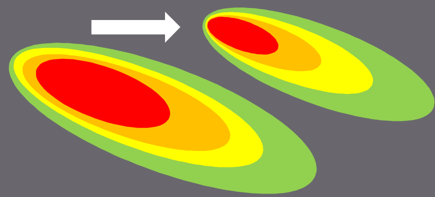


Natural Loss Processes

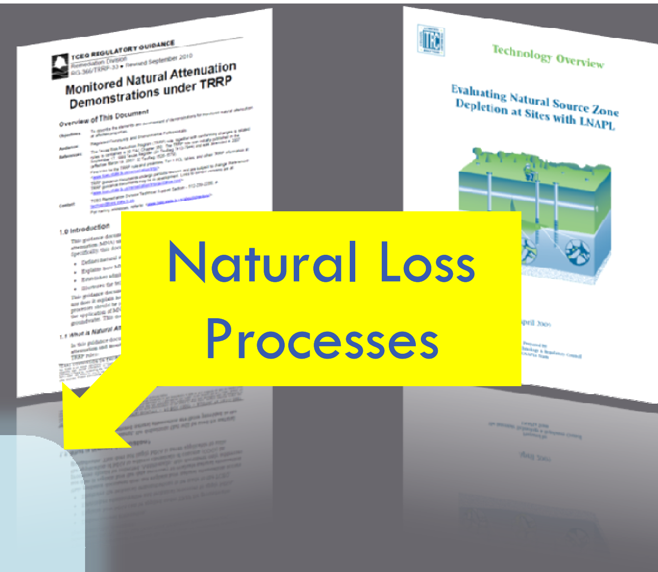
NATURAL LOSSES:
Remediation Strategies in Texas

H2A

Summary



LNAPL Body
Life Cycle



Natural Loss
Processes

NATURAL LOSSES:
Remediation
Strategies in Texas

Quantitative
Methods

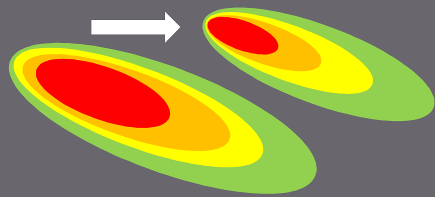
Moments

Mass Flux

Trends

H₂A

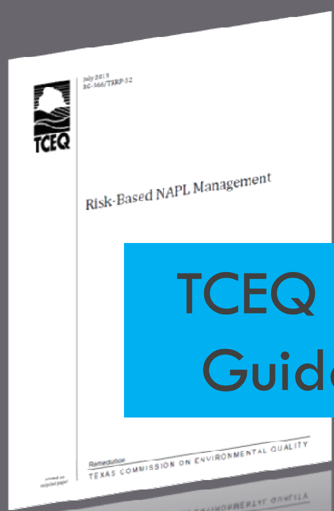
Summary



LNAPL Body Life Cycle

Natural Loss Processes

NATURAL LOSSES: Remediation Strategies in Texas



TCEQ NAPL Guidance

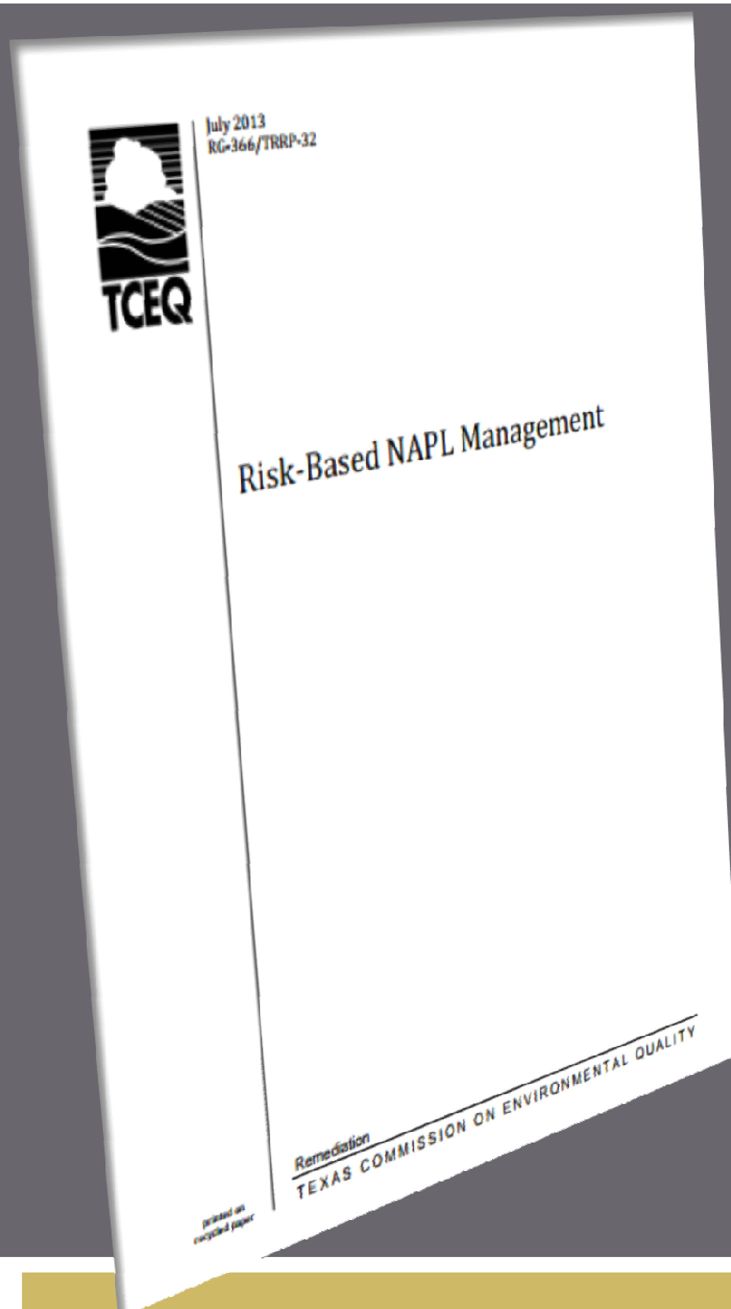
Quantitative Methods

Trends

Moments

H_2A

Summary



TRRP-32

TCEQ TRRP-32

TCEQ* Response Action Plan (RAP)

- Response Action Objectives
- Response Action Design
- Response Action Performance

* Texas Commission on Environmental Quality

TCEQ

H2A

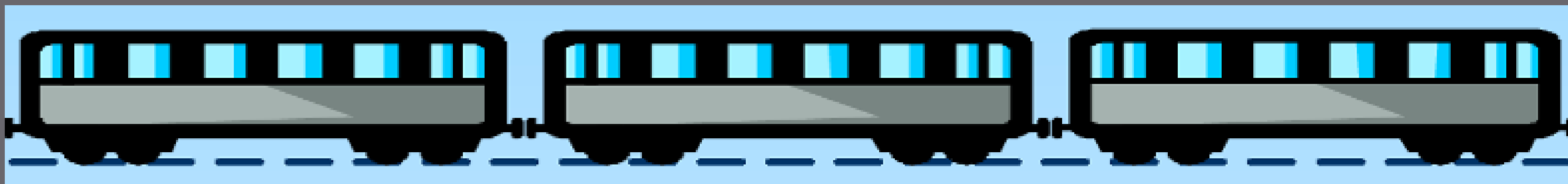
TCEQ RAP Components

TCEQ Response Action Plan (RAP)

- Response Action Design

Timeframe to Attain Remedial Goal(s)

