

Abiotic and Biotic Dechlorination of Carbon Tetrachloride and Chloroform by In Situ Chemical Reduction

Worley: Débora Toledo Ramos, Tiago Takeuti, Yumi Mori, Marcelo Silveira, Sander Eskes and Paulo Rego

Jacobs: Jim Arthur

University of Toronto: Elizabeth Edwards and Line Lomheim

Corteva: Paloma Carvalho and Elizabeth Erin Mack

2024 Battelle Chlorinated Conference

Denver | Colorado | USA

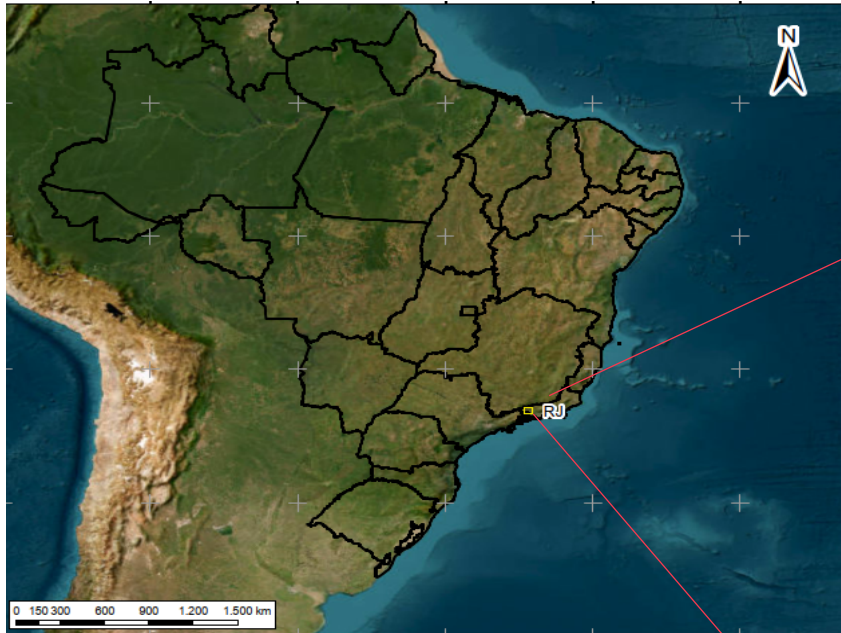
June | 4 | 2024



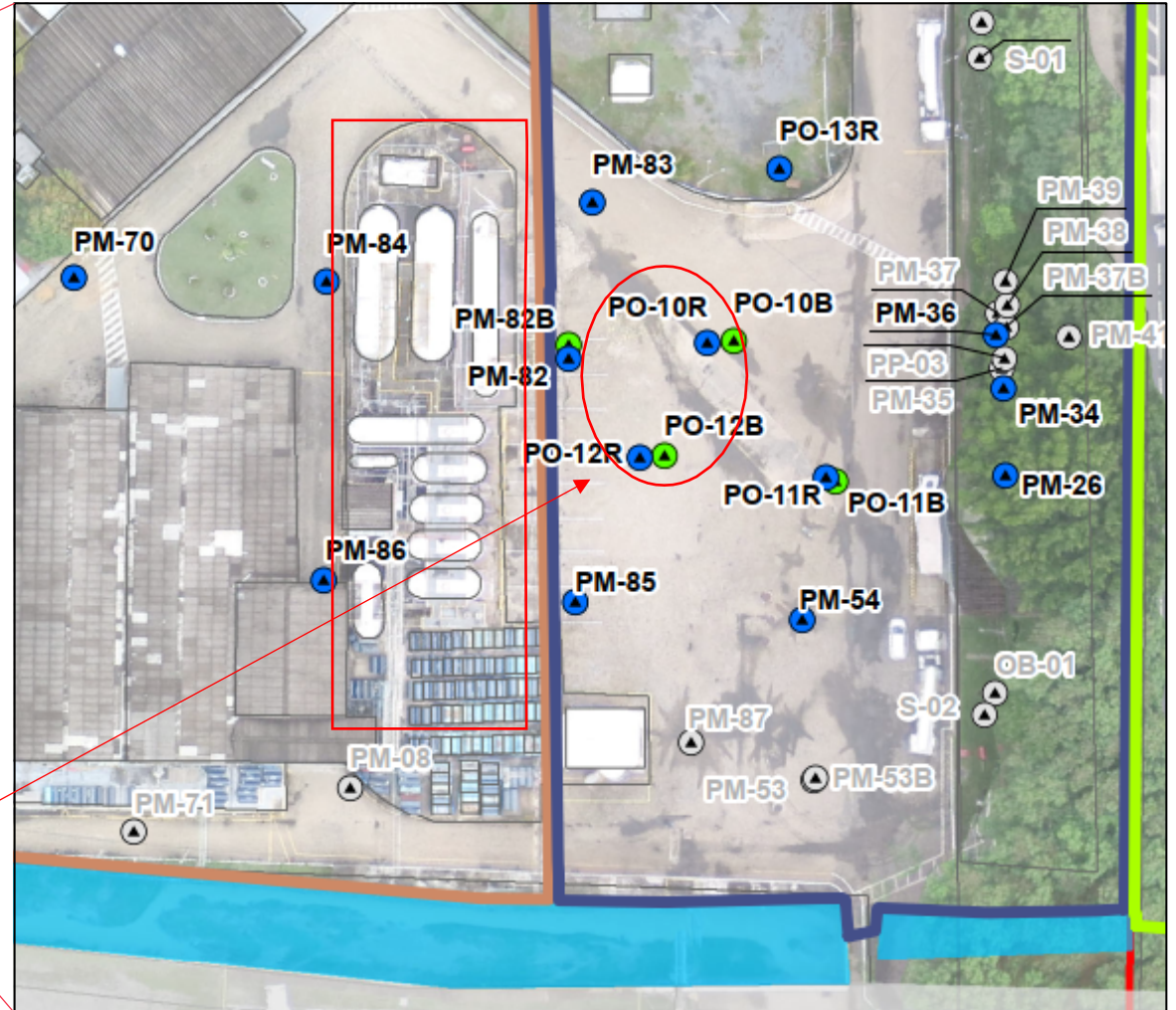
Agenda

- **Site Context**
- **Historical Interventions**
- **Remedial Strategy**
- **Project Timeline and Approach**
- **Performance Evaluation**
- **Conclusions and Lessons Learned**

Site Context

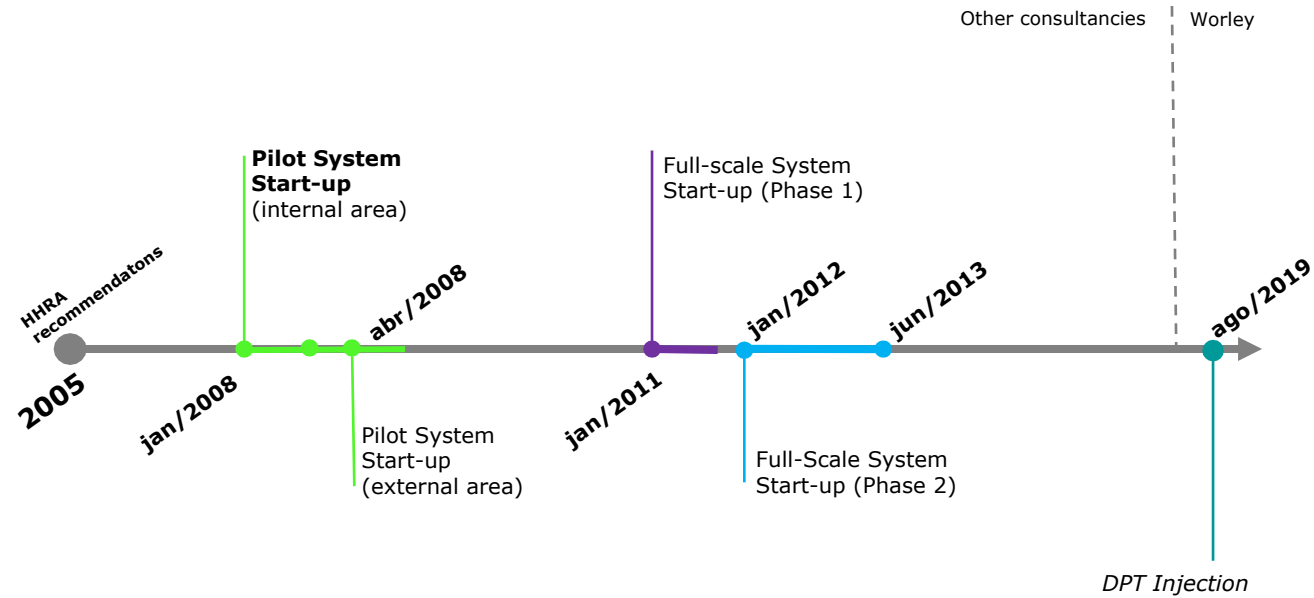


Former Above-Ground Storage Tanks Area



○ Former Above-Ground Storage Tank Area

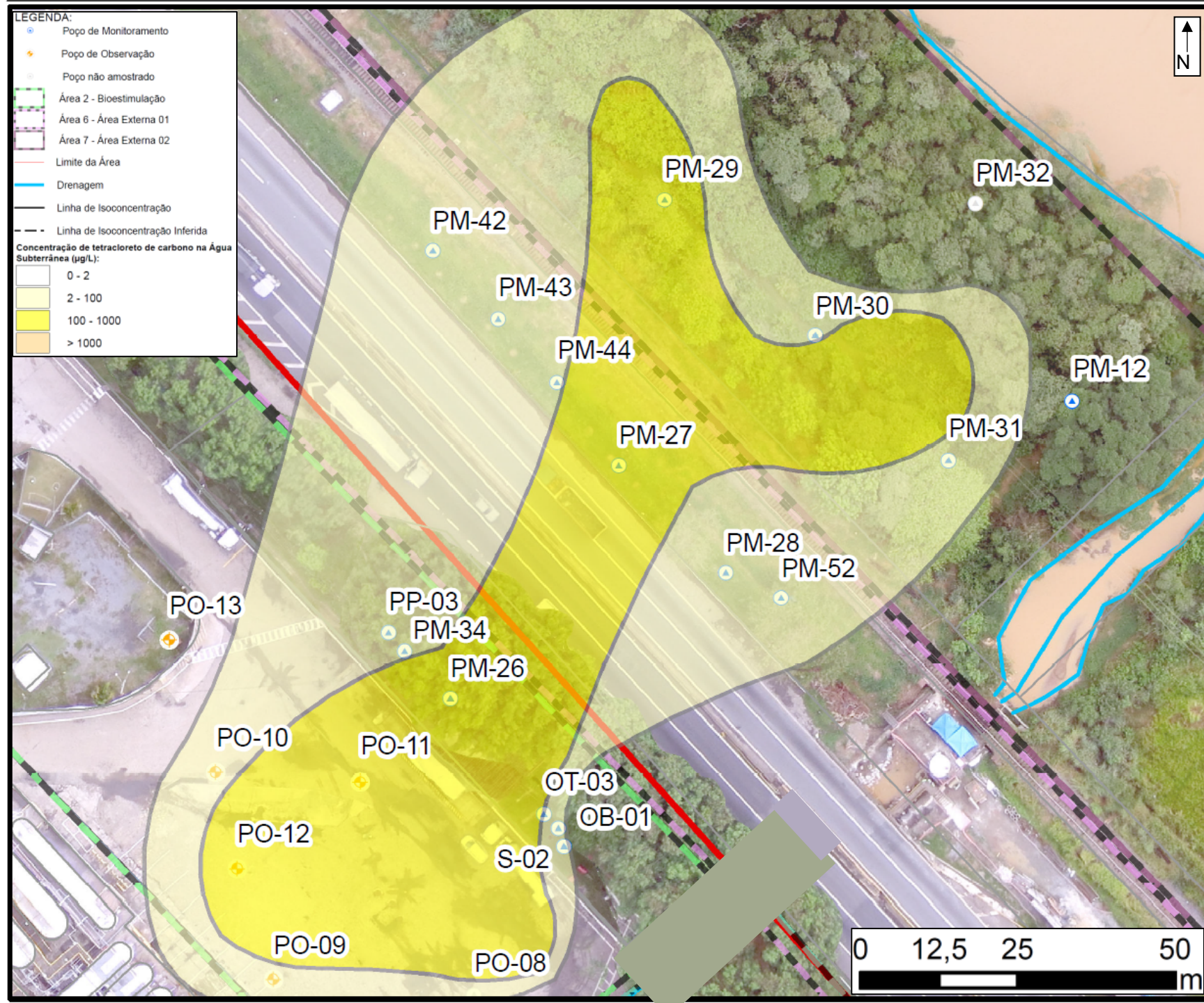
Intervention History



- Compounds identified in HHRA (2005) include carbon tetrachloride, chloroform and 1,1,2,2-TeCA;
- Pilot System molasses injections (green squares)
- Full-scale molasses injections performed (2011 – 2019)
- Limited success and strategy was reassessed.