LNAPL Life Cycle



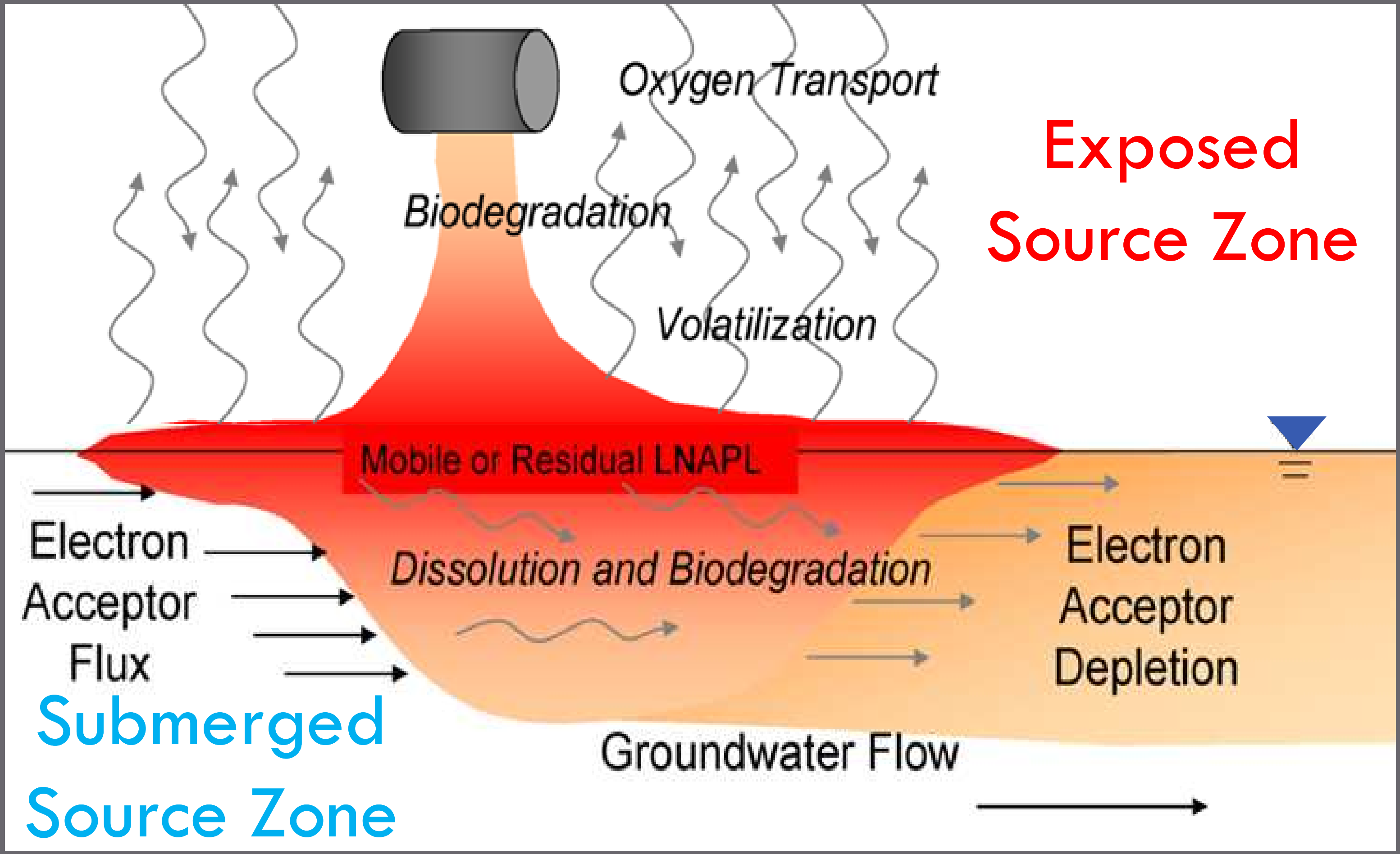
Conventional Tech

Hydraulic Recovery *(T_n-Limited)* (+) Soil Vapor Extraction

Alternative Tech

NSZD
MNA

TRRP-32

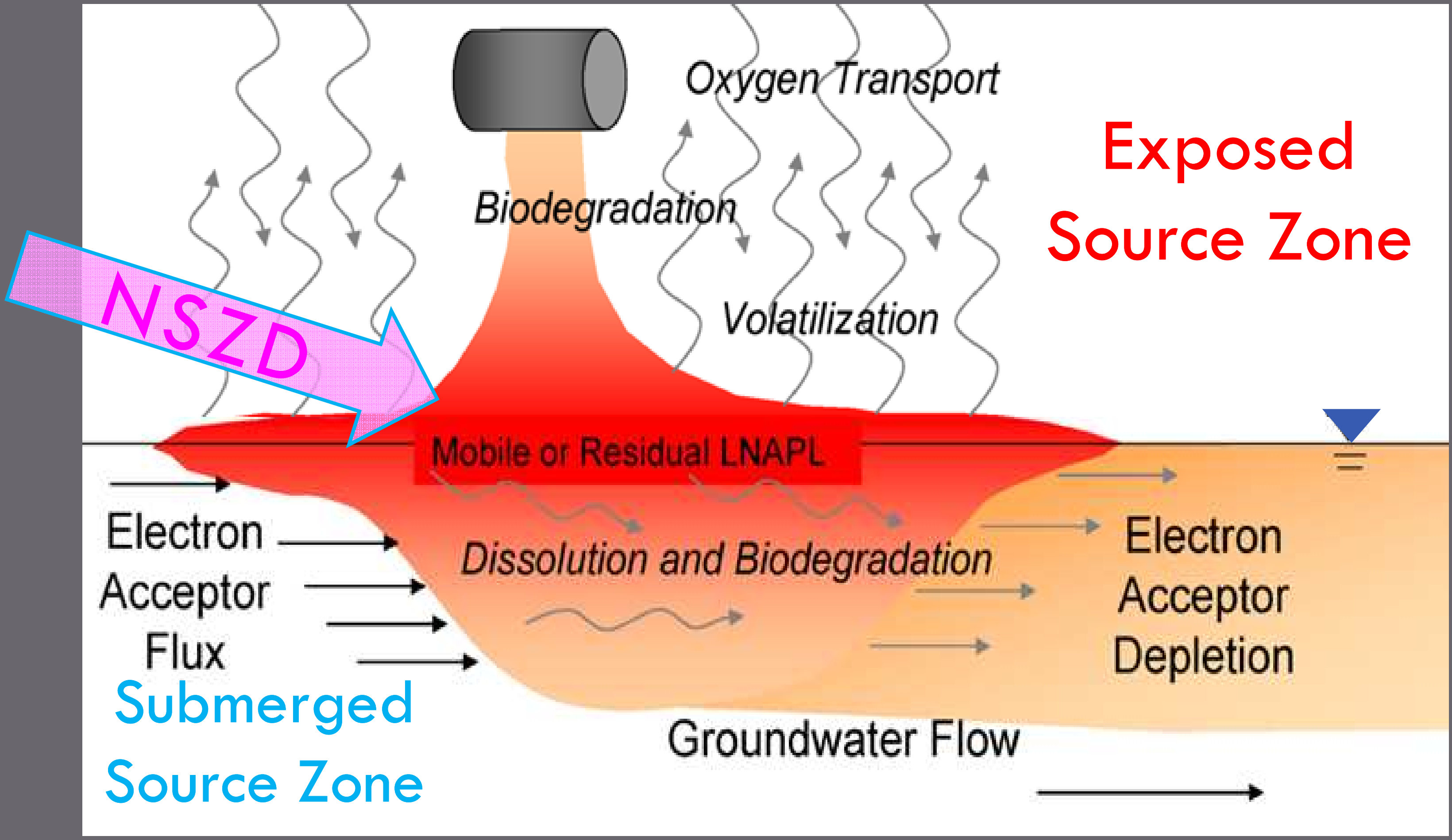


ITRC 2009

Natural Losses = NSZD + MNA

H2A

LNAPL Natural Loss Processes

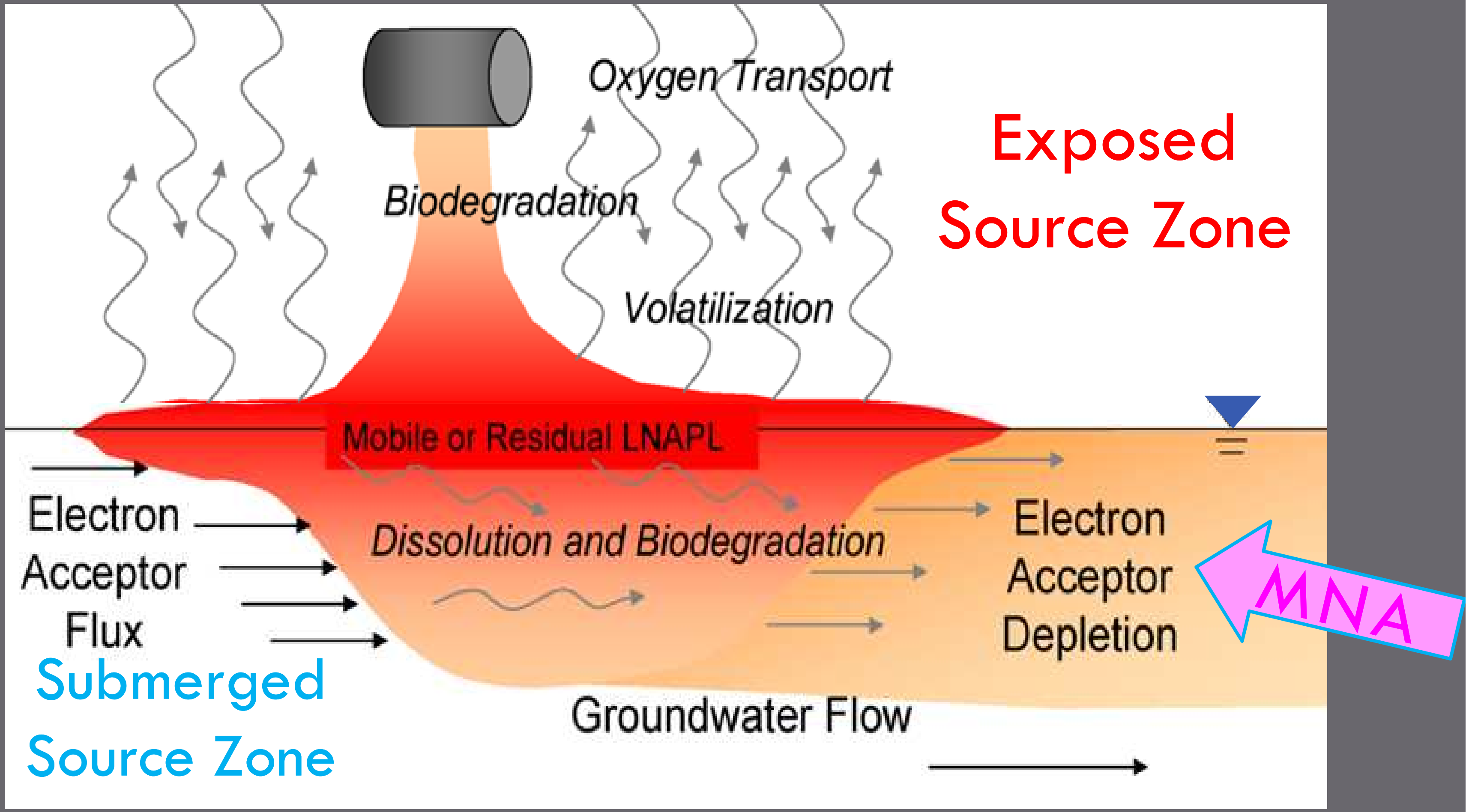


Natural Losses = NSZD + MNA

ITRC 2009

H₂A

LNAPL Natural Loss Processes

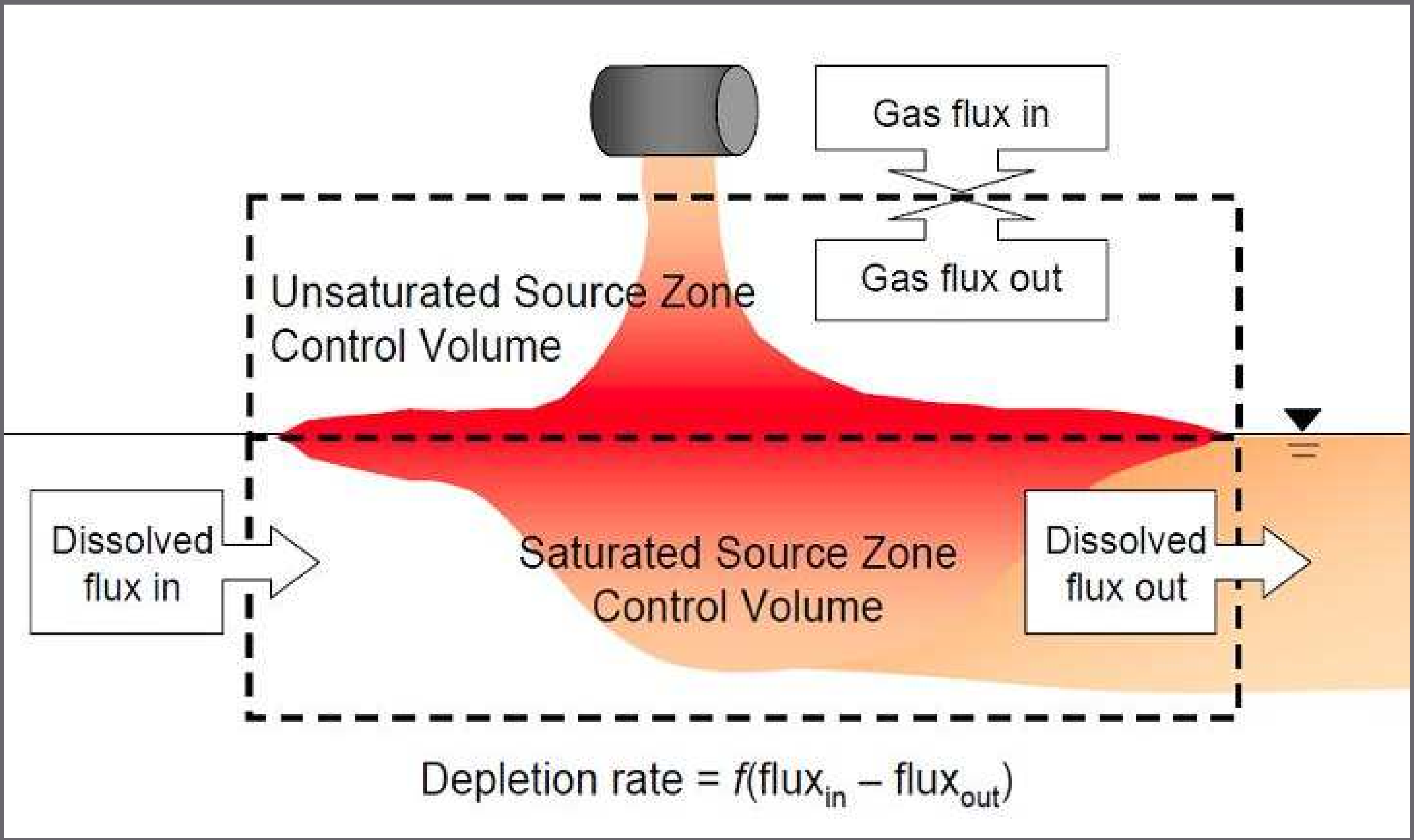


ITRC 2009

Natural Losses = NSZD + MNA

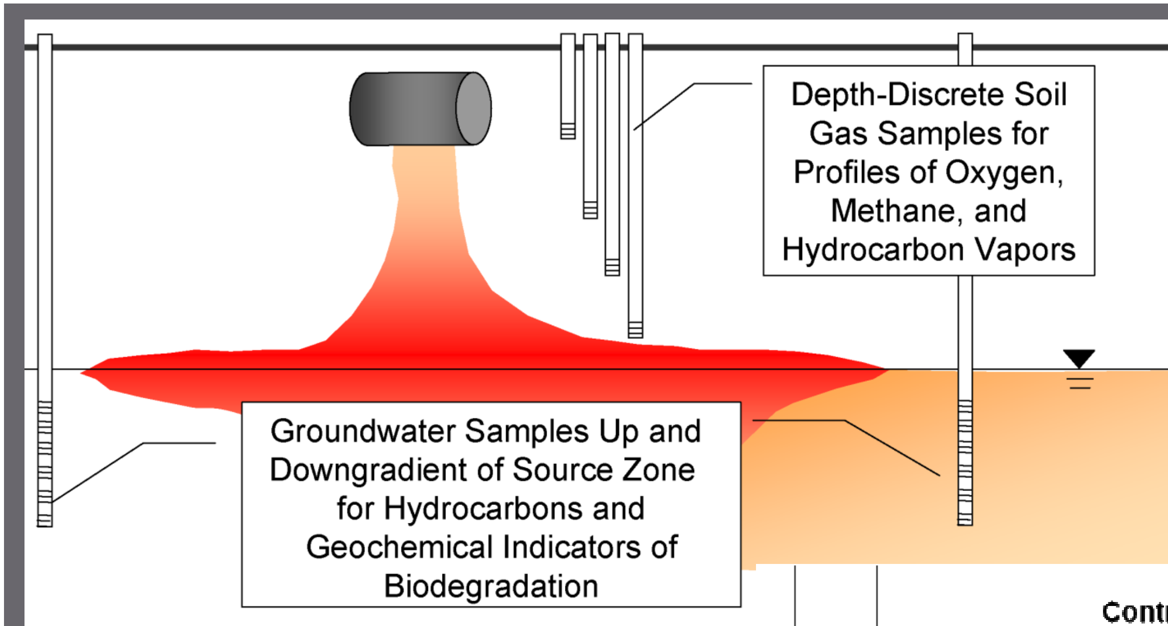
H2A

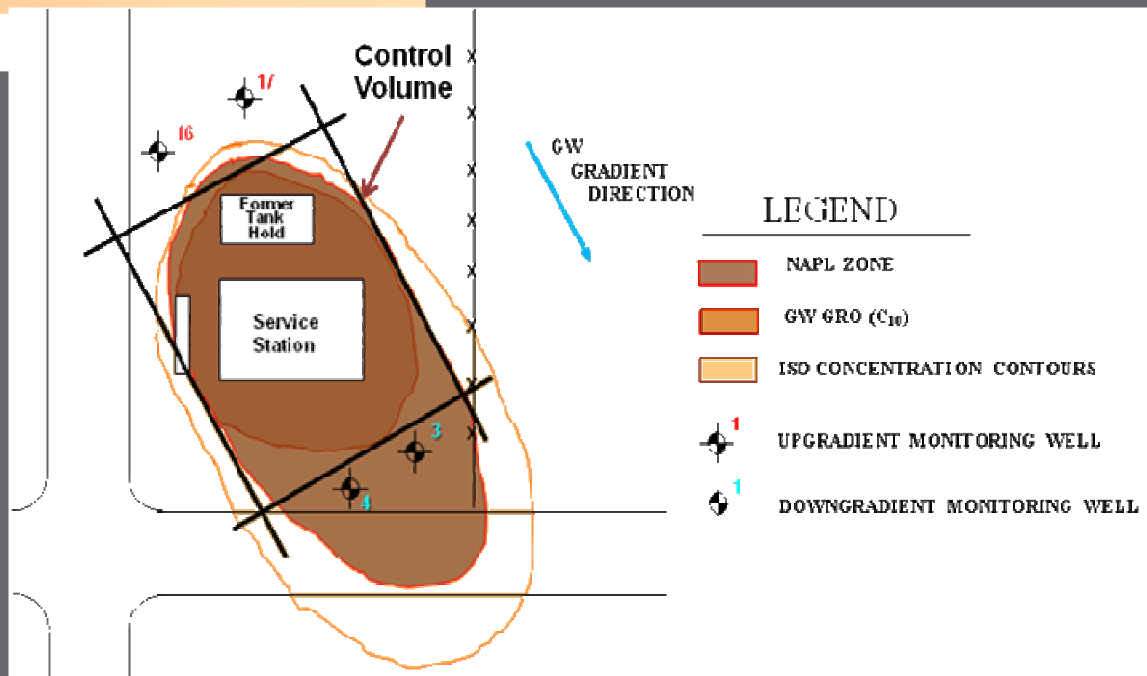
LNAPL Natural Loss Processes



ITRC 2009

NSZD: Mass Flux Accounting





INTERSTATE TECHNOLOGY REGULATORY COUNCIL ITRC 2009

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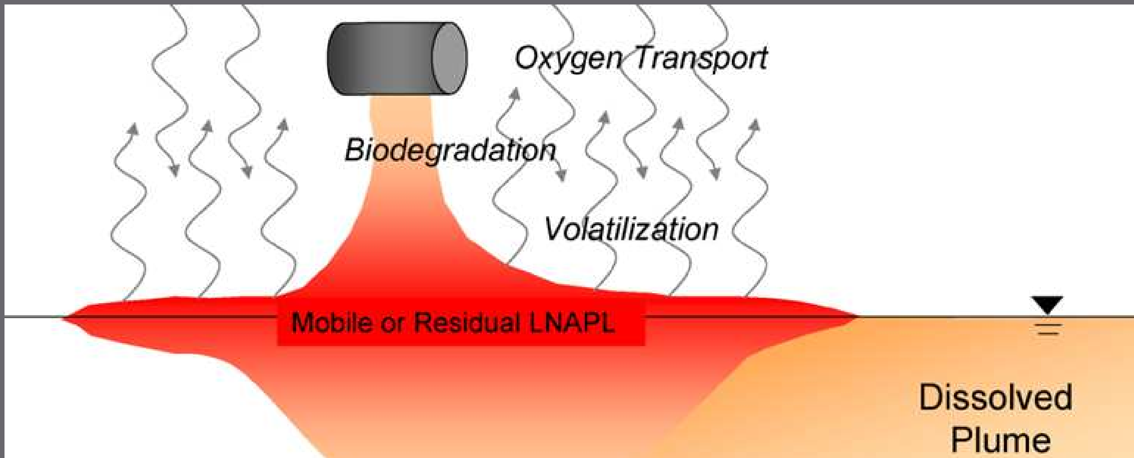
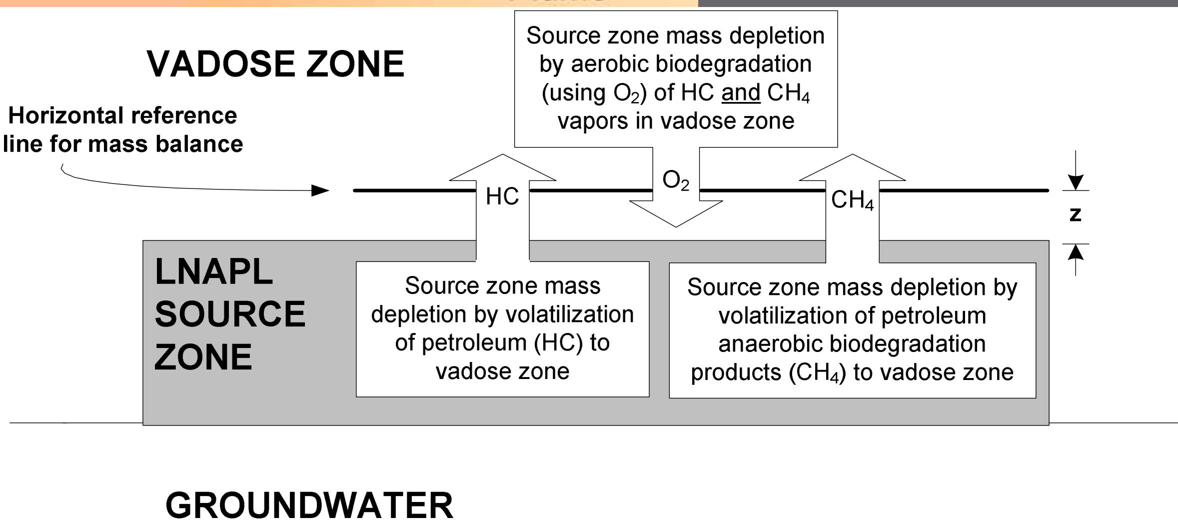
NSZD Monitoring Network

Exposed Source Zone





Control Volume "Box" - Exposed Source Zone

Source zone mass depletion by vapor transport processes = Horizontal area of source zone (Mass flux of HC vapor to vadose zone below reference line + HC mass flux equivalent of CH_4 vapor to vadose zone below reference line - HC mass flux equivalent of O_2 vapor to vadose zone below reference line)

2009

NSZD: Exposed Source Zone Mass Flux

LNAPL Source Zone Vapor Phase Mass Flux

$$R_{vapor} \approx WL\left\{-D_{HC}(C_{HC})_z - S_M D_{CH_4}\left(C_{CH_4}\right)_z + S_O D_{O_2}\left(C_{O_2}\right)_z\right\} \quad [1]$$

At Depth where: $C_{HC} = 0; \quad C_{CH_4} = 0$

$$R_{vapor} \approx WL\left\{S_{O_2} D_{O_2}^T \left(\frac{C_{O_2}^{atm} - C_{O_2}(d)}{d}\right)\right\} \quad [2]$$

$$\frac{D_{O_2}^T}{d} = \left[\sum_{i=1}^{n} \frac{d_i}{D_{O_2}}\right]^{-1}; d = \sum_{i=1}^{n} d_i$$

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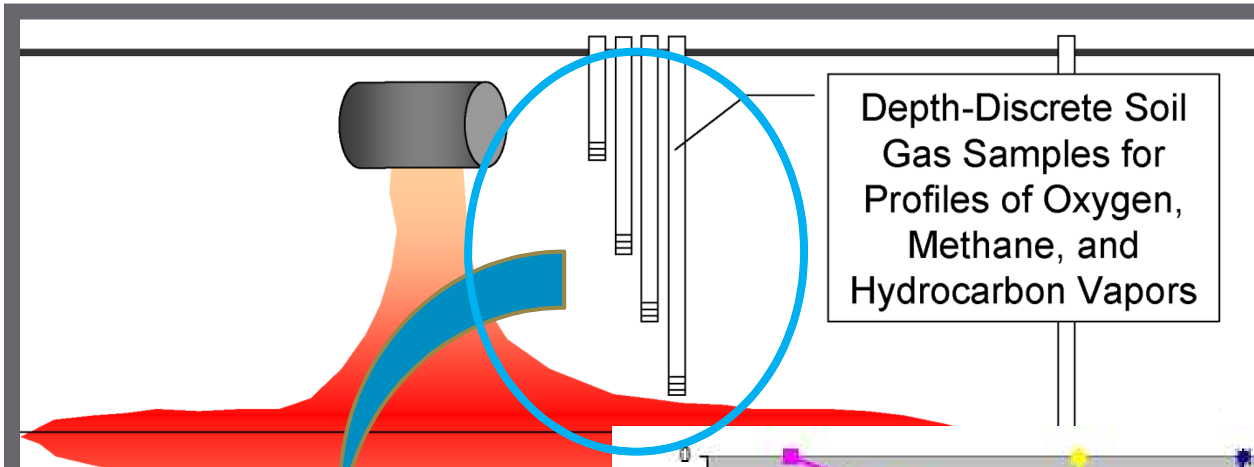
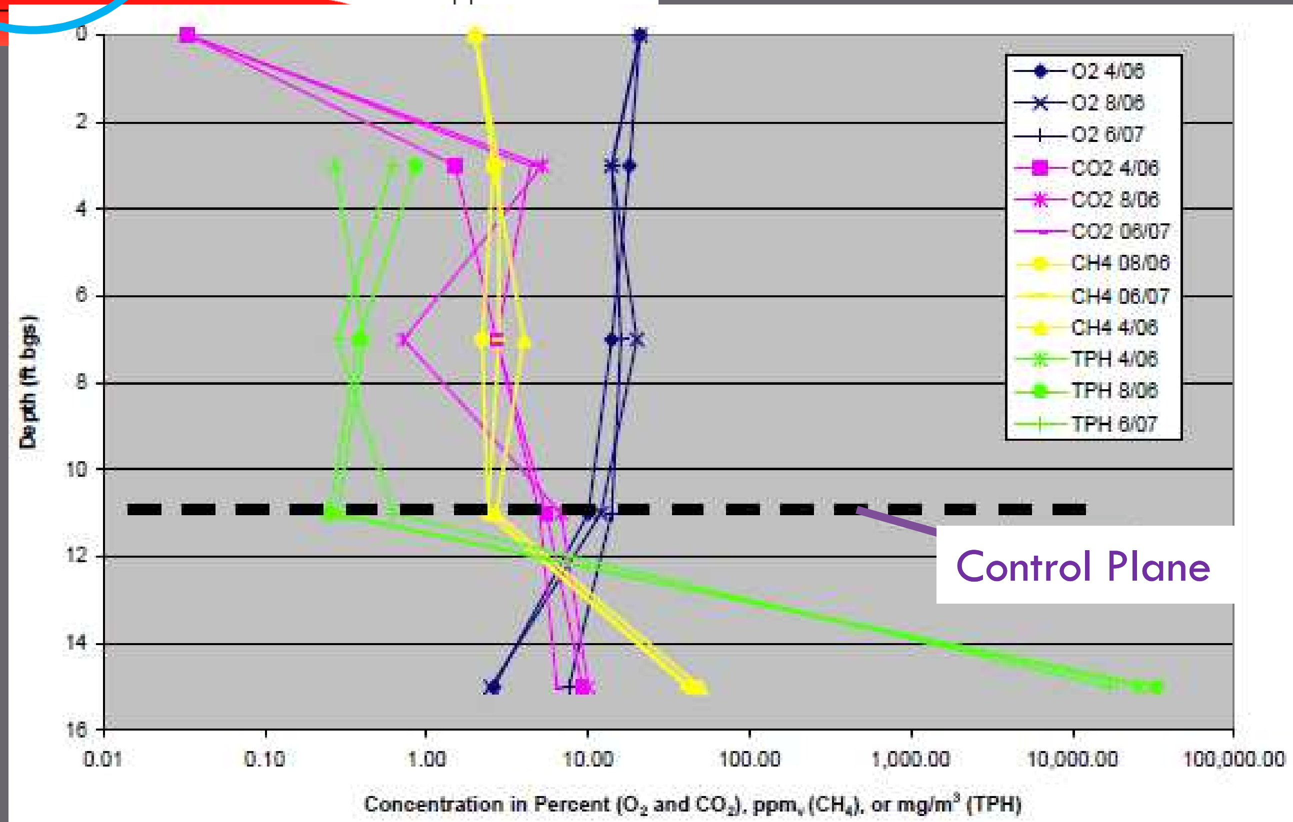
NSZD: Exposed Source Zone Mass Flux





$$\frac{D^T_{O_2}}{d} = \left[\sum_{i=1}^{n} \frac{d_i}{D_{O_2}}\right]^{-1} ; d = \sum_{i=1}^{n} d_i$$

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NSZD: Exposed Source Zone Mass Flux

Exposed LNAPL Source Zone Depletion Rate

Soil Probe (V-1) Depth		Interval Depth	Measured Effective O_2 Diffusivity (D_{eff})	Average O_2 Concentration			Average Effective O_2 Diffusivity (D_{eff}^T)	Biodegradation Rate
(ft)	(m)	(m)	(cm^2/s)	(%)	(ppm_v)	(kg O_2/m^3)	(cm^2/s)	(kg HC/m^2-yr)
3.0	0.91	0.91	0.018	15.3%	153,000	0.200	0.018	1.35
7.0	2.13	1.22	0.020	16.7%	167,000	0.219	0.019	0.46
11.0	3.35	1.22	0.023	12.0%	120,000	0.157	0.020	0.65
15.0	4.57	1.22	0.026	4.2%	42,000	0.055	0.022	0.95

Stoichiometric Coefficient (O_2)

S_O = 0.29 kg HC/kg O2

Total Depth Below Ground Surface

d = 4.57 m

Effective Vapor Phase Diffusion Coefficient (O_2) at depth, d

D_O^T = 0.022 cm2/s

Unit Biodegradation Rate

R = 0.95 kg HC/m2-yr

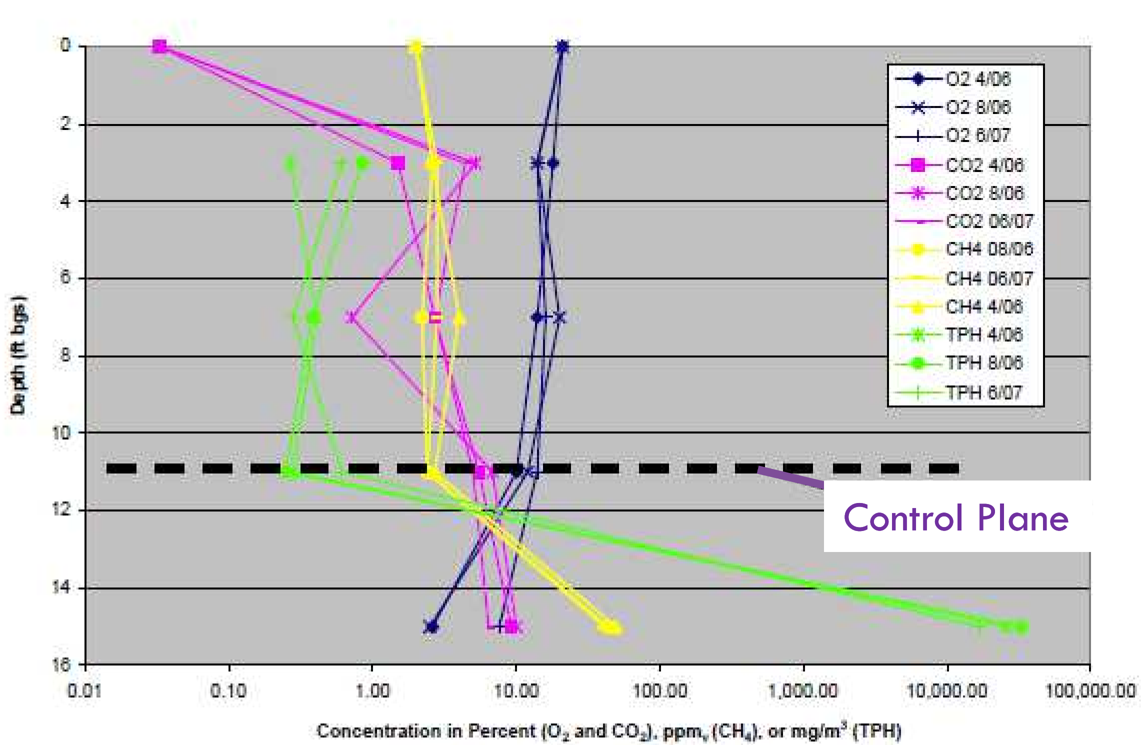
Exposed LNAPL Zone Dimensions

Length = 42.0 m

Width = 35.0 m

Estimated Exposed LNAPL Mass Depletion Rate

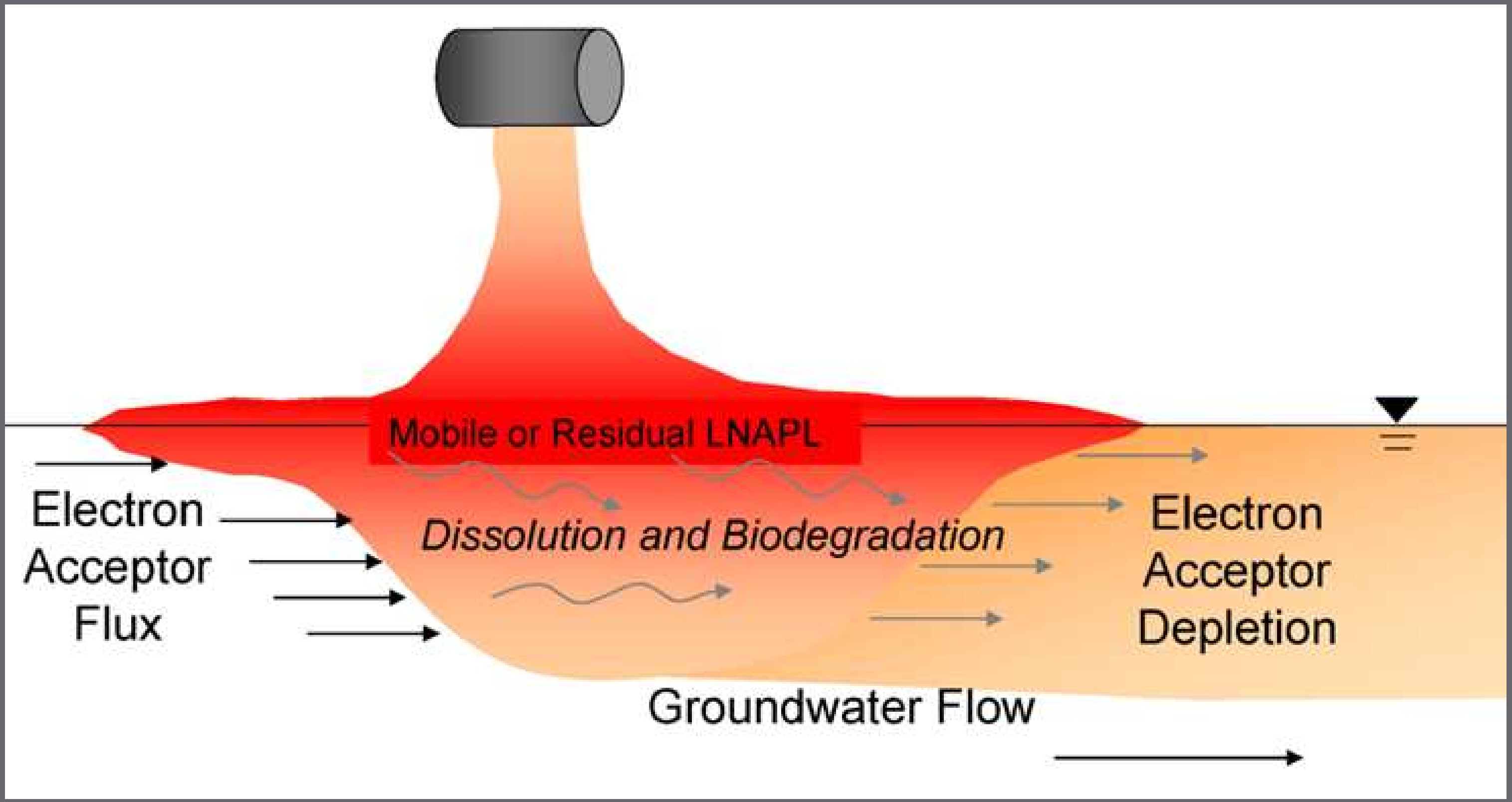
R_{vapor} = 1,398 kg HC/yr



~~2009~~

NSZD: Exposed Source Zone Mass Flux

Submerged Source Zone



$$R_{Submerged} \approx R_{Dissoln} + R_{Bio-Sat}$$

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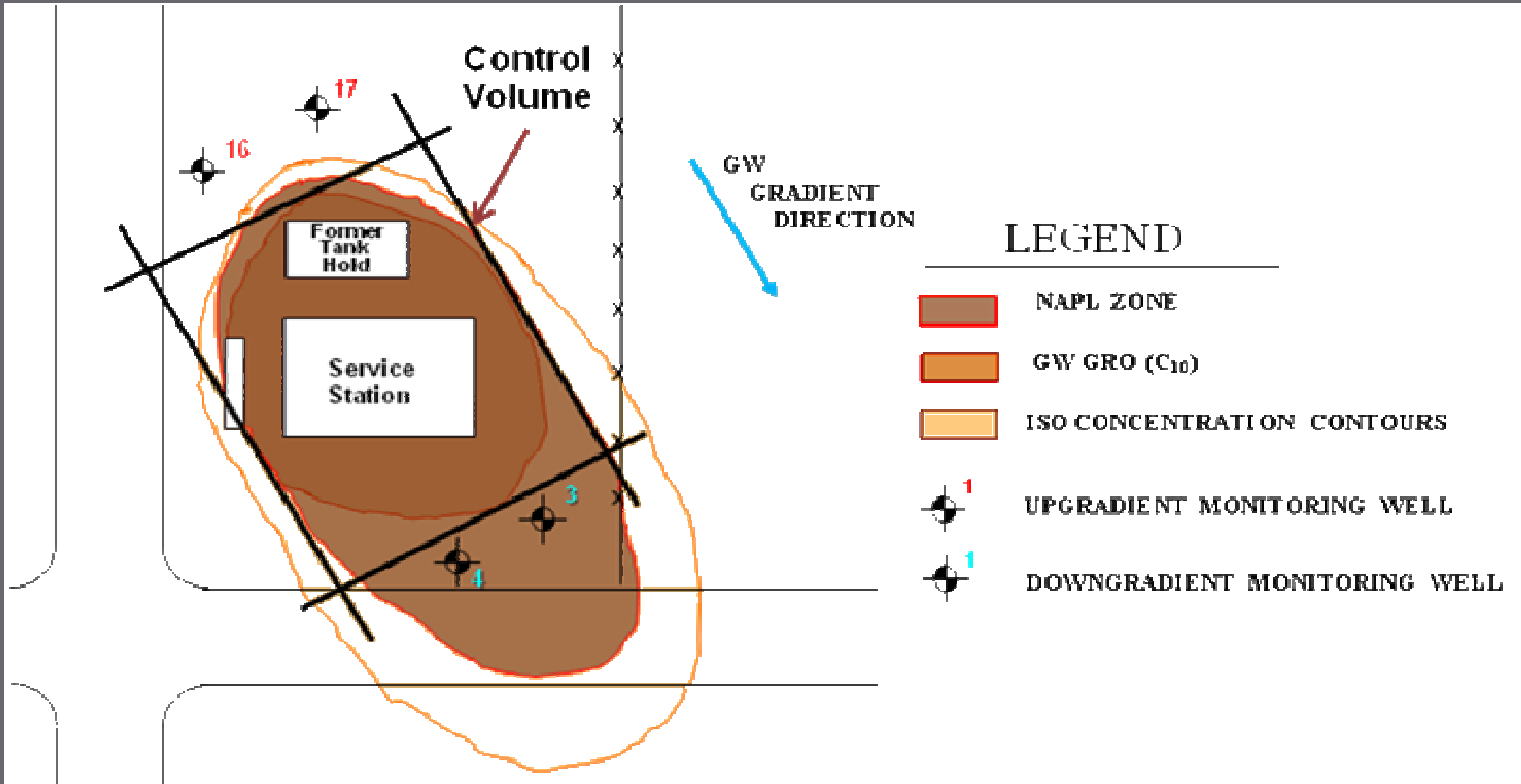
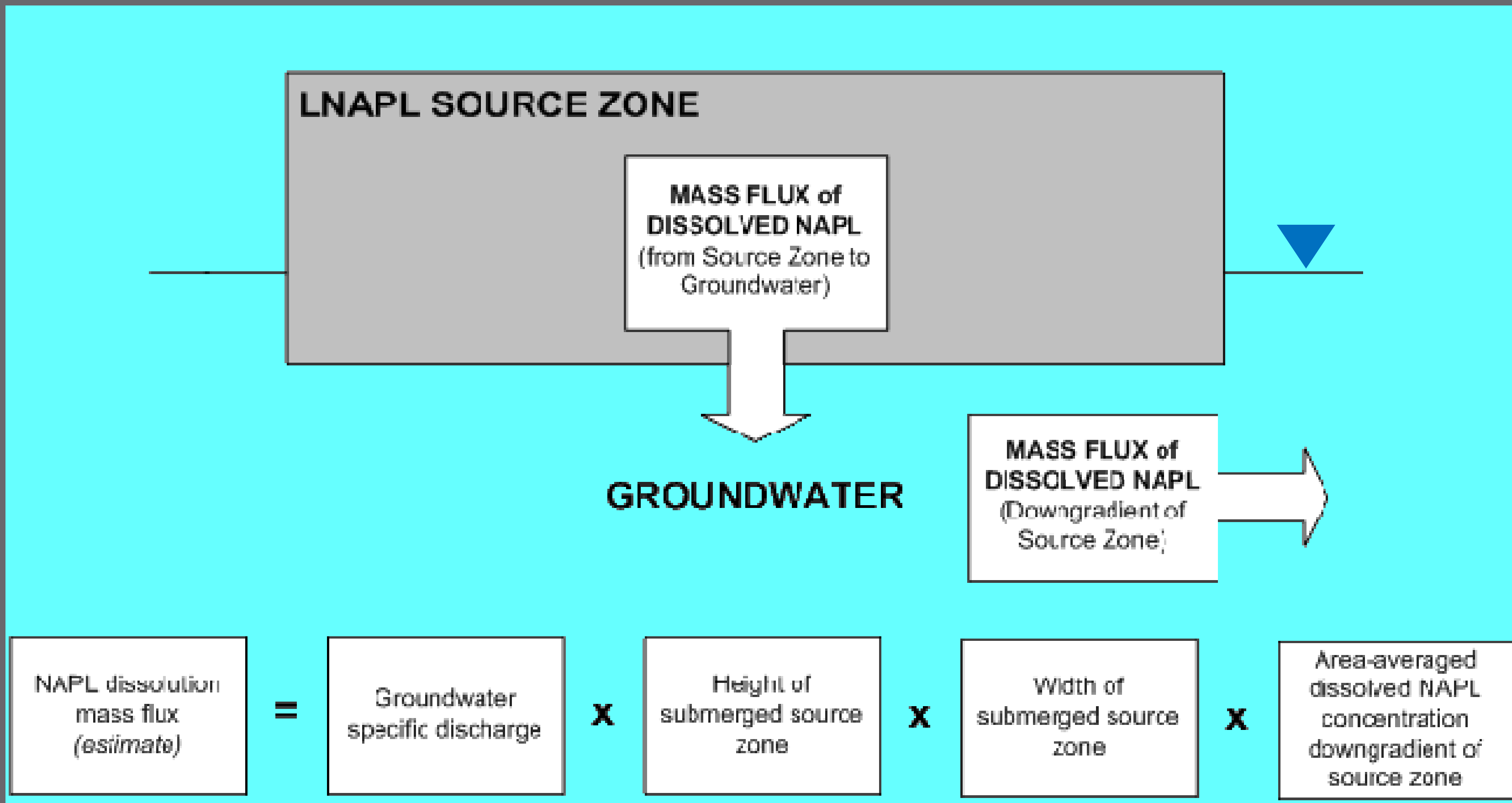
NSZD: Submerged Source Zone Mass Flux