Evolution of Carbon Tetrachloride Plume



2010 / August

2011 / August

2012 / February

2013 / March

2014

2015

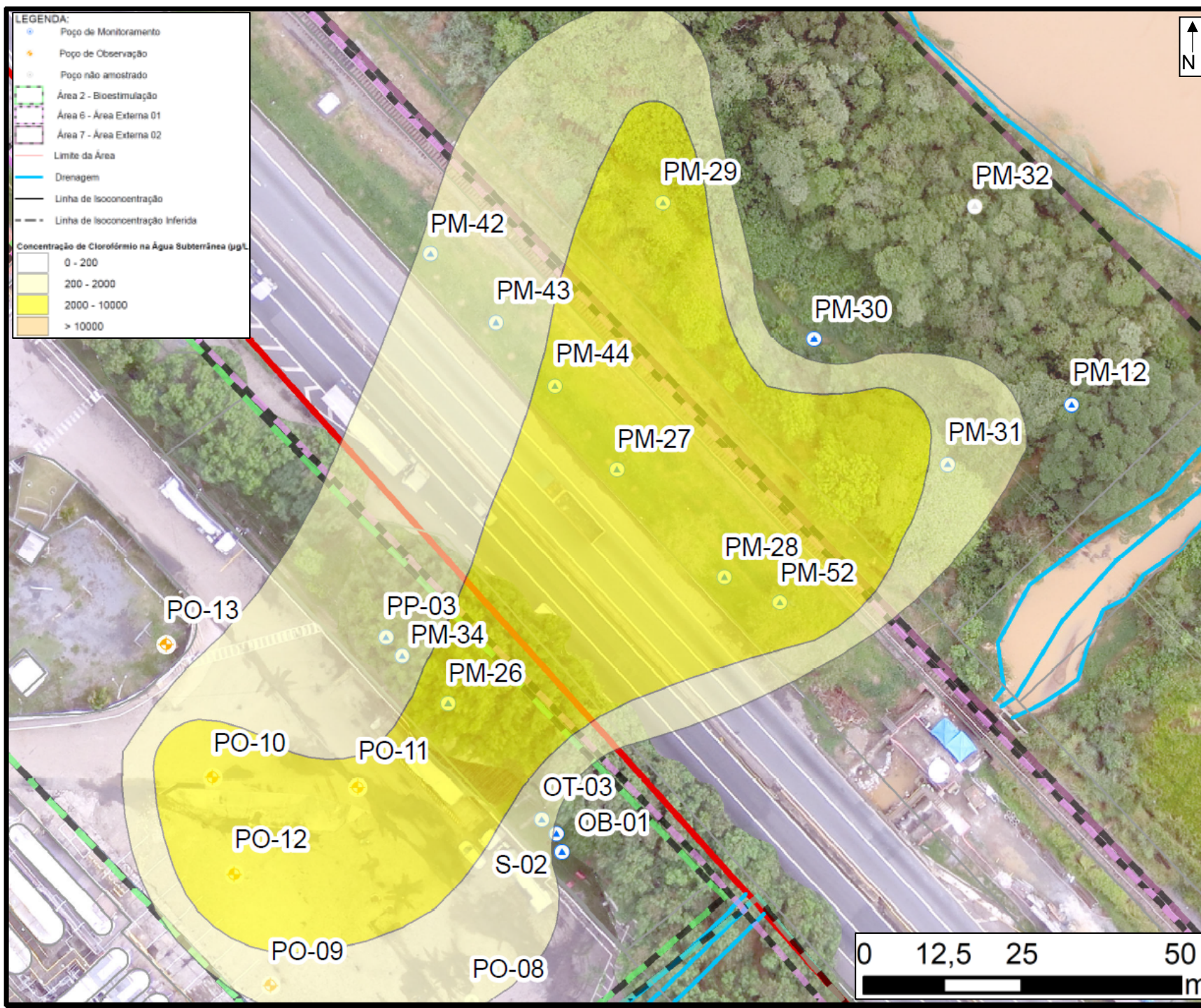
2016

2017 / Nov-Dec

2018 / Apr-Jun

2019 / Feb-Mar

Evolution of Chloroform Plume



2010 / August

2011 / August

2012 / February

2013

2014 / June

2015 / January

2016

2017 / Nov-Dec

2018 / Apr-Jun

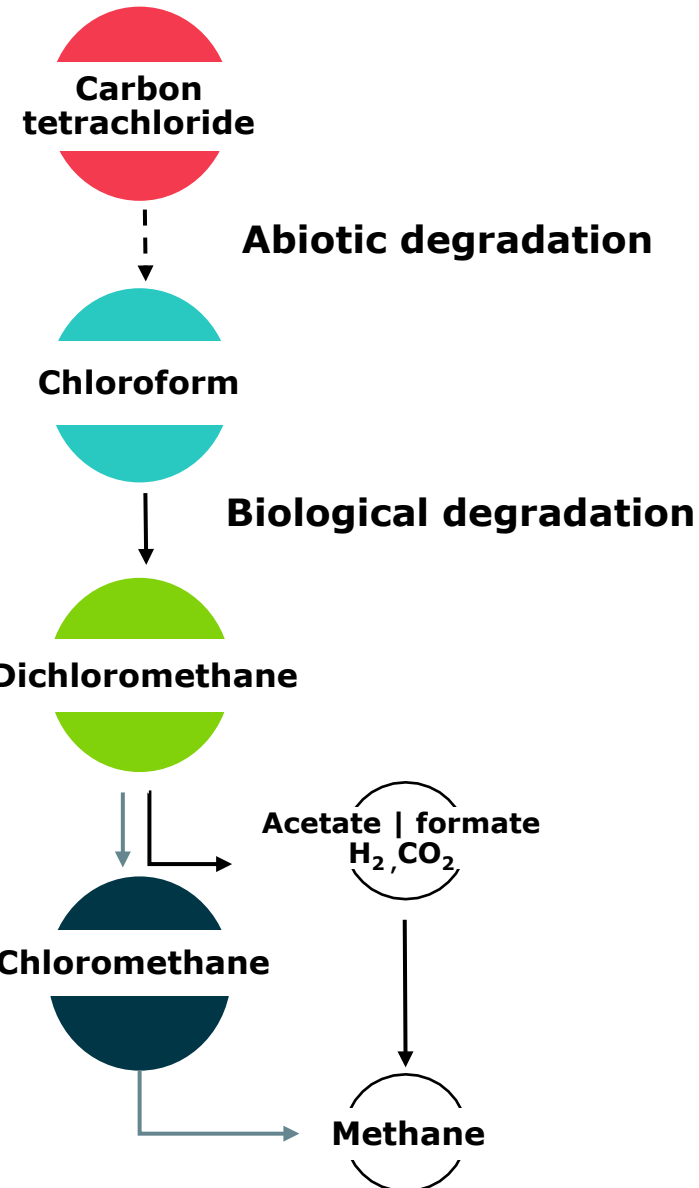
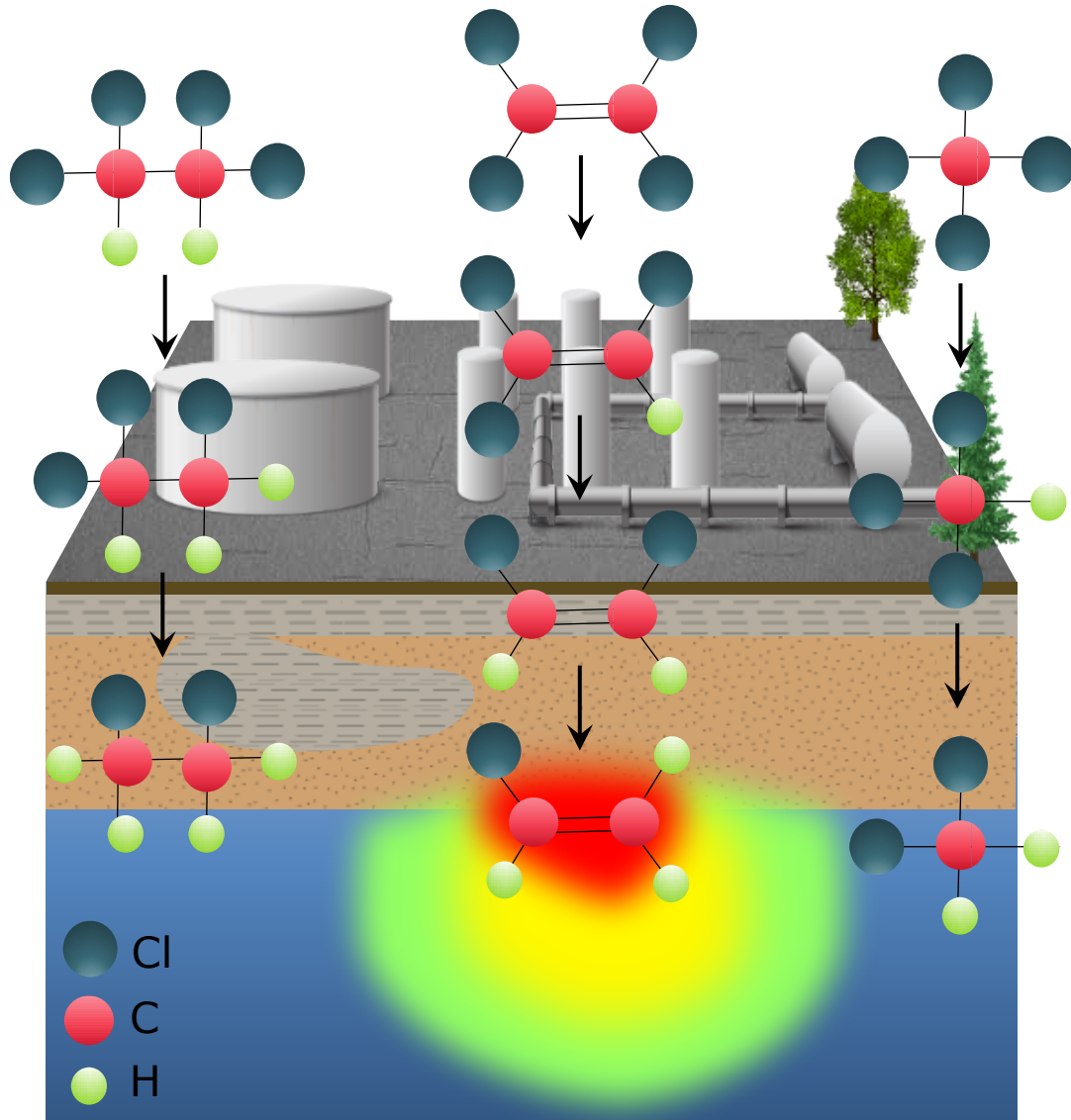
2019 / Feb-Mar

The Challenge and Our Solution

Chlorinated ethanes

Chlorinated ethenes

Chlorinated methanes



Commingled plume

Solution?

Combine biotic and
abiotic strategies to
optimize COIs
degradation

ISCR-IR:
ZVI + Organic
components

ISCR-IR Injection Event

Phase 1 – Executed in Nov/2020

Injection points	Quantity		Radius of influence (m)
	Injection points	Layers per point	
IP (plume)	10	4	4.0
PRB (permeable reactive barrier)	5	4	3.0
Total	15	-	-

 Phase 1 Injection Points

Phase 2 – Executed in Aug/2022

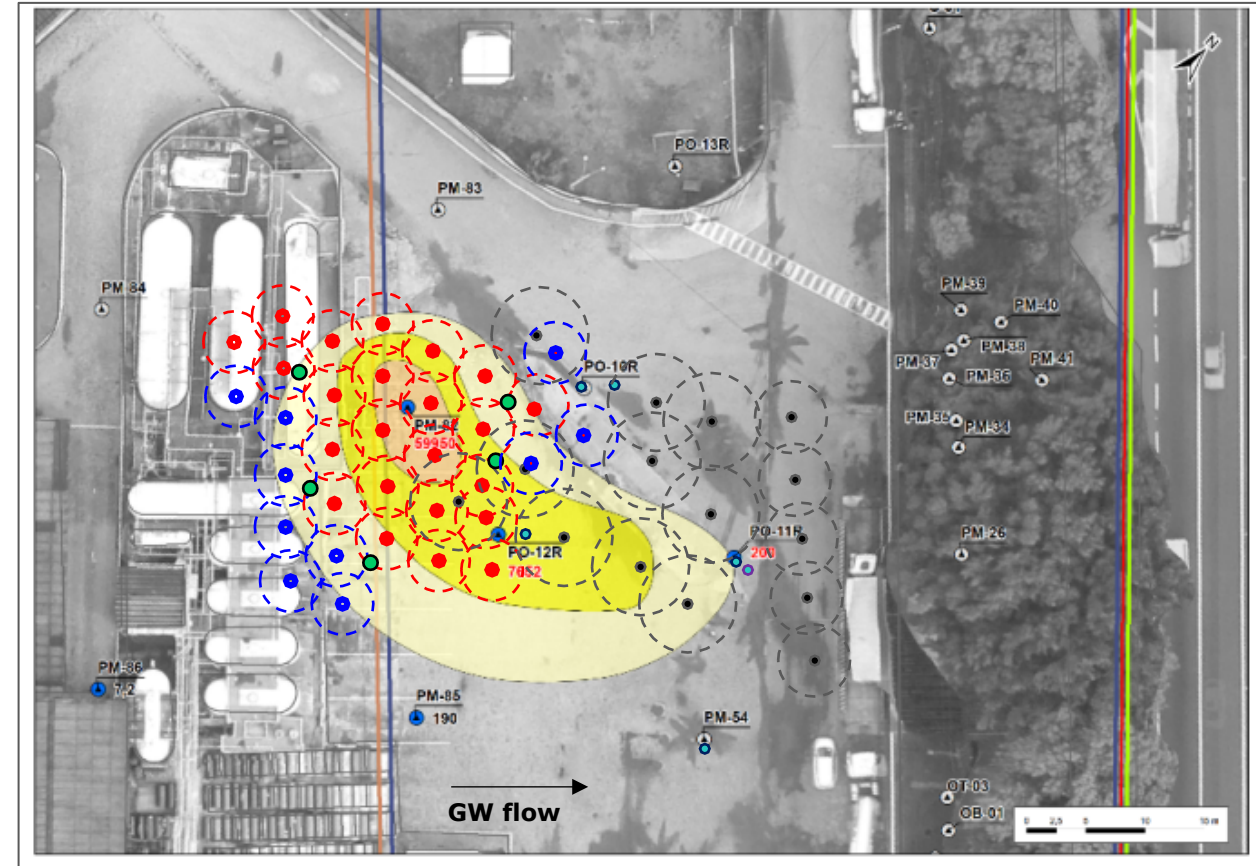
Injection points	Quantity		Radius of influence (m)
	Injection points	Layers per point	
IP (plume)	33	4	2.5

1st step:

 **Grab samples in rush time** to refine plumes and optimize injection points distribution

2nd step:

• **ISCR-IR injection** in **10 additional points**, based on grab sample results (results > ref. values)



Phase I (2020/2021)

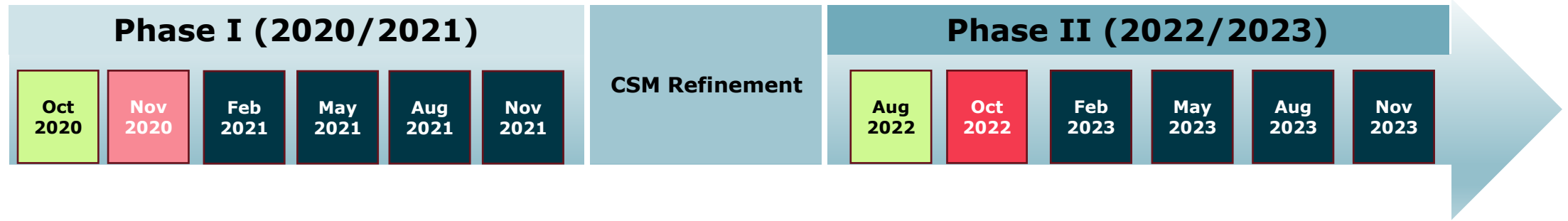
CSM Refinement

Phase II (2022/2023)

 Phase 1 Injection Points

  Phase 2 Injection Points

Monitoring Program



- Field parameters (monthly): ORP, DO, EC, pH;
- Geochemical parameters (quaterly): TOC | NO_3^- | dissolved iron | SO_4^{2-} | S^{2-} | CH_4 ;
- COIs concentrations (quaterly);
- Microbial analysis (quaterly): qPCR (Total bacteria, *Dehalobacter*, *crfA/dcrA/tmrA*) | Next Generation Sequencing.



Baseline sampling



ISCR Injection event – smaller scale (15 IPs)



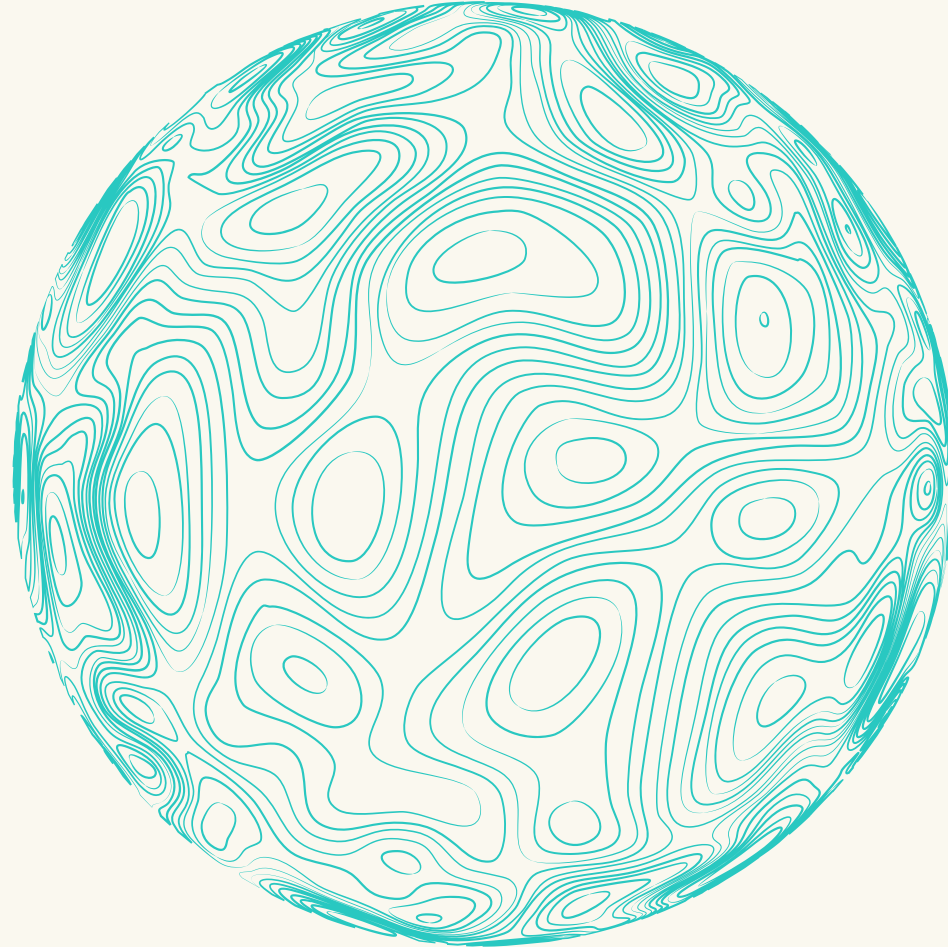
Analytical Monitoring



ISCR Injection event – 33 IPs

Phase II Performance Evaluation

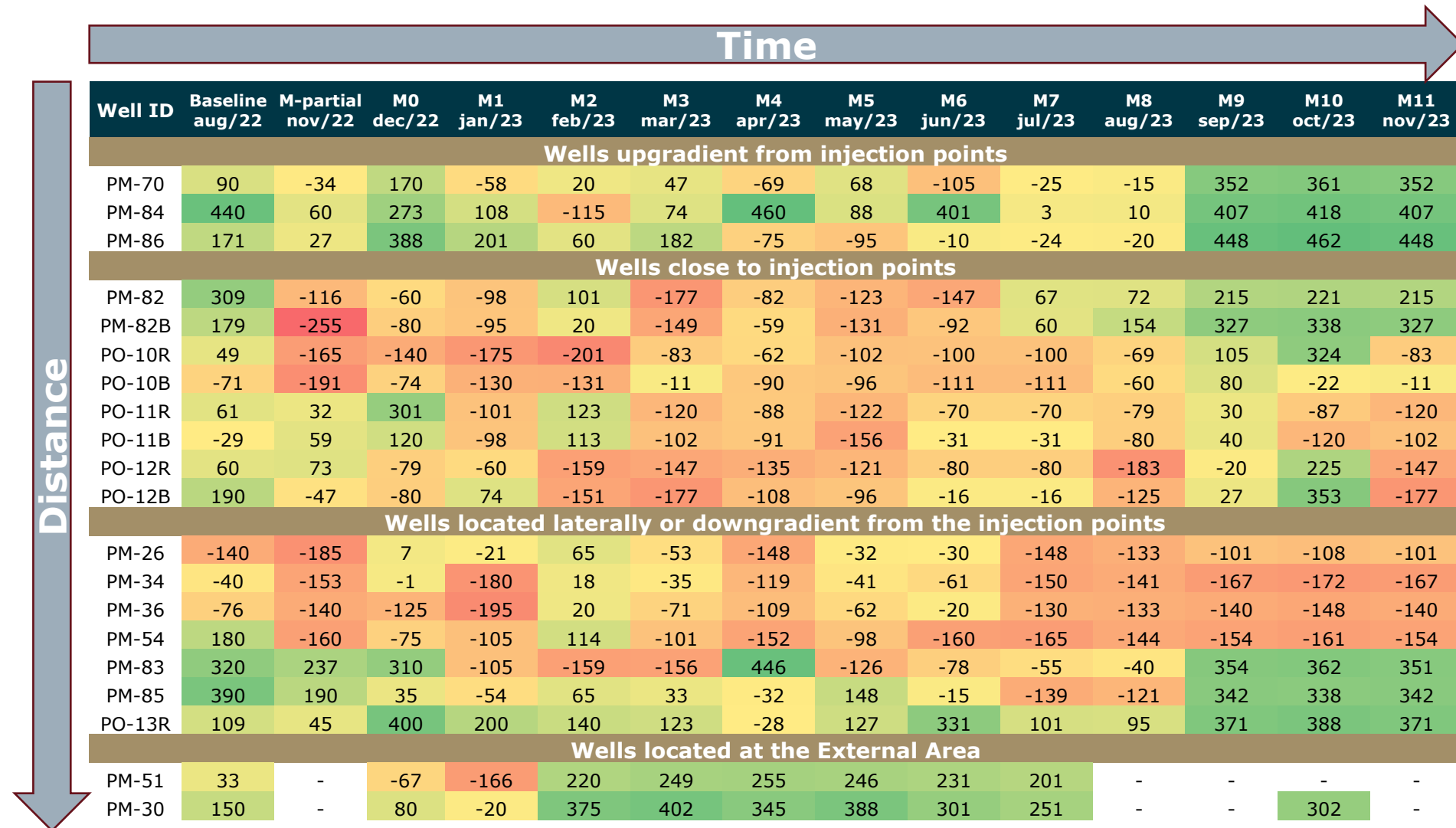
December -2022 to
November - 2023



Field Parameters

ORP (Oxidation-Reduction Potential)