ITRC 2009

Submerged Source Zone Monitoring Network

NSZD: Submerged Source Zone Mass Flux

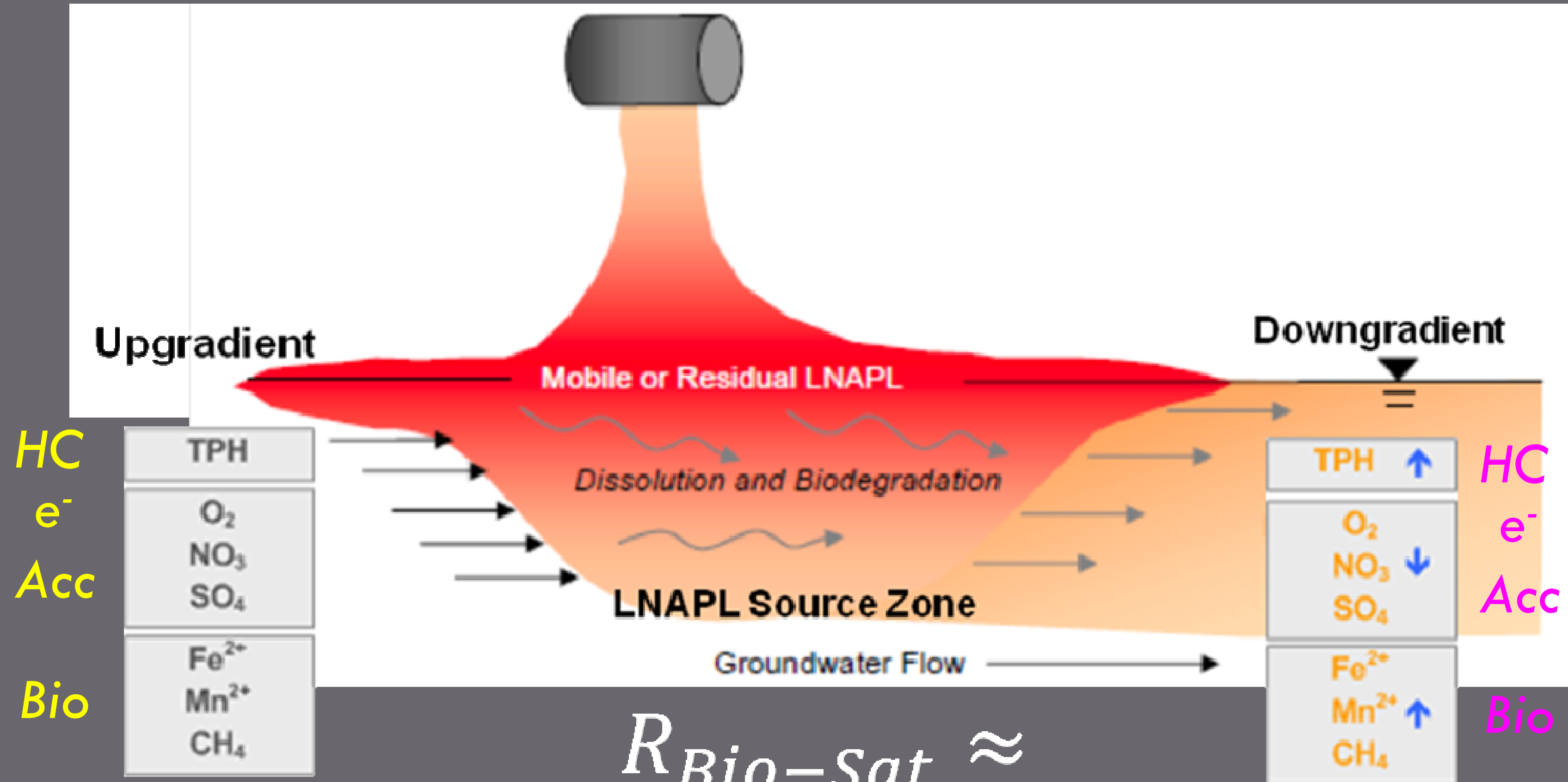


$$R_{Submerged} = R_{Dissoln} + R_{Bio-Sat}$$

$$R_{Dissoln} \approx WHq_d\langle C_d\rangle$$

2009

NSZD: Submerged Source Zone Mass Flux



$$R_{Bio-Sat} \approx$$

$$WHq_u \cdot m[e^- \, Acc - Bio]_{IN} - WHq_d \cdot m[e^- \, Acc - Bio]_{OUT}$$

ITRC 2009

NSZD: Submerged Source Zone Mass Flux

$$mHC = \sum S_i \cdot e^- \, Acc_i \;\; \& \;\; \sum S_i \cdot Bio_i$$

Representative stoichiometric coefficients (S_i) for biodegradation of a reference hydrocarbon constituent ($C_{10}H_{22}$)

Biodegradation process	Biodegradation component	Stoichiometric coefficient (S_i)
Aerobic biodegradation	**O_2**	**0.29 kg-HC/kg-O_2**
Nitrate reduction	NO_3^-	0.19 kg-HC/kg-NO_3^-
Iron reduction	Fe^{2+}	0.041 kg-HC/kg-Fe^{2+}
Sulfate reduction	SO_4^{2-}	0.19 kg-HC/kg-SO_4^{2-}
Manganese reduction	Mn^{2+}	0.083 kg-HC/kg-Mn^{2+}
Methanogenesis	CH_4	1.1 kg-HC/kg-CH_4

(after Johnson, Lundegard, and Liu 2006)

2009

HC Stoichiometric Conversion

TCEQ Response Action Plan (RAP)

- Response Action Design

Timeframe to Attain LNAPL Recovery Goal

$$R_{mass} \approx R_{exposed} + R_{submerged}$$

$$\frac{dR_{mass}}{dt} \approx \frac{dR_{exposed}}{dt} + \frac{dR_{submerged}}{dt}$$

TCEQ

TRRP-31

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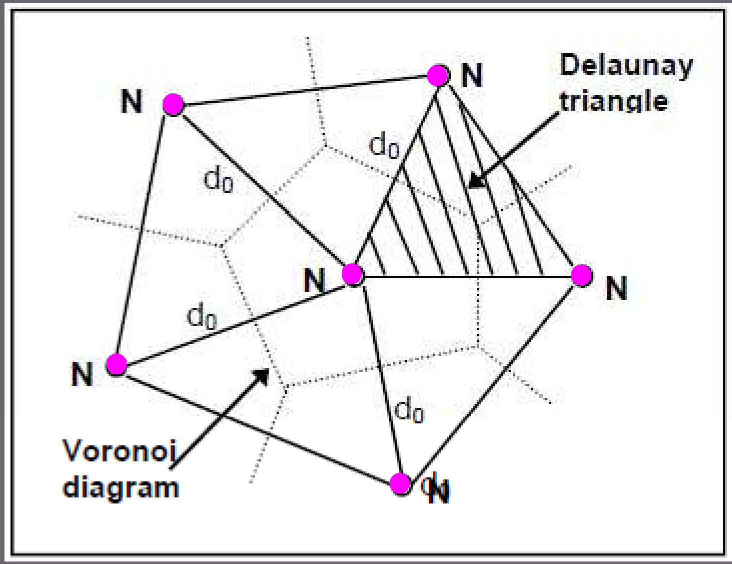
Spatial Mass Moments

Zeroith Moment:

estimate of total mass

$$Mass_{Diss\ COC} \approx \sum A \cdot h \cdot C_{COC} \cdot \eta$$

$$Mass_{LNAPL} \approx \sum A \cdot h_{LNAPL} \cdot \delta \cdot \eta \cdot S^*$$



First Moment:

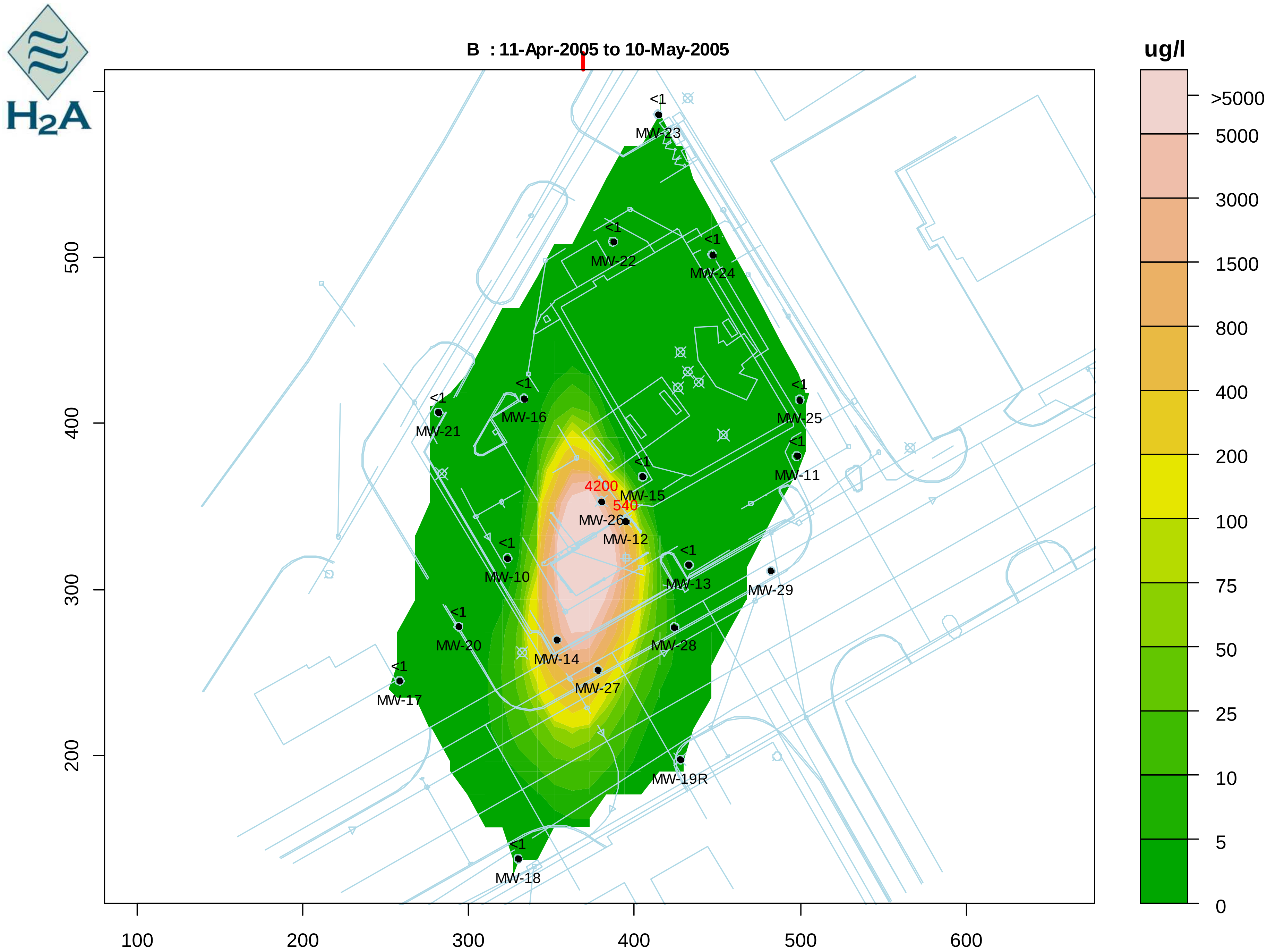
centroid of total mass

S^* – *estimated LNAPL saturation*

2012

Dissolved Benzene Concentrations:

April 2005 – September 2012



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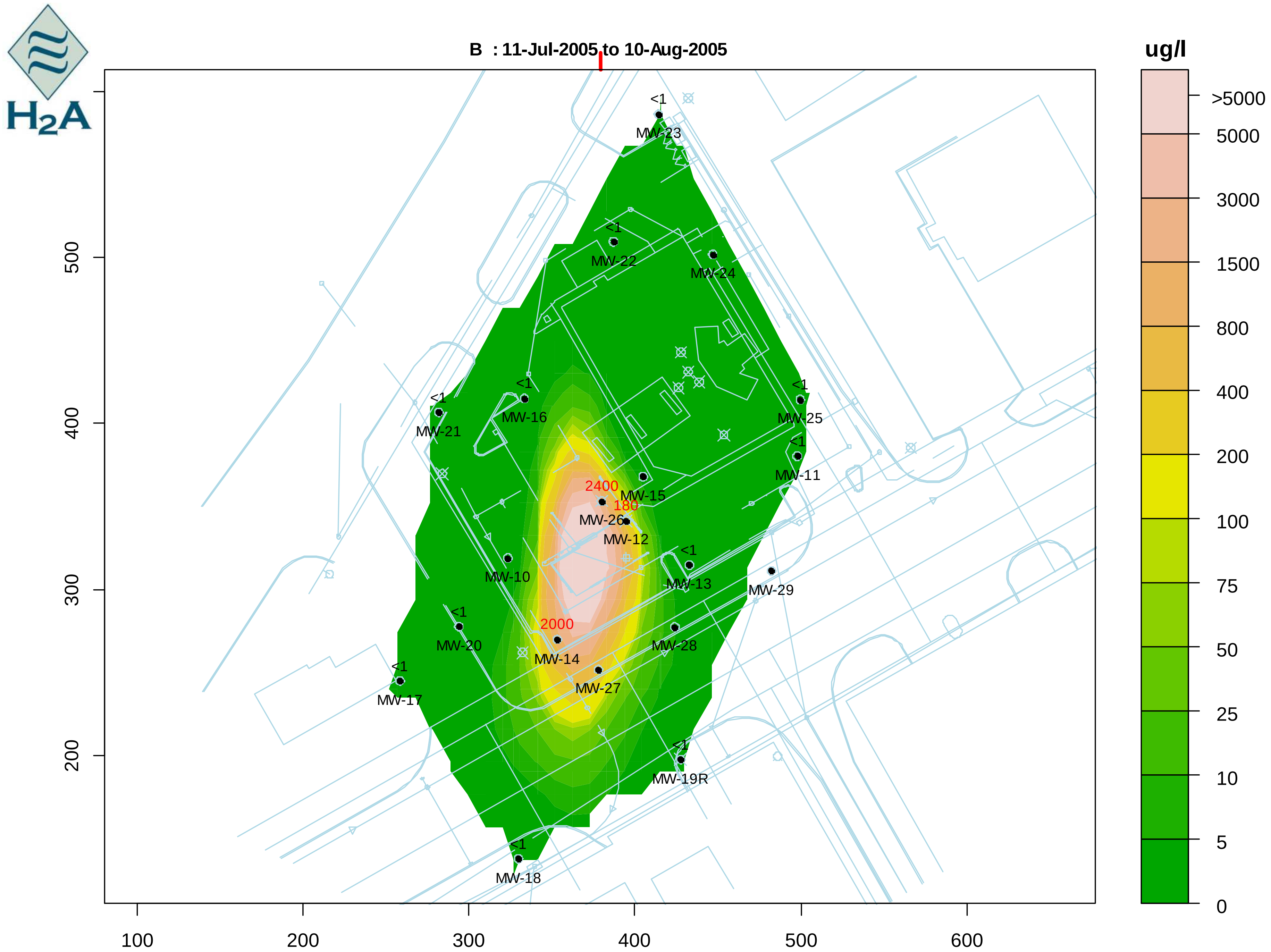