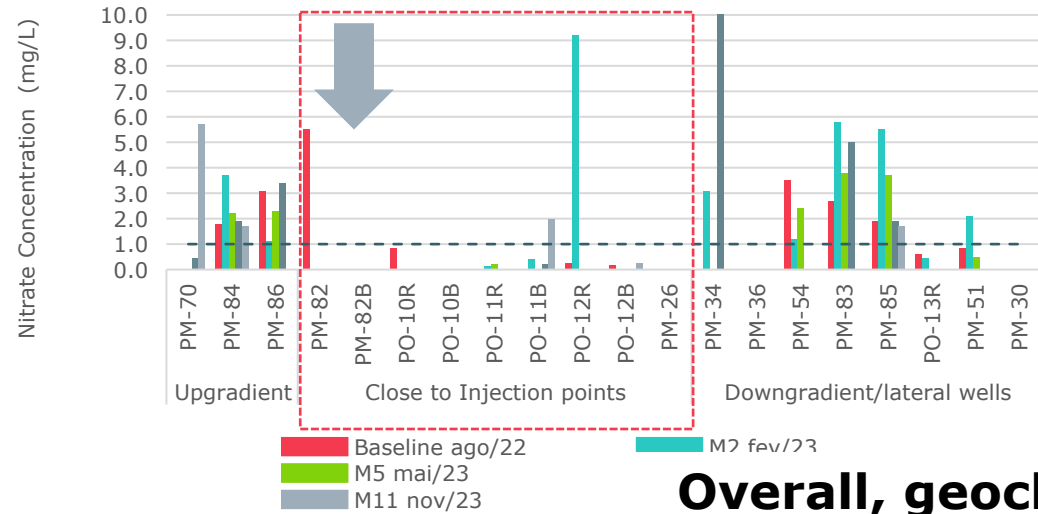
- ORP values decreased significantly right after the injection.
- Wells located close to the injection: lowest ORP values (mean value: -93mV)
- Upgradient wells and wells located at the external area presented positive values (mean values of +59 mV and +299 mV, respectively).



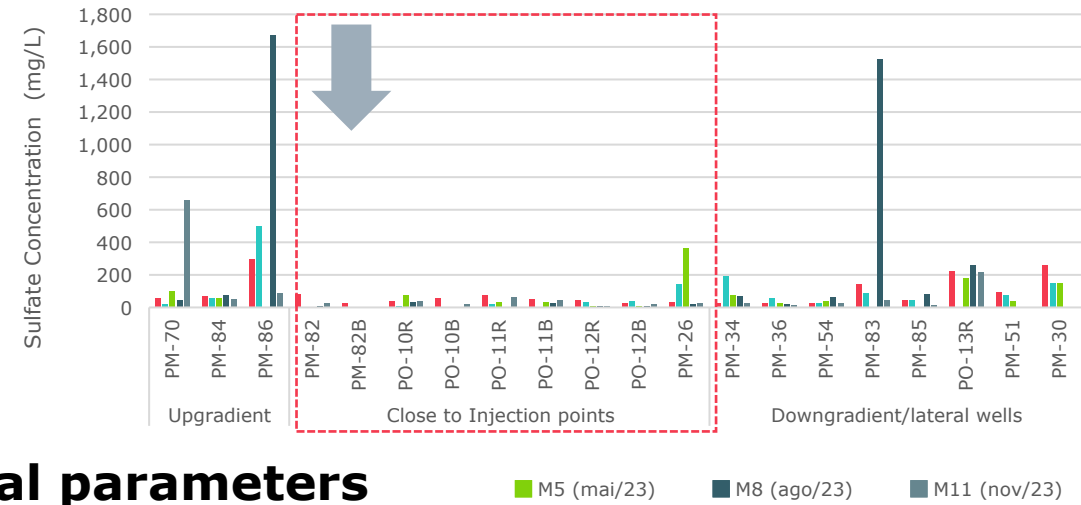
Geochemical Parameters

Nitrate, sulfate, sulfide and methane

Nitrate

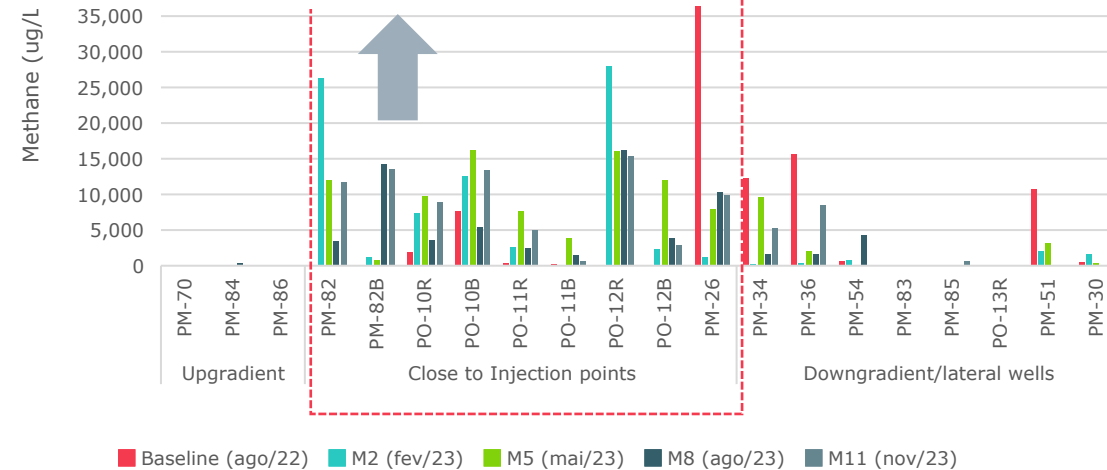
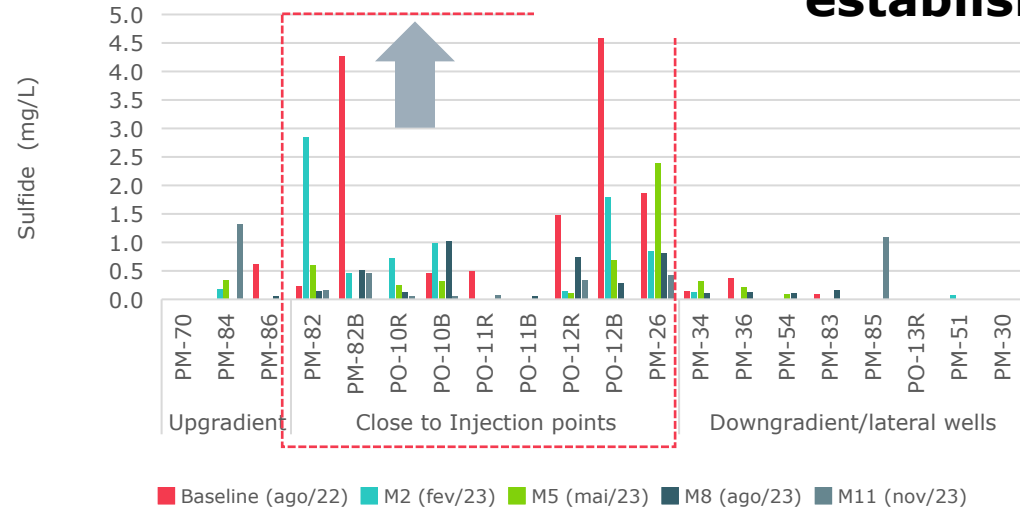


Sulfate



Overall, geochemical parameters indicate that anaerobic conditions were established at the site

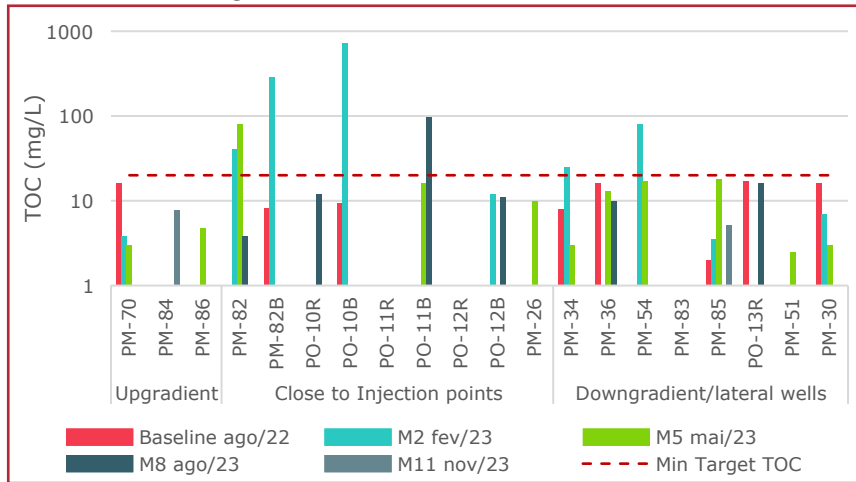
Sulfide



Geochemical Parameters

TOC and Dissolved Iron

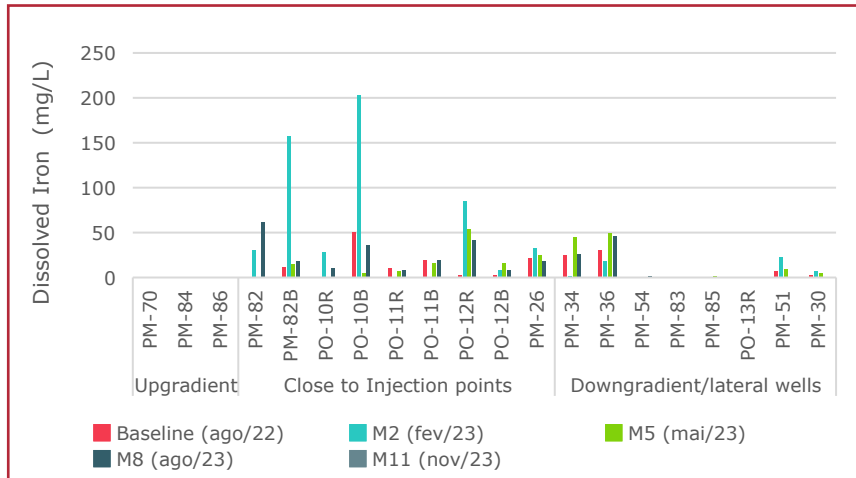
TOC (Total Organic Carbon)



TOC

- Evidence for the distribution of ISCR reagent is based on TOC concentration (ISCR-IR has more than 40% of organic ingredients in the formula).
- Significant increase in TOC (≥ 20 mg/L) indicates that ISCR reagent reached a monitoring well.
- Results demonstrated increase in TOC after injection event, mainly at wells close to injection points

Dissolved Iron

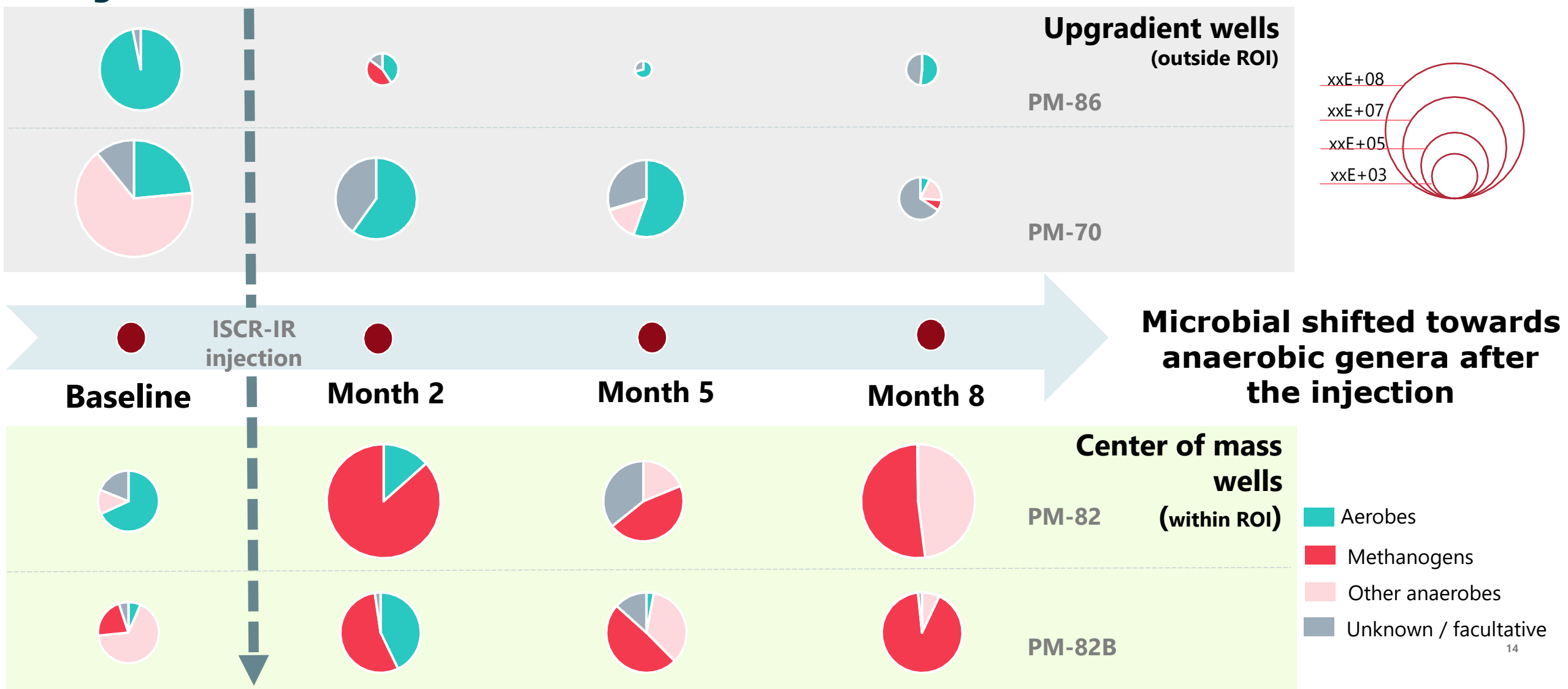


Dissolved iron

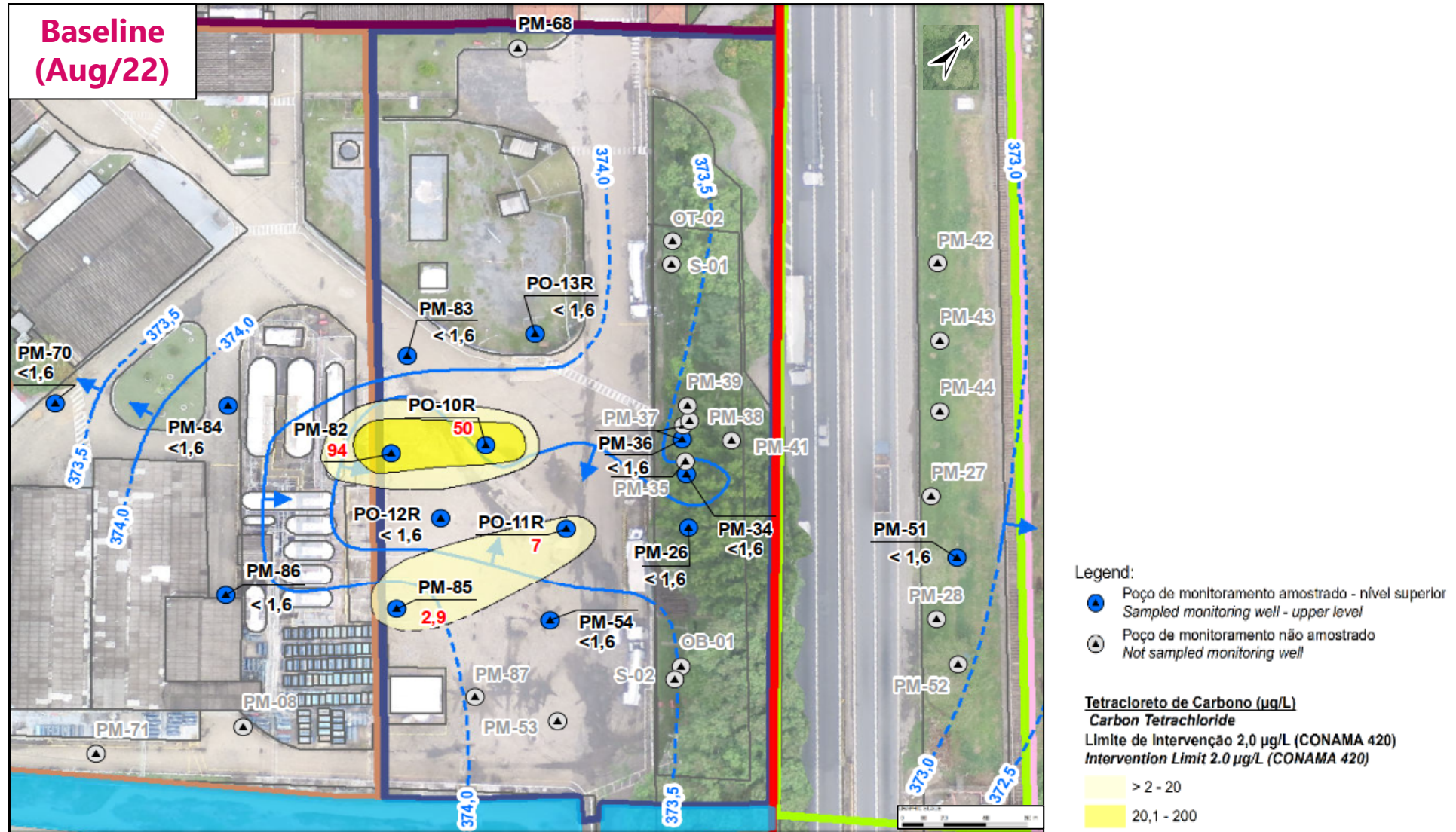
- Ferrous iron greater than 1 mg/L are typically observed:
 - Fe^{2+} is produced during Fe^{3+} reduction in anaerobic environments.
 - Zero-valent iron is converted to Fe^{2+} after reaction with chlorinated compounds
- Dissolved iron (assumed Fe^{2+}) increased at wells close to the injection points.

Overall, both TOC and dissolved iron results suggest presence of the remedial agent mainly at the locations close to the injection points.

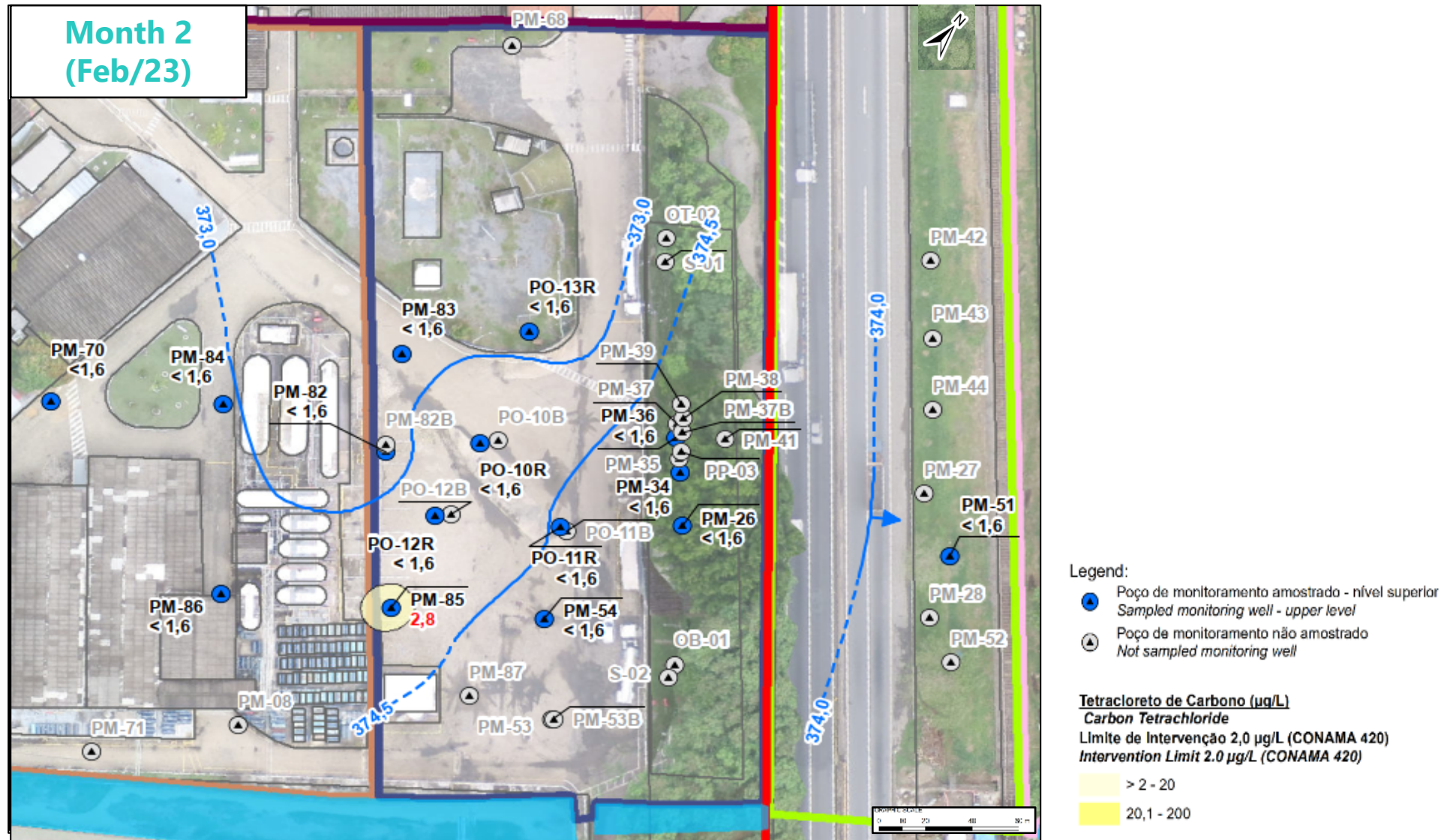
Microbial Shifts Over Time – Influence of ISCR Injections