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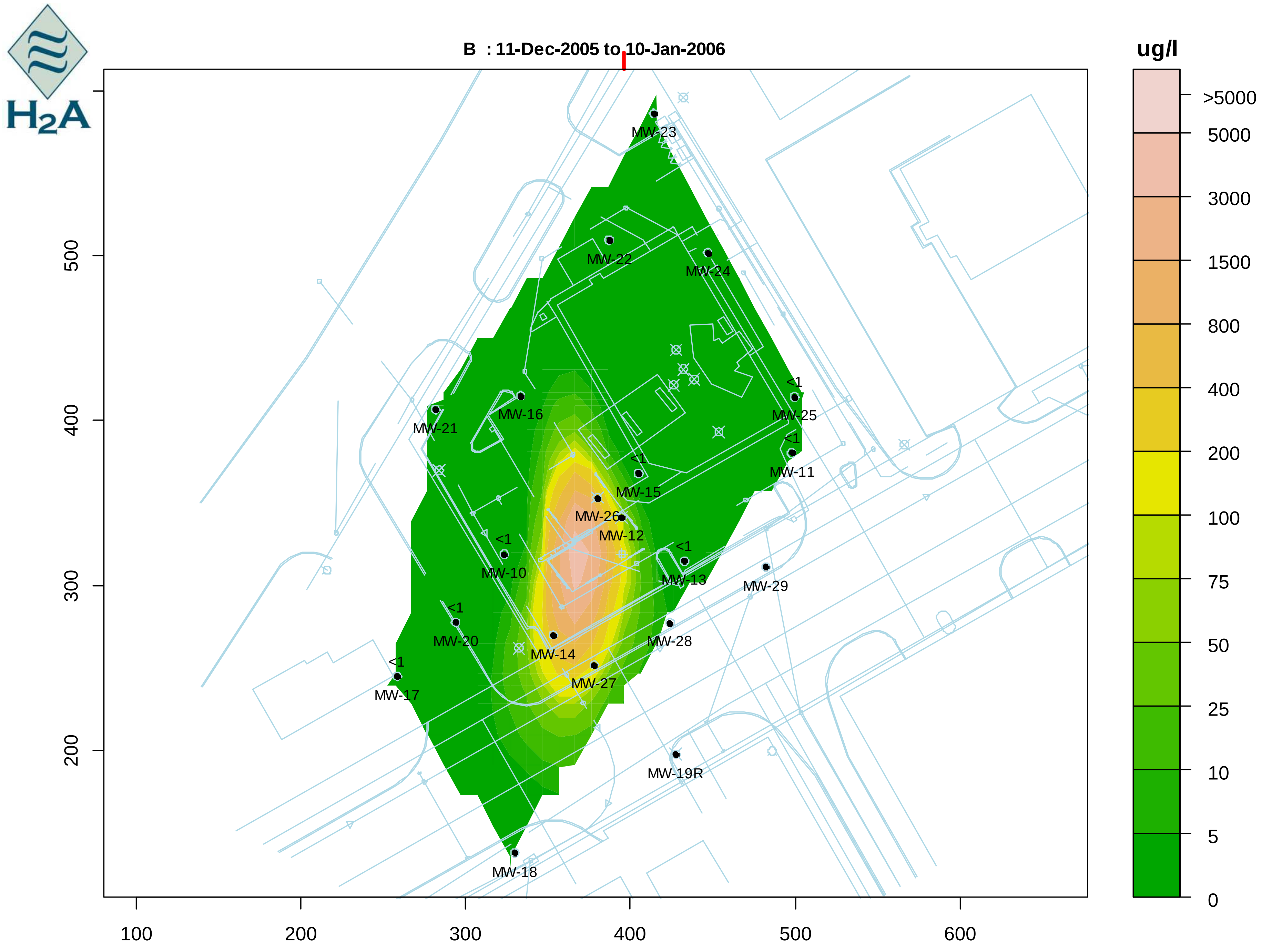

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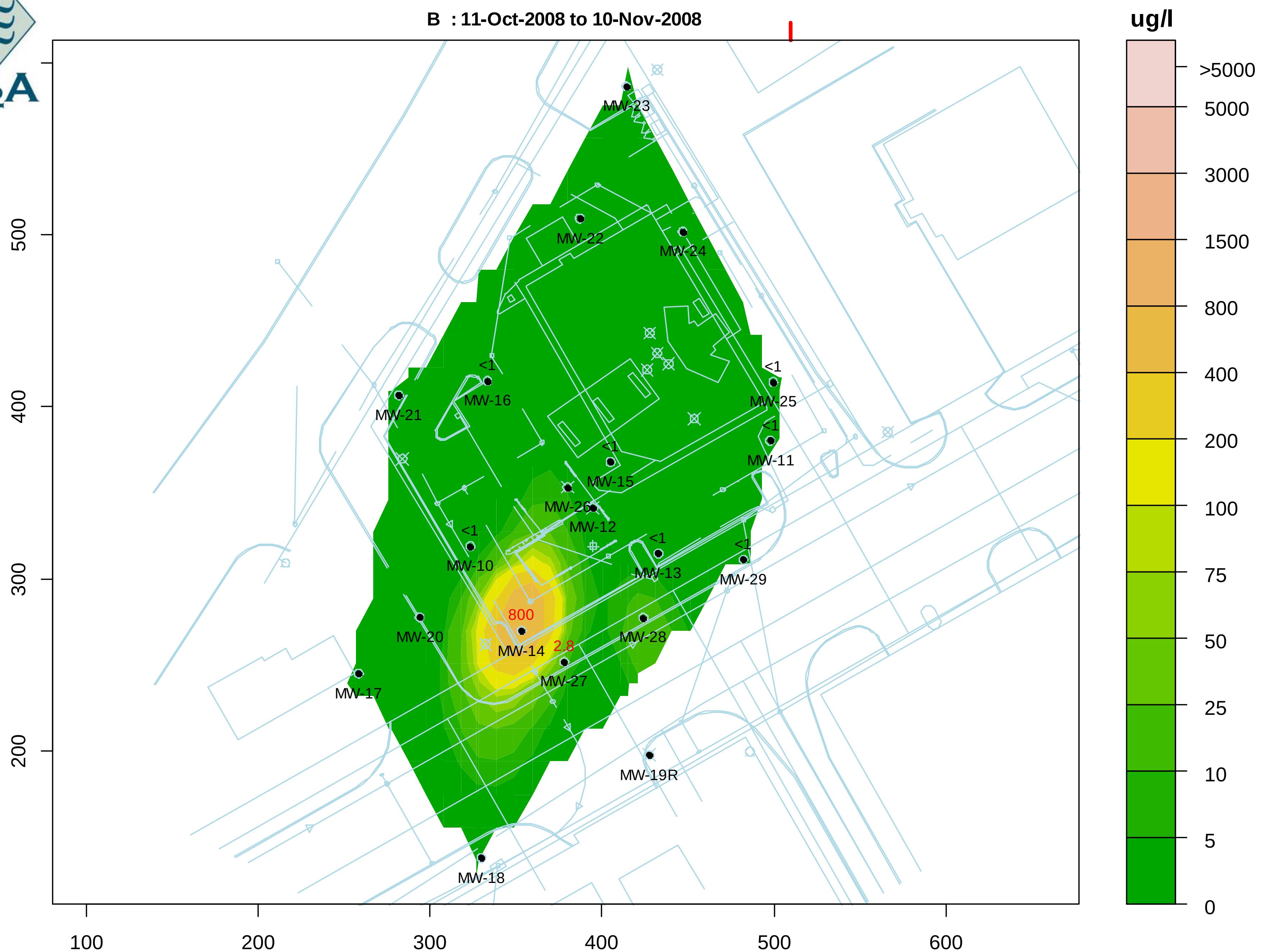
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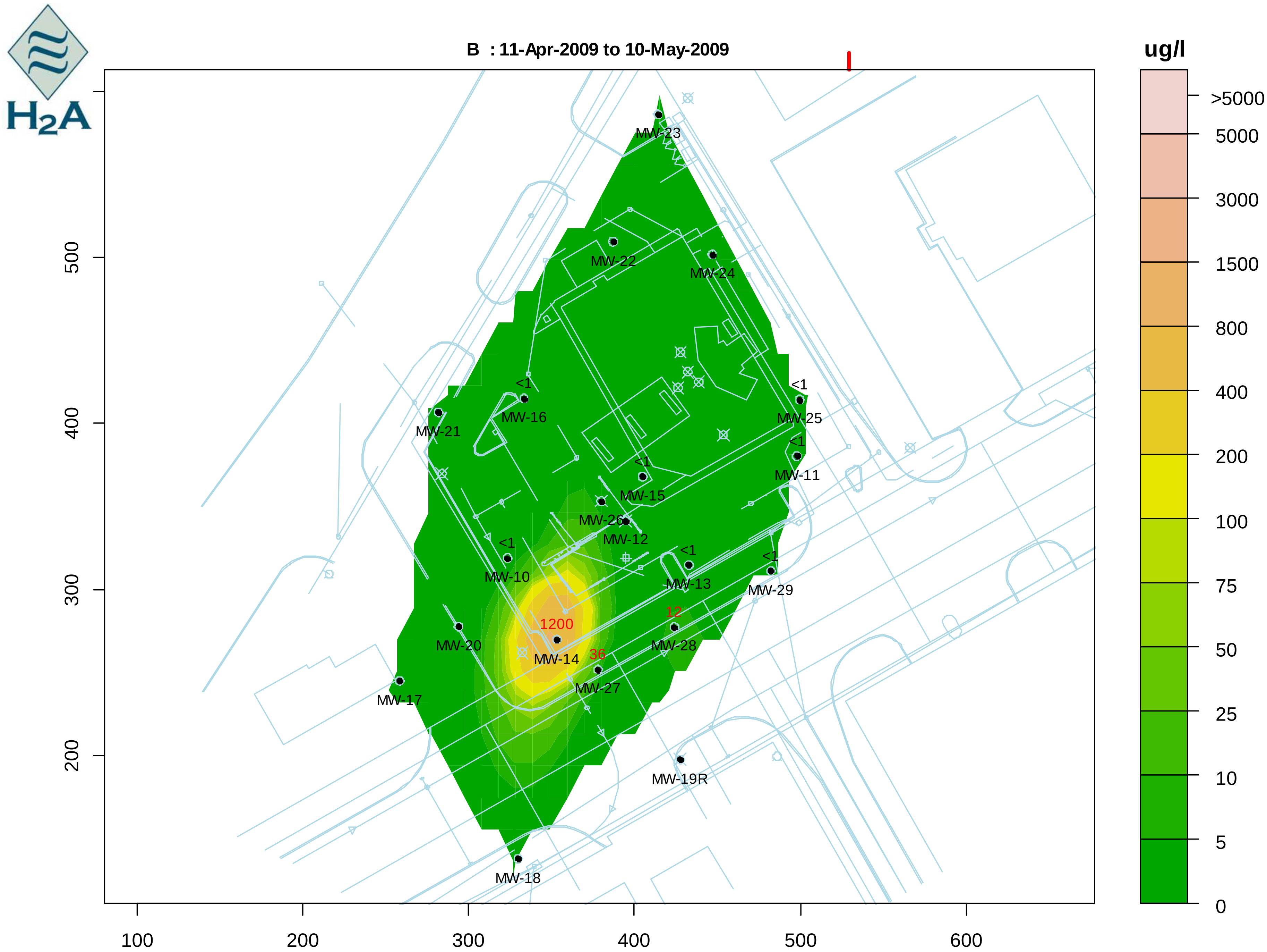

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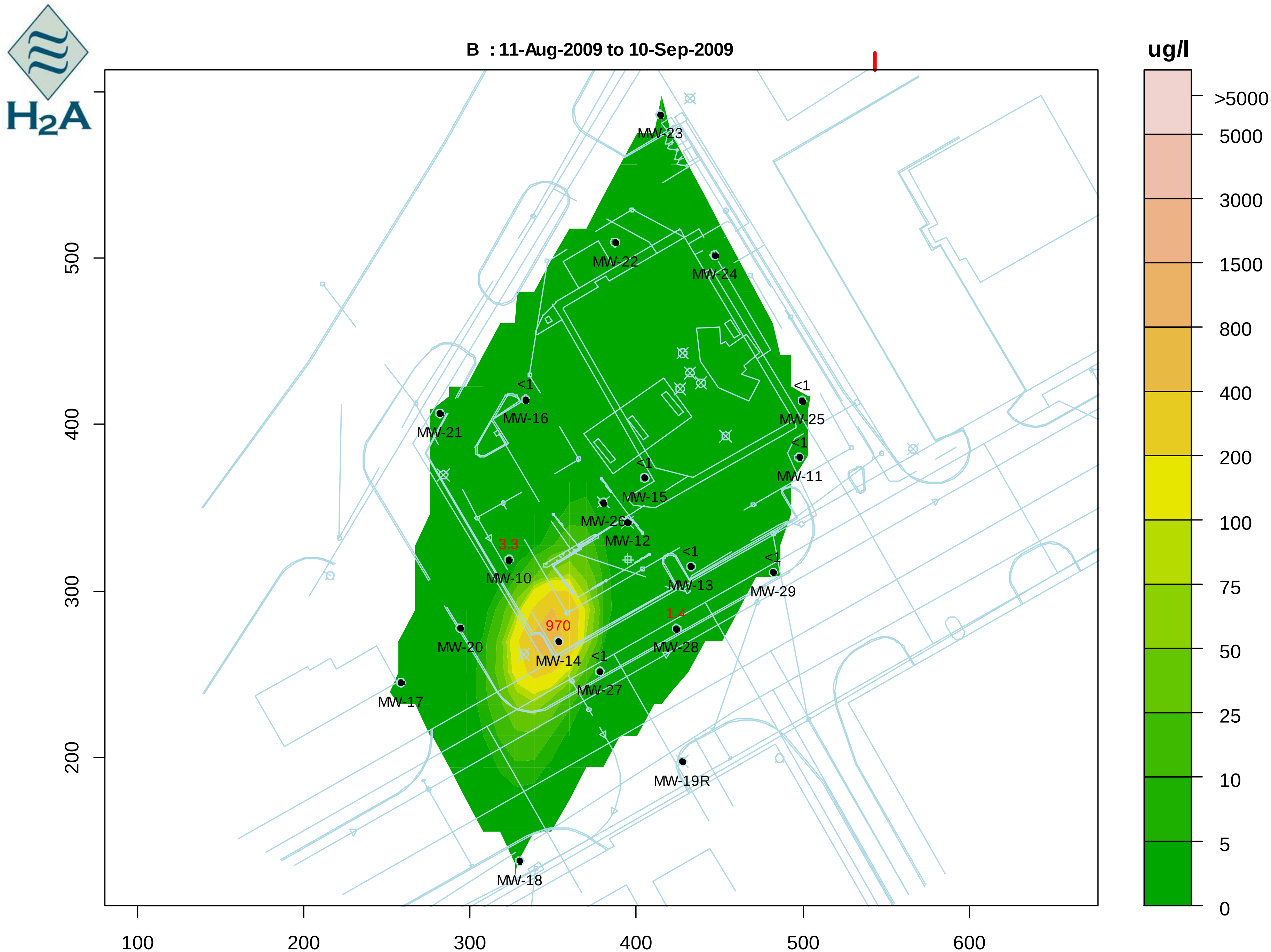