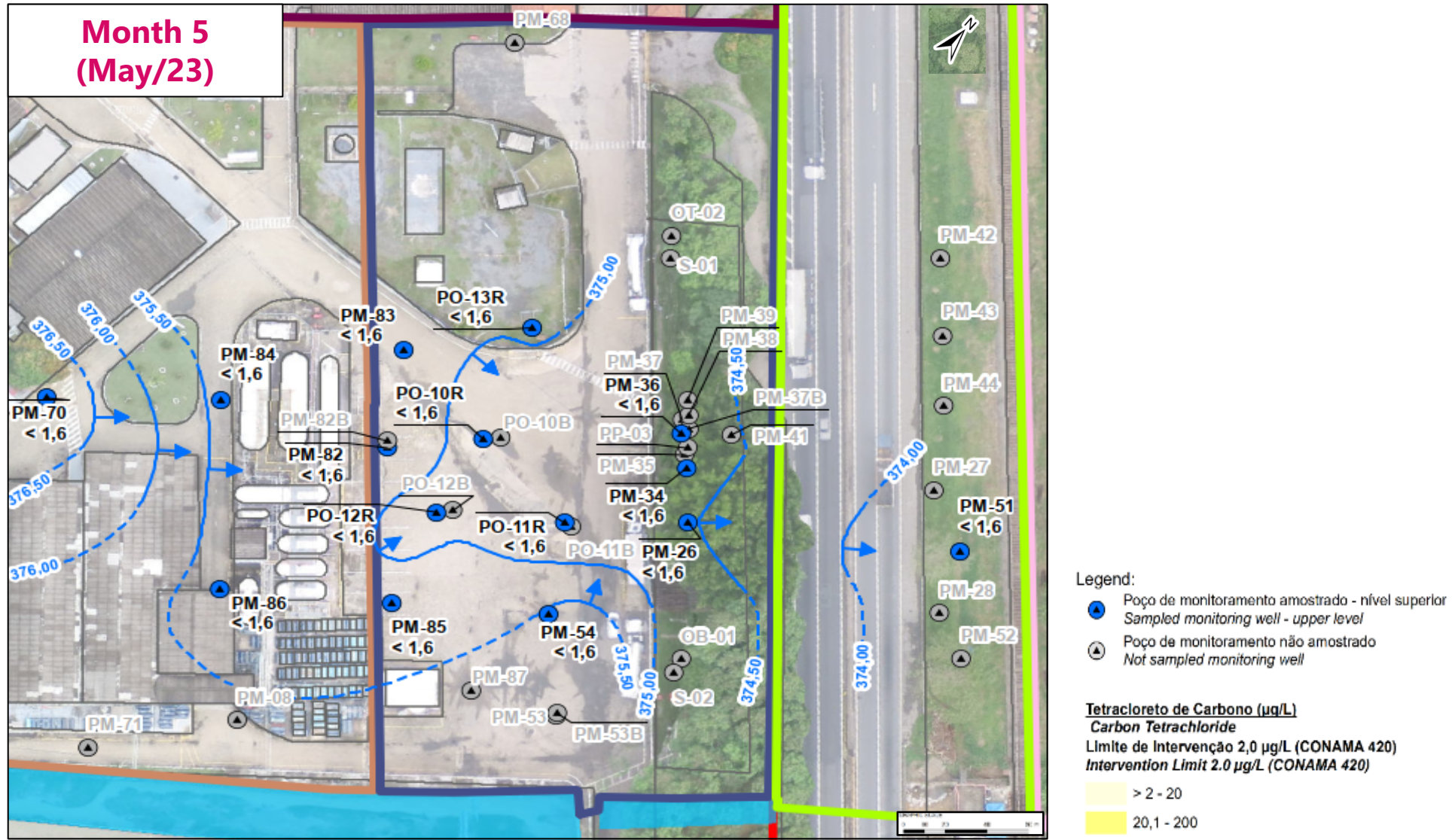
Chlorinated Methanes – Carbon Tetrachloride (CT) Upper Aquifer Level



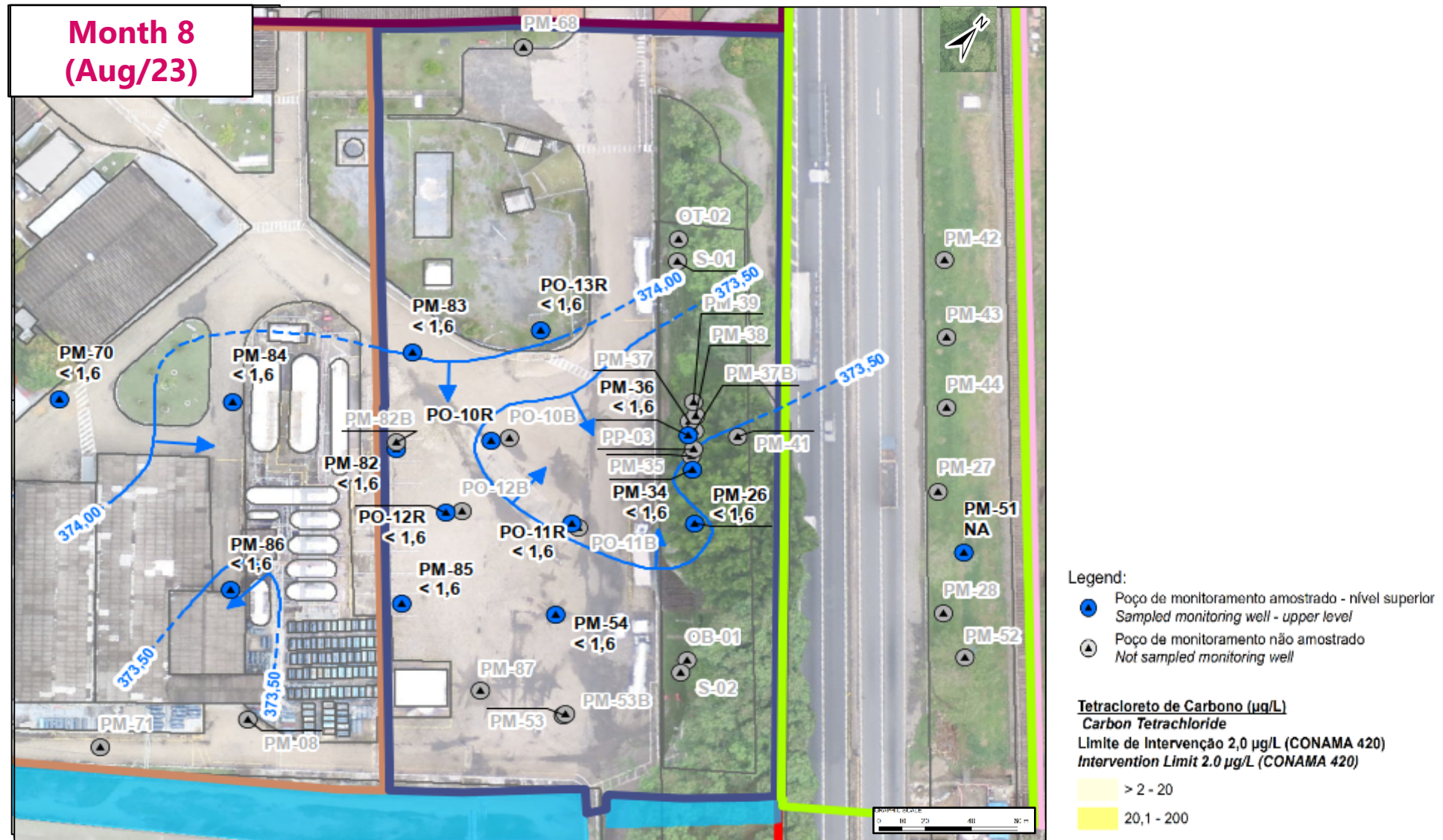
Chlorinated Methanes – Carbon Tetrachloride (CT) Upper Aquifer Level



Chlorinated Methanes – Carbon Tetrachloride (CT) Upper Aquifer Level

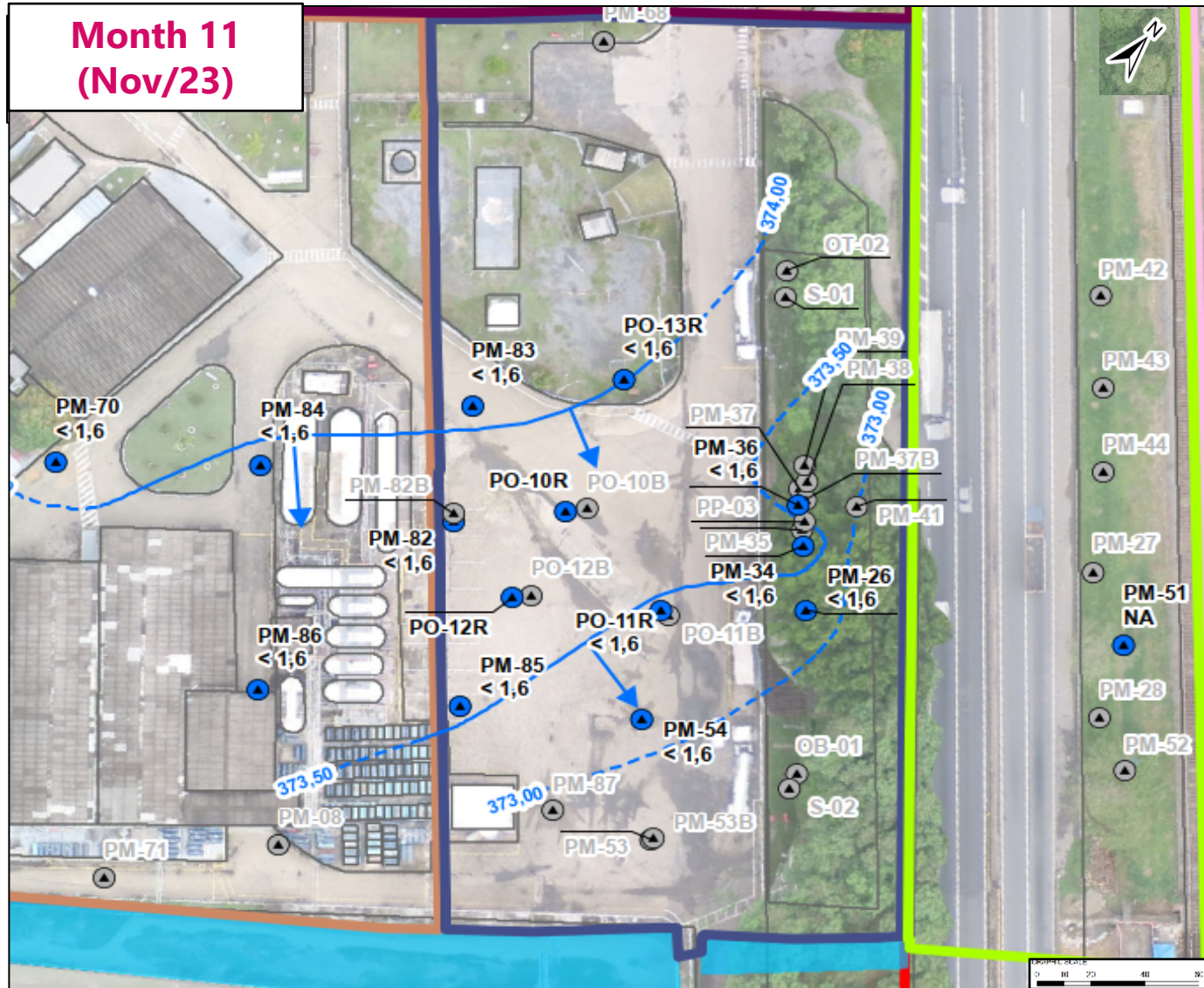


Chlorinated Methanes – Carbon Tetrachloride (CT) Upper Aquifer Level



Chlorinated Methanes – Carbon Tetrachloride (CT)

Upper Aquifer Level



Legend:

- Poço de monitoramento amostrado - nível superior
Sampled monitoring well - upper level
- ⊙ Poço de monitoramento não amostrado
Not sampled monitoring well

Tetracloreto de Carbono (µg/L)

Carbon Tetrachloride

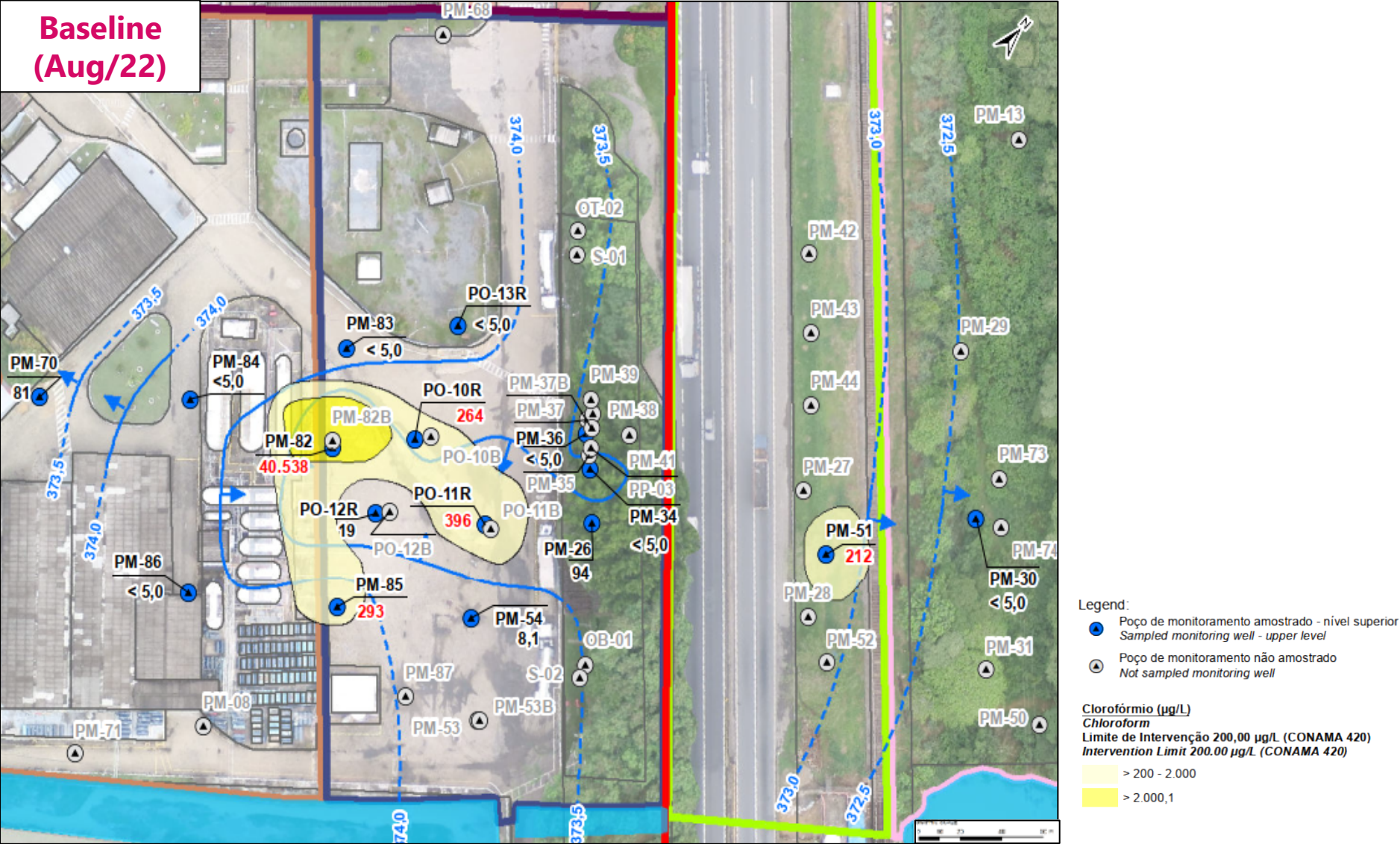
Limite de Intervenção 2,0 µg/L (CONAMA 420)

Intervention Limit 2.0 µg/L (CONAMA 420)

- > 2 - 20
- 20,1 - 200

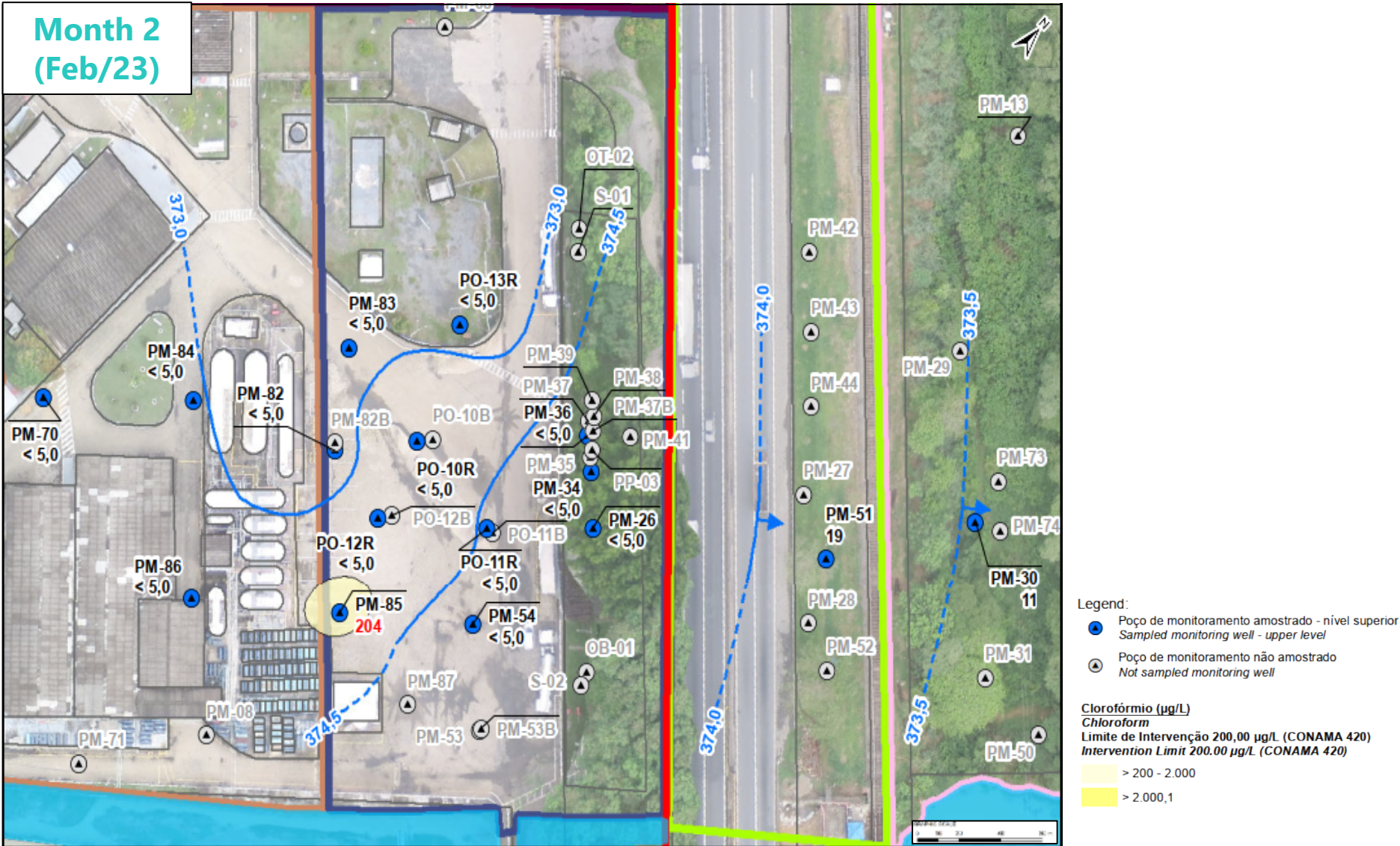
Chlorinated Methanes – Chloroform (CF)

Upper Aquifer Level



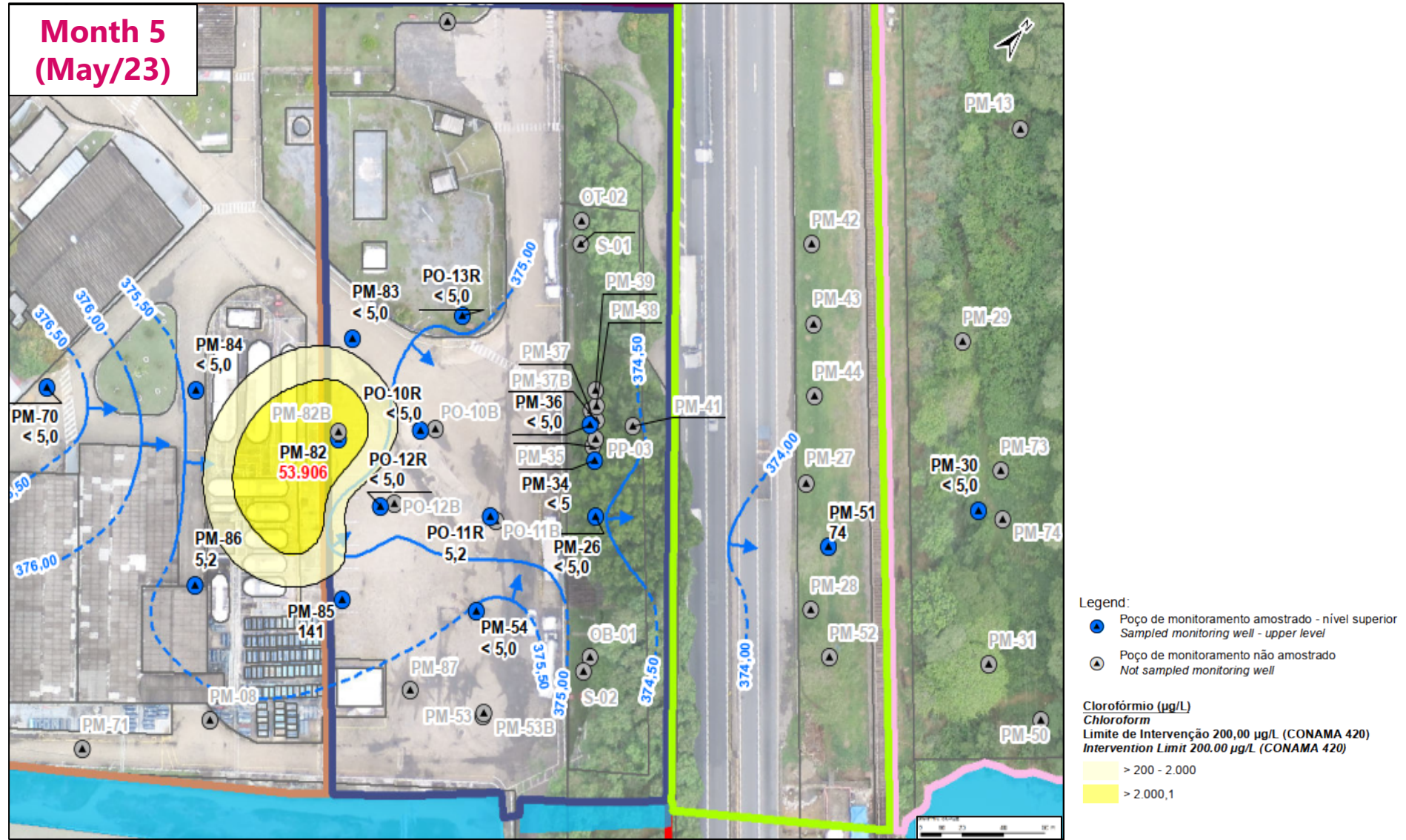
Chlorinated Methanes – Chloroform (CF)