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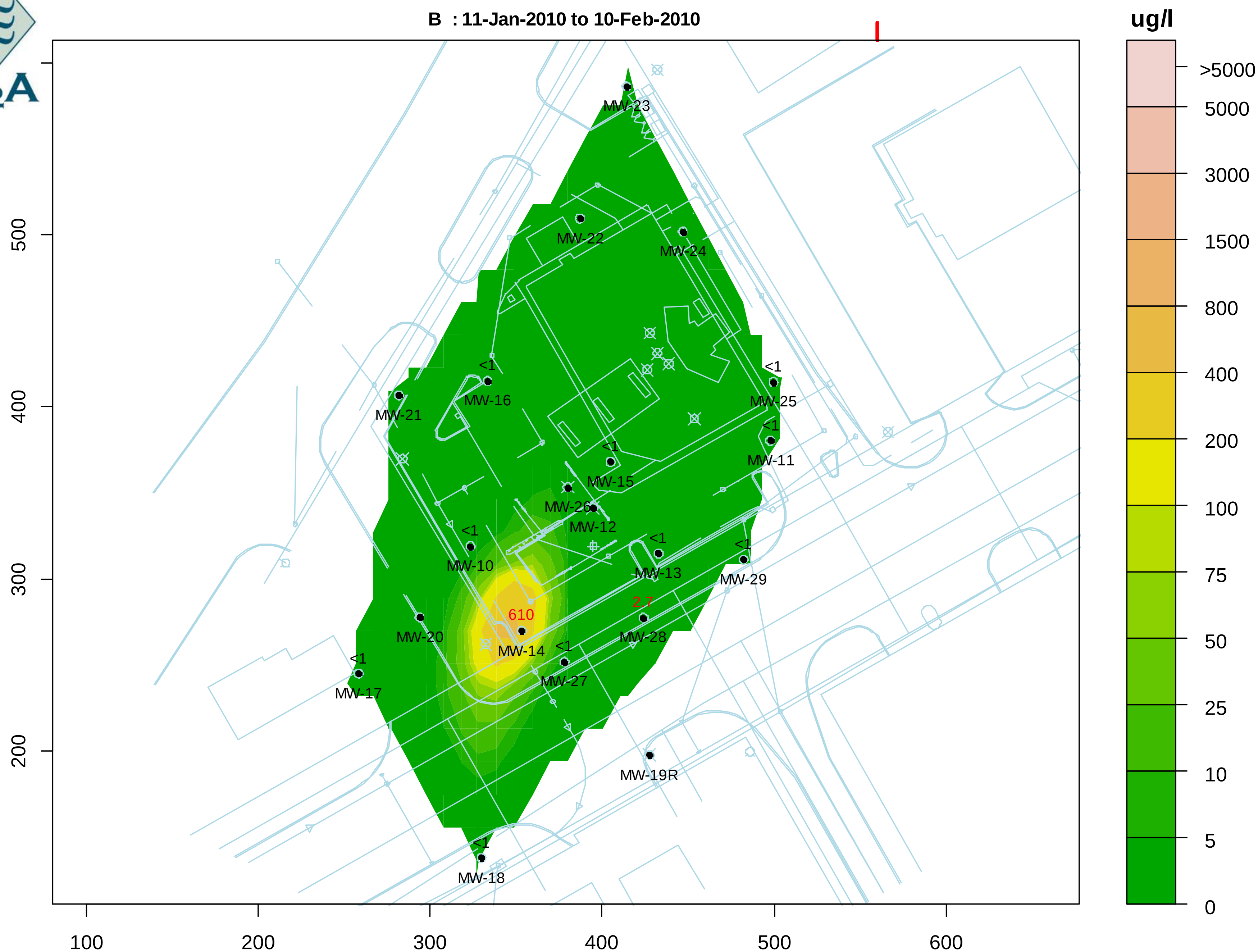
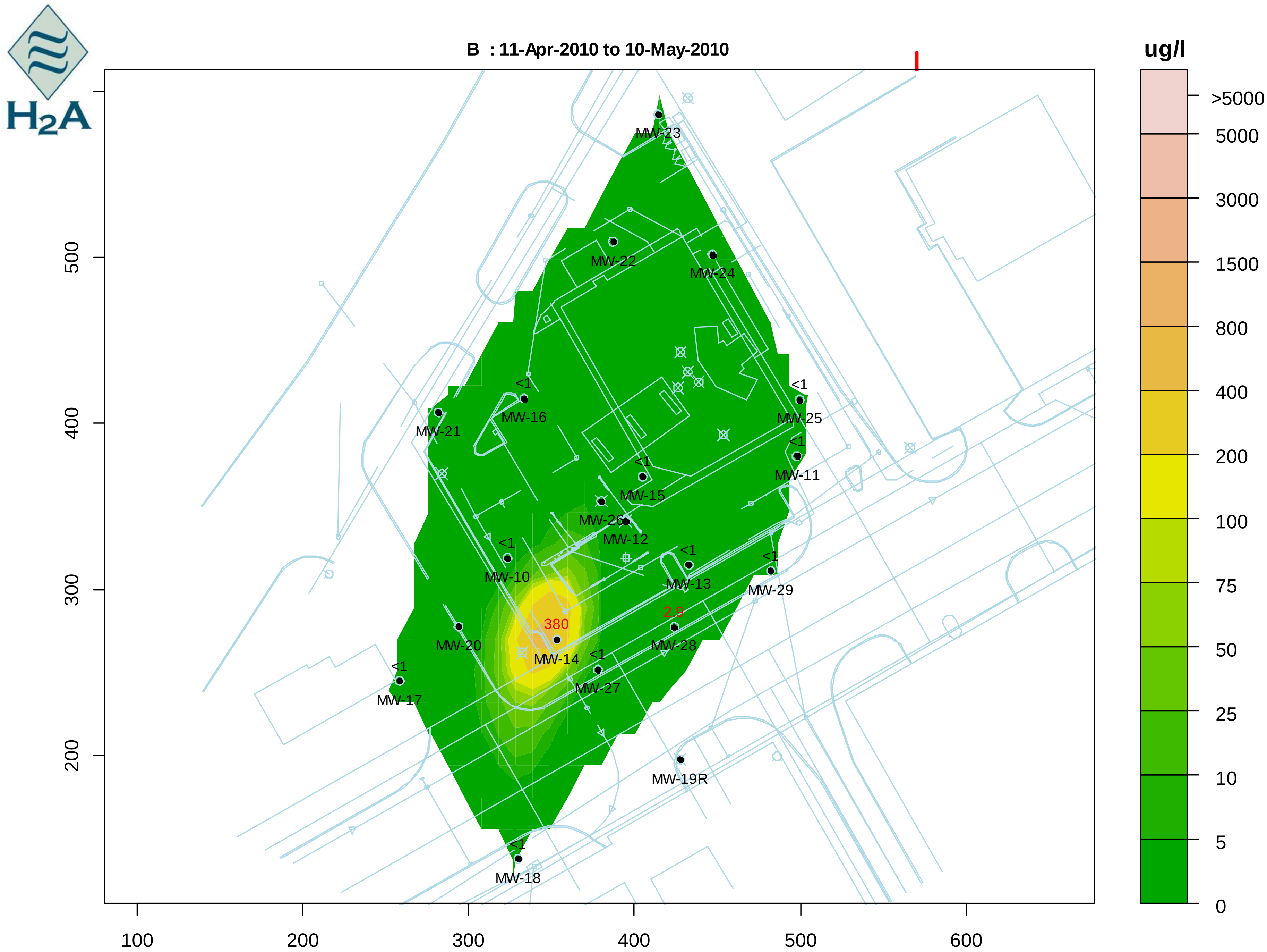


B : 11-Jan-2010 to 10-Feb-2010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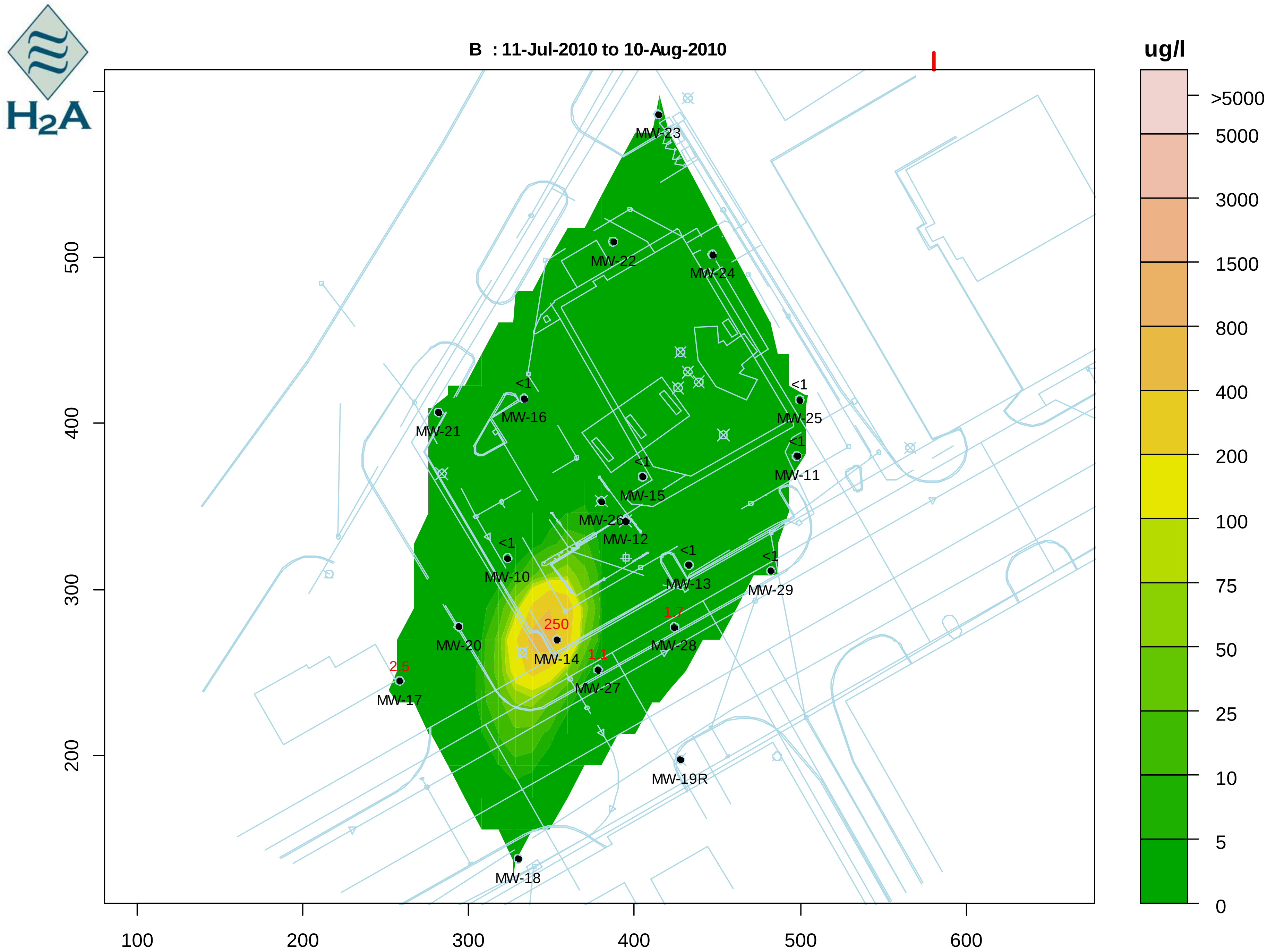
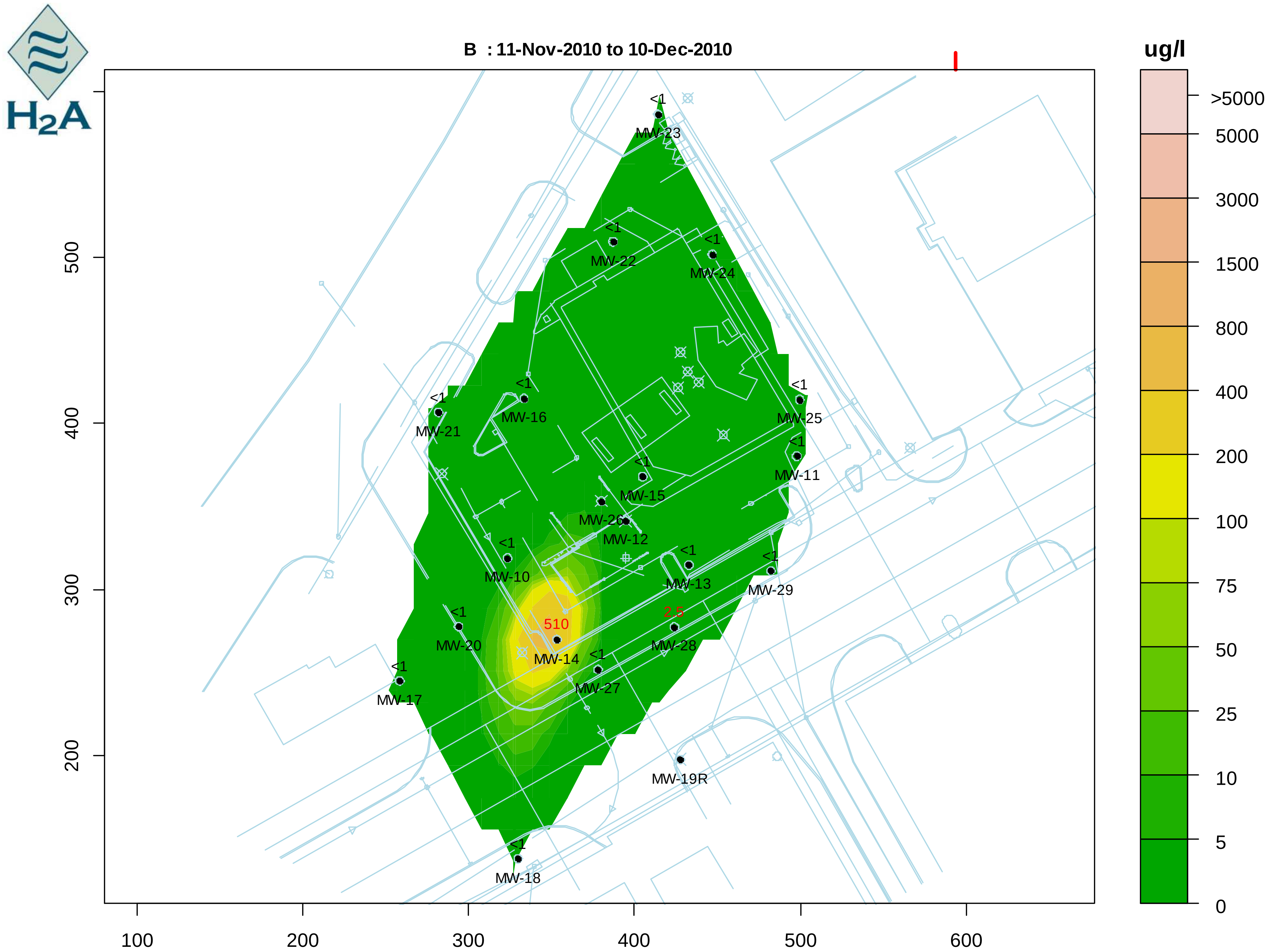
B : 11-Jul-2010 to 10-Aug-2010





H2A
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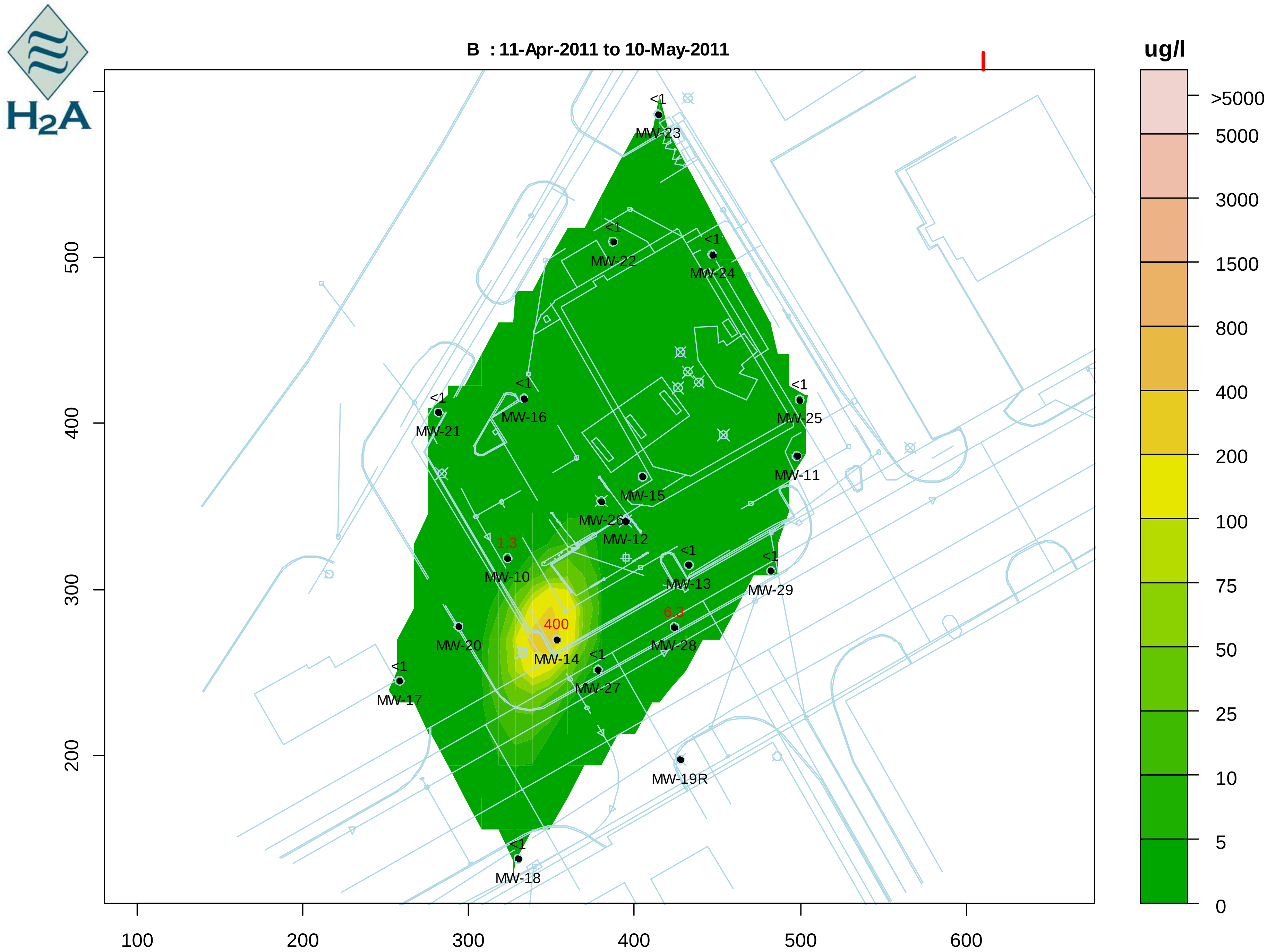

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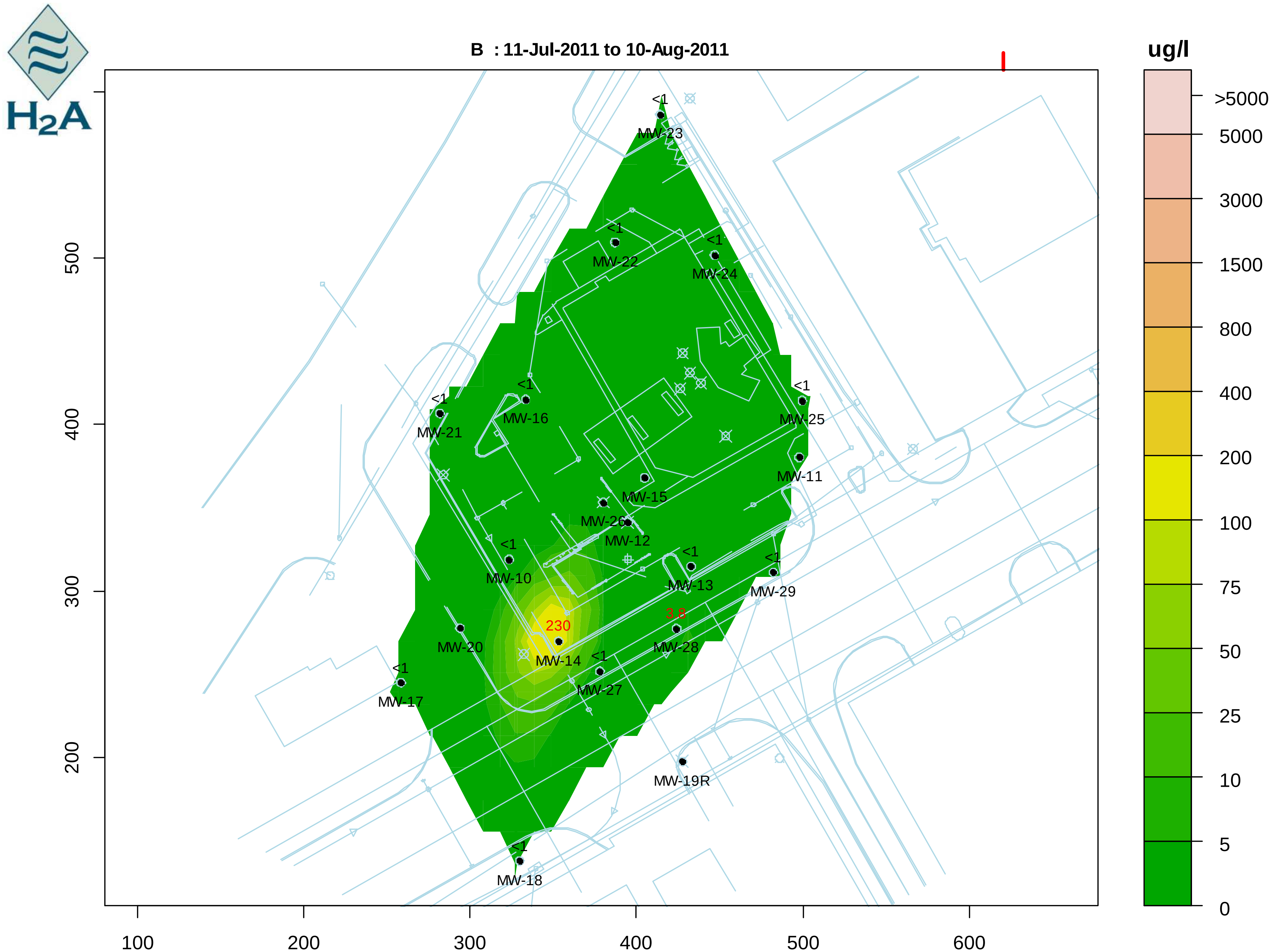

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MW-29
MW-20
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MW-17
MW-27
MW-19R
MW-18
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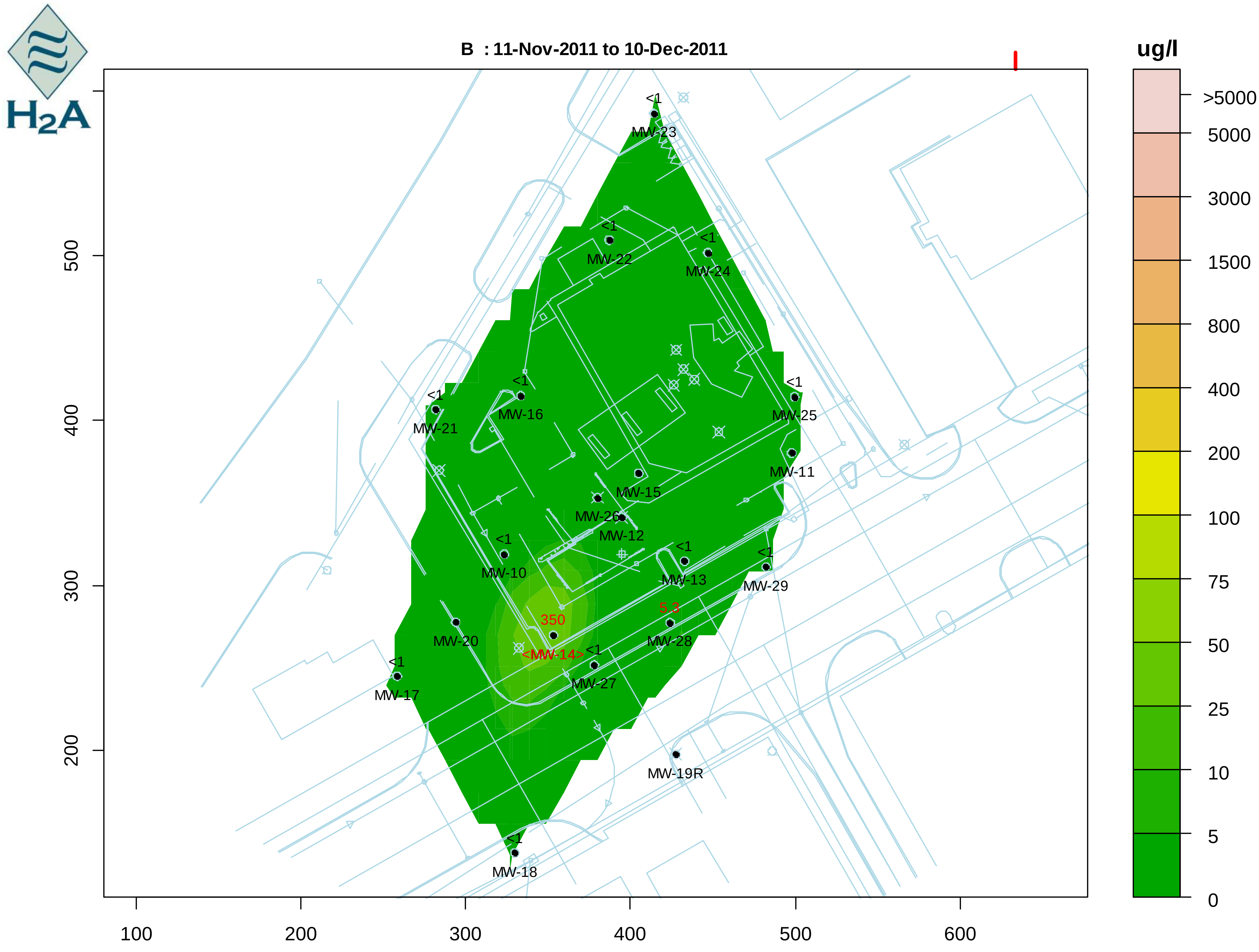
300
400
500
600



H2A
B : 11-Nov-2011 to 10-Dec-2011
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10
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MW-25
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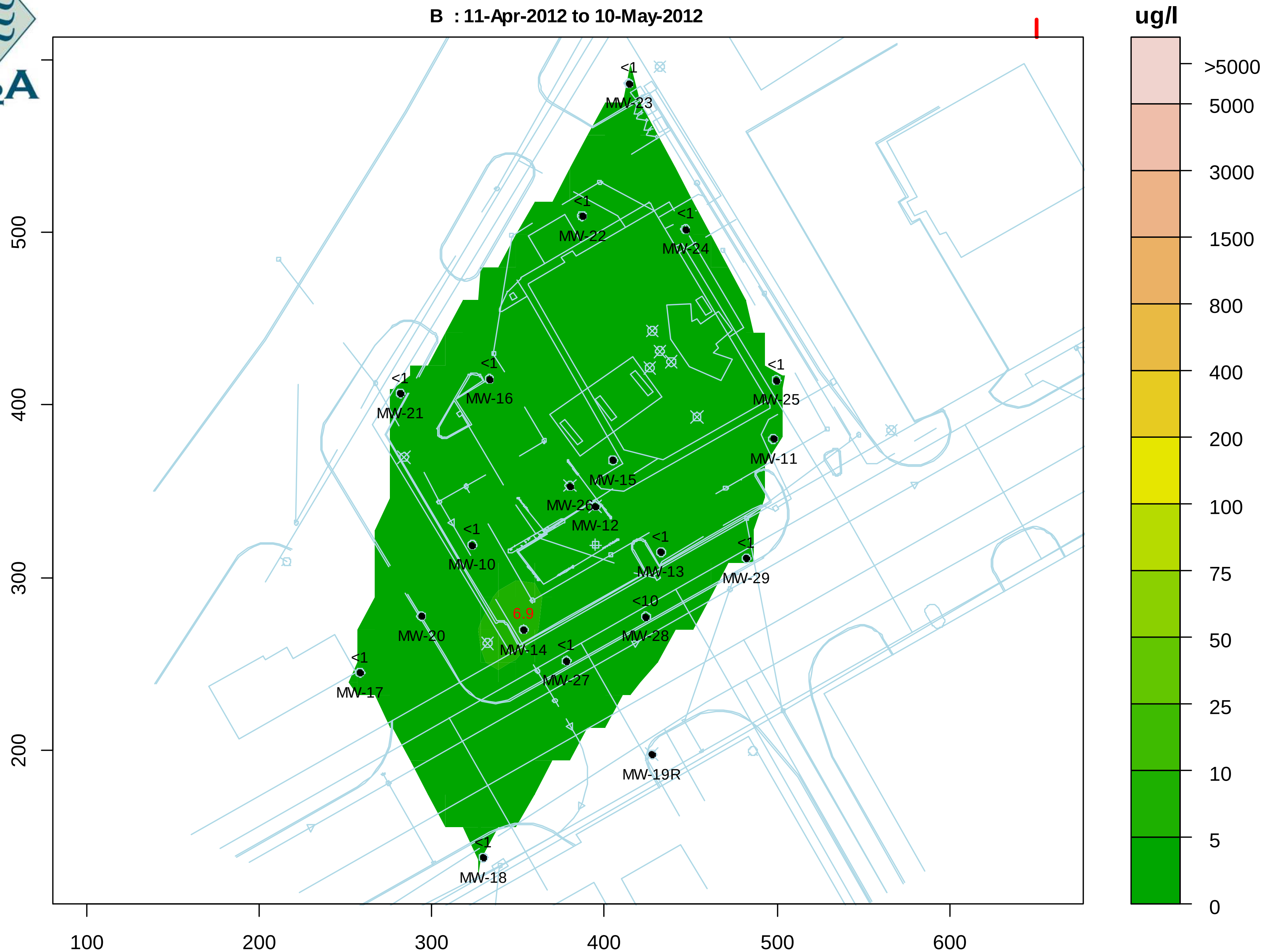

B : 11-Apr-2012 to 10-May-2012
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400
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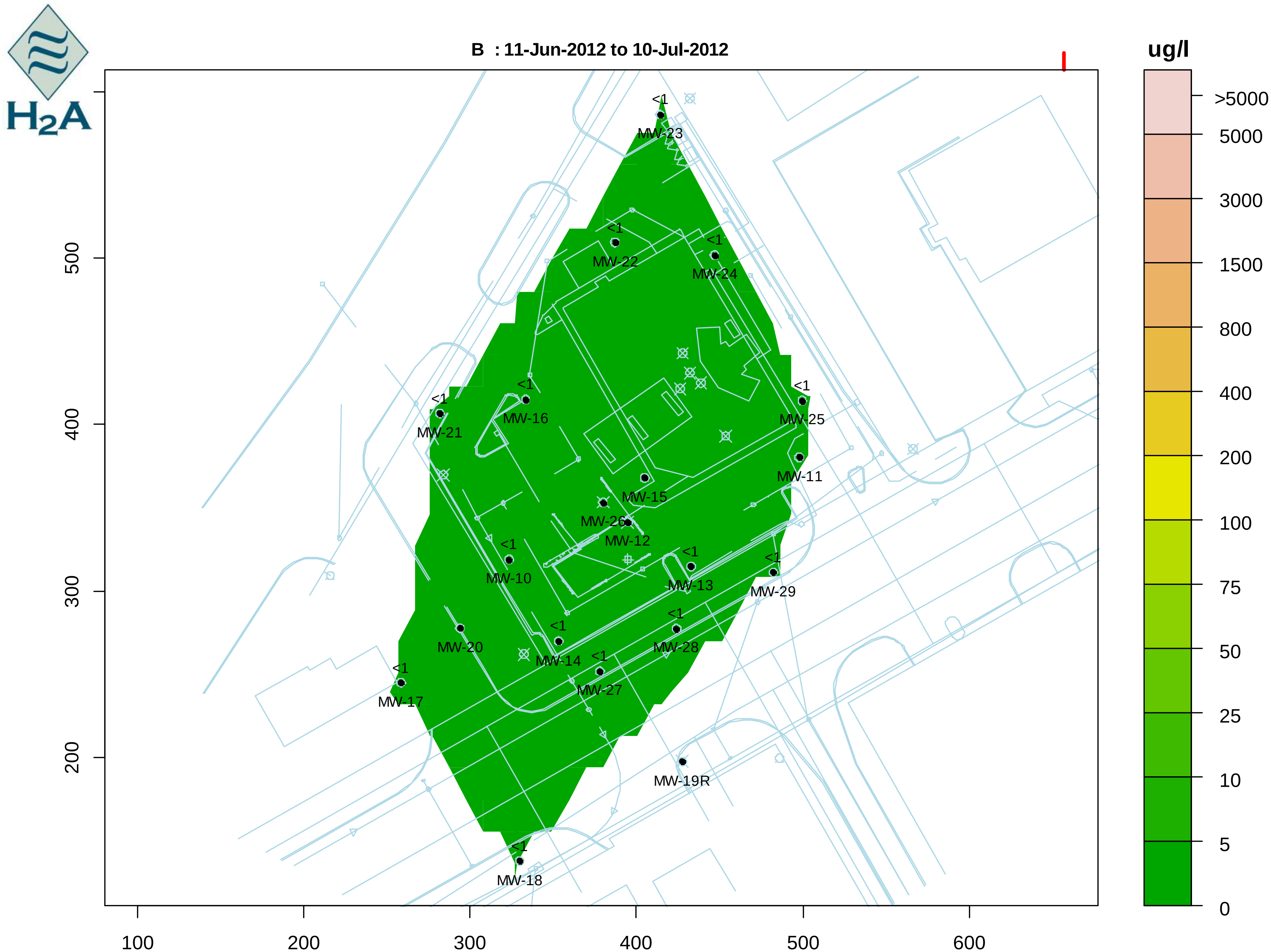
H2A
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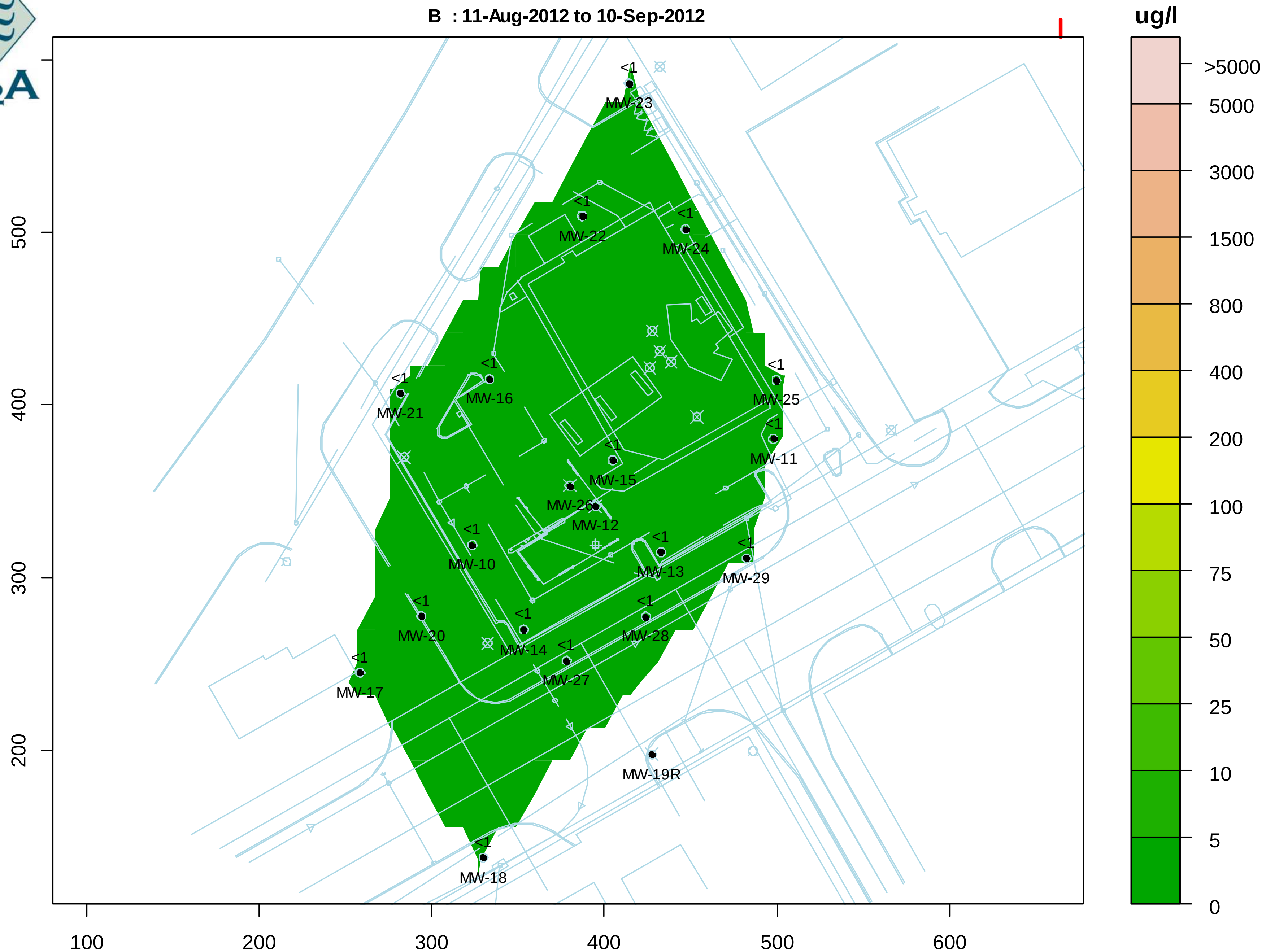
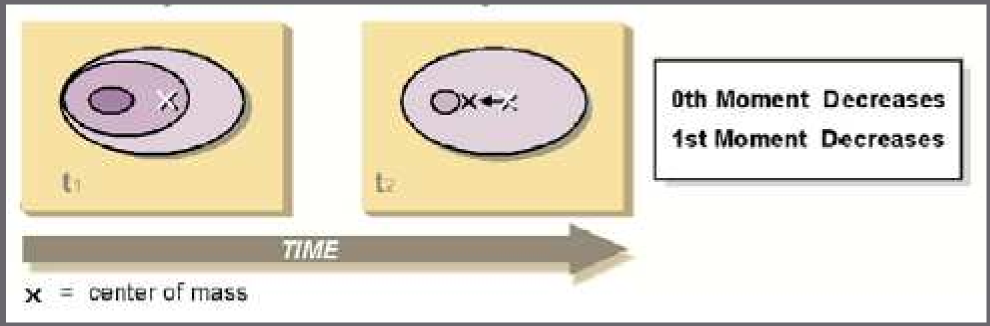
MW-17
MW-19R
<1
MW-18
100
200
300
400
500
600

B : 11-Aug-2012 to 10-Sep-2012

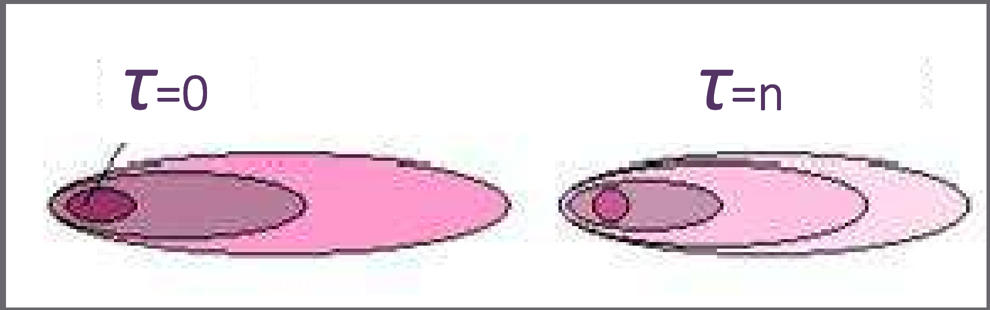


Time Series Data Trend Analysis

Spatial Mass Moments



GW Concentrations



Stable / Decreasing Trend

$$\lambda_m = -\frac{dm}{dt} \qquad \lambda_C = -\frac{dC}{dt}$$

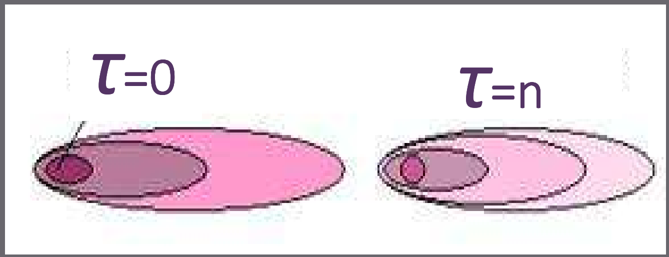
Time-Series Data Analysis: Mann-Kendall Statistic

Mann-Kendall S Statistic	Confidence in Trend	Coefficient of Variation	Interpretation
S > 0	> 95% 90% - 95% < 90%	- - -	Increasing Probably Increasing No Trend
S ≤ 0	< 90%	COV ≥ 1 COV < 1	No Trend Stable
S < 0	90% - 95% > 95%	- -	Probably Decreasing Decreasing

2012

GW Concentration Attenuation Rates

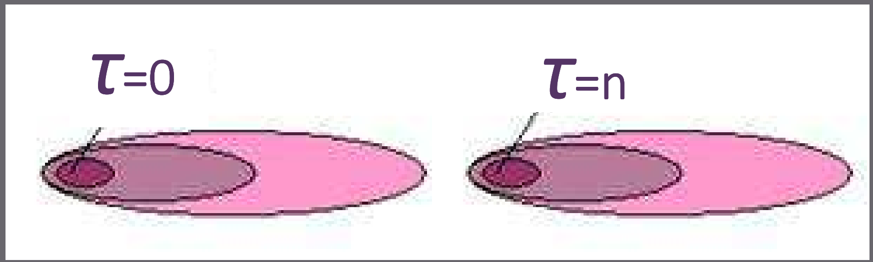
Decreasing Trend



concentration vs time

$$C(t) = C_i e^{-\lambda t}$$

Stable Trend



concentration vs distance

$$C(x) = C_0 e^{-\lambda \frac{x}{v}}$$

TCEQ TRRP-33

TCEQ Response Action Plan (RAP)

- Response Action Design

Timeframe to Attain LNAPL Recovery Goal

$$R_{mass} \approx R_{exposed} + R_{submerged}$$

$$\frac{dR_{mass}}{dt} \approx \frac{dR_{exposed}}{dt} + \frac{dR_{submerged}}{dt}$$

TCEQ NAPL Response Triggers

NAPL Response Trigger	Description of Trigger	Reference
NAPL Generating Vapors	*NAPL vapor accumulations that are potentially explosive or exceed inhalation PCLs at applicable POE -* $^{Air}Air_{Inh-V}$	Sec 2.1.1
Migrating NAPL Zone	*NAPL zone is observed to grow or move*	Sec 2.1.2
Mobile NAPL Zone	*NAPL in vadose zone with concentrations exceeding* $Soil_{Res}$	Sec 2.1.3
NAPL Aesthetic Impact or Nuisance Condition	*NAPL causes objectionable characteristics (e.g., taste, odor, color, etc.) making a natural resource or soil unsuitable for intended use*	Sec 2.1.4
NAPL Contact with Groundwater	*NAPL is in contact with saturated zone or capillary fringe of a Class 1, 2 or 3 groundwater-bearing unit (GWBU)*	Sec 2.1.5
NAPL Contact with Surface Water	*Liquid with COC concentrations exceeding the aqueous solubility that is in contact with surface water*	Sec 2.1.6
NAPL Contact with Sediment	*Liquid with COC concentrations exceeding the aqueous solubility that has impacted sediments*	Sec 2.1.7

TCEQ

TRRP-32

H₂A

TRRP-32: NAPL Response Triggers

TCEQ NAPL Response Triggers

NAPL Response Trigger	Description of Trigger	Reference
NAPL Generating Vapors	*NAPL vapor accumulations that are potentially explosive or exceed inhalation PCLs at applicable POE - $^{Air}Air_{Inh\text{-}V}$*	Sec 2.1.1
Migrating NAPL Zone	*NAPL zone is observed to grow or move*	Sec 2.1.2
Mobile NAPL Zone	*NAPL in vadose zone with concentrations exceeding $Soil_{Res}$*	Sec 2.1.3
NAPL Aesthetic Impact or Nuisance Condition	*NAPL causes objectionable characteristics (e.g., taste, odor, color, etc.) making a natural resource or soil unsuitable for intended use*	Sec 2.1.4
NAPL Contact with Groundwater	*NAPL is in contact with saturated zone or capillary fringe of a Class 1, 2 or 3 groundwater-bearing unit (GWBU)*	Sec 2.1.5
NAPL Contact with Surface Water	*Liquid with COC concentrations exceeding the aqueous solubility that is in contact with surface water*	Sec 2.1.6
NAPL Contact with Sediment	*Liquid with COC concentrations exceeding the aqueous solubility that has impacted sediments*	Sec 2.1.7

TCEQ

TRRP-32

H₂A

TRRP-32: NAPL Response Triggers

NAPL Contact with Groundwater Trigger

Site Condition *(from STEP 2)*	NAPL Response Objective	NAPL Response Endpoint	
		Recovery Endpoint	Control Endpoint
❑ NAPL contact w/ Class 1 groundwater ❑ NAPL contact w/ Class 2 / Class 3 groundwater <u>not</u> in PMZ	Groundwater restoration (Sec 3.6.1)	RECOVERY ONLY ❑ Recover soluble NAPL fraction sufficient to eliminate source contributions to GW PCLE zone (Sec 3.6.1.1)	CONTROL (via TI) ❑ Control soluble NAPL fraction sufficient to create stable (or shrinking) PCLE zone (Sec 3.6.1.2)
❑ NAPL contact w/ Class 2 / Class 3 groundwater, in PMZ	Compliance with PMZ performance criteria at NAPL zone (Sec 3.6.2)	RECOVERY ❑ Recover readily recoverable NAPL fraction (Sec 3.6.2.1)	(only address recovery endpoint, if applicable) (Sec 3.6.2.2)

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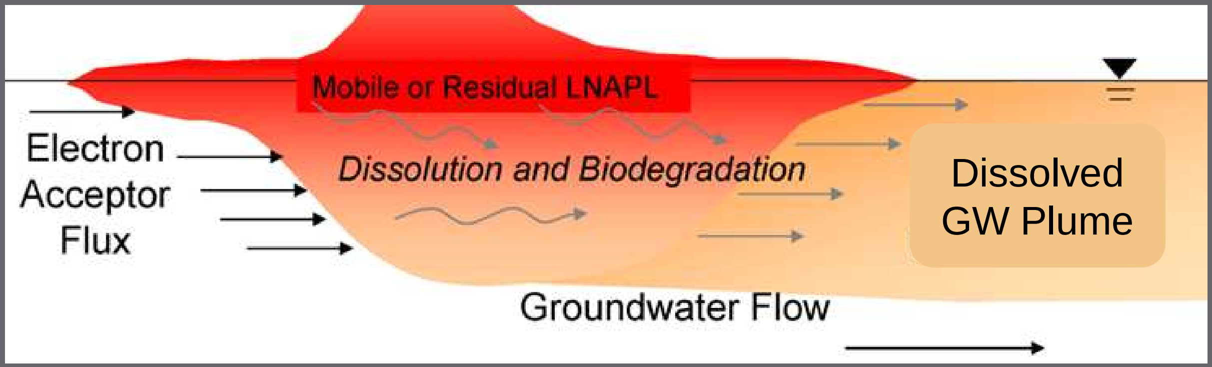
TRRP-32

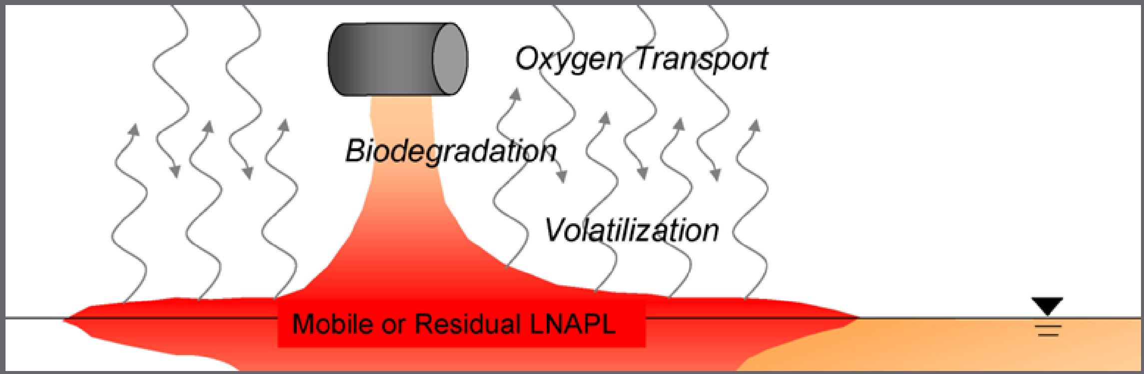
Submerged Source Zone

NAPL Trigger	NAPL Response Objective	Recovery Endpoint	NAPL RAP Design (Recovery)
NAPL Contact w/ GW – no institutional controls	**Restore Groundwater**	Recover soluble LNAPL fraction sufficient to eliminate GW exceedance zone	• GW plume is decreasing by M-K • GW attenuation rate determined • IF GW MNA rate projected to attain GW goal in reasonable timeframe • THEN LNAPL NSZD rate can achieve NAPL Recovery Endpoint and satisfies NAPL Response Objective



Exposed Source Zone

NAPL Trigger	NAPL Response Objective	Recovery Endpoint	NAPL RAP Design (Recovery)
NAPL Generating Vapors – Exceed protective inhalation standards at POE	**Abate Inhalation Exposure**	Recover volatile LNAPL fraction sufficient to eliminate exceedance of inhalation standards	• Vapor mass flux decreasing by M-K • Vapor attenuation rate determined • IF vapor attenuation rate projected to attain inhalation goal in reasonable timeframe • THEN LNAPL NSZD rate can achieve NAPL Recovery Endpoint and satisfies NAPL Response Objective



NAPL RAP Design: Recovery by NSZD

This is …

H_2A