Upper Aquifer Level



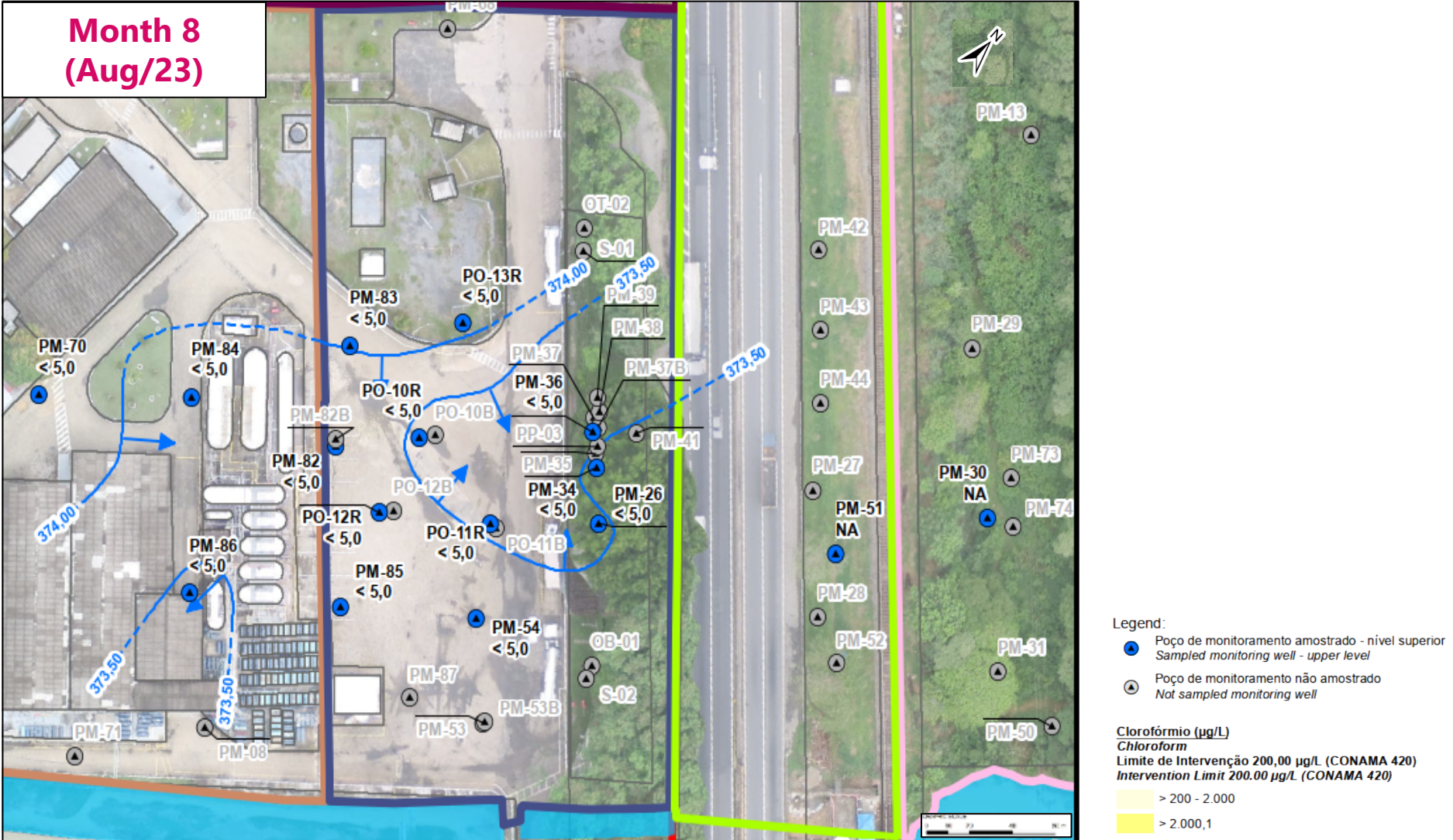
Chlorinated Methanes – Chloroform (CF)

Upper Aquifer Level



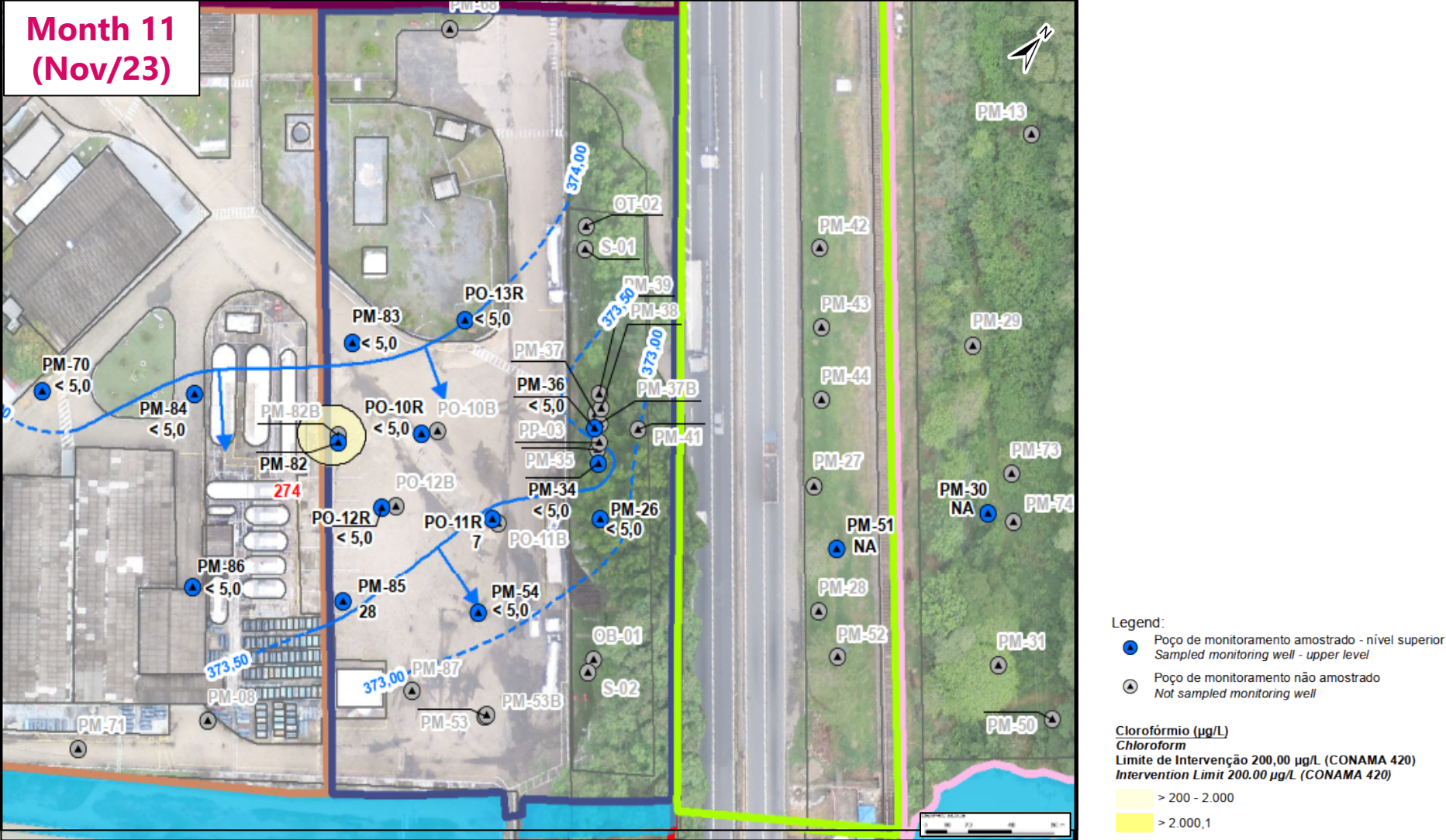
Chlorinated Methanes – Chloroform (CF)

Upper Aquifer Level

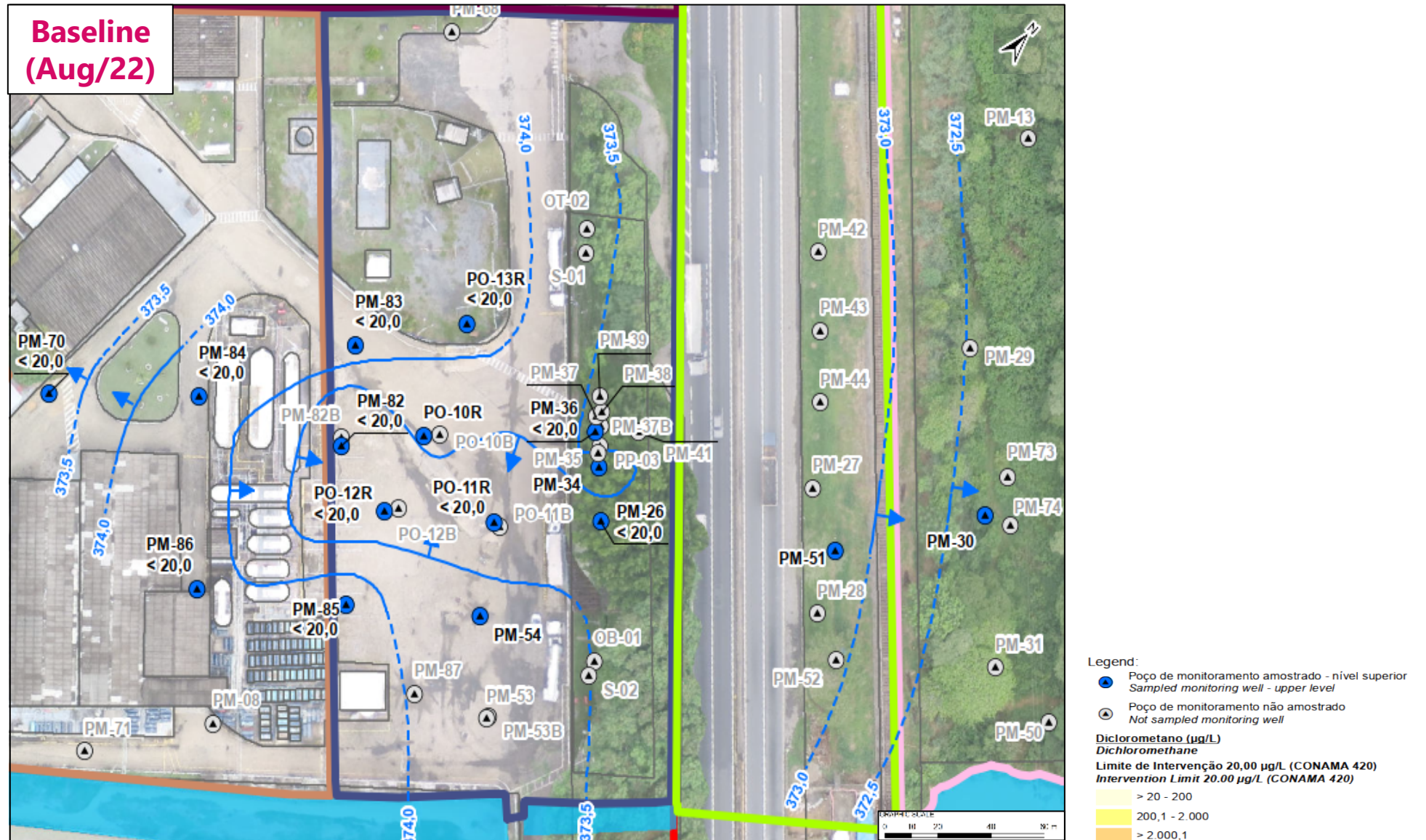


Chlorinated Methanes – Chloroform (CF)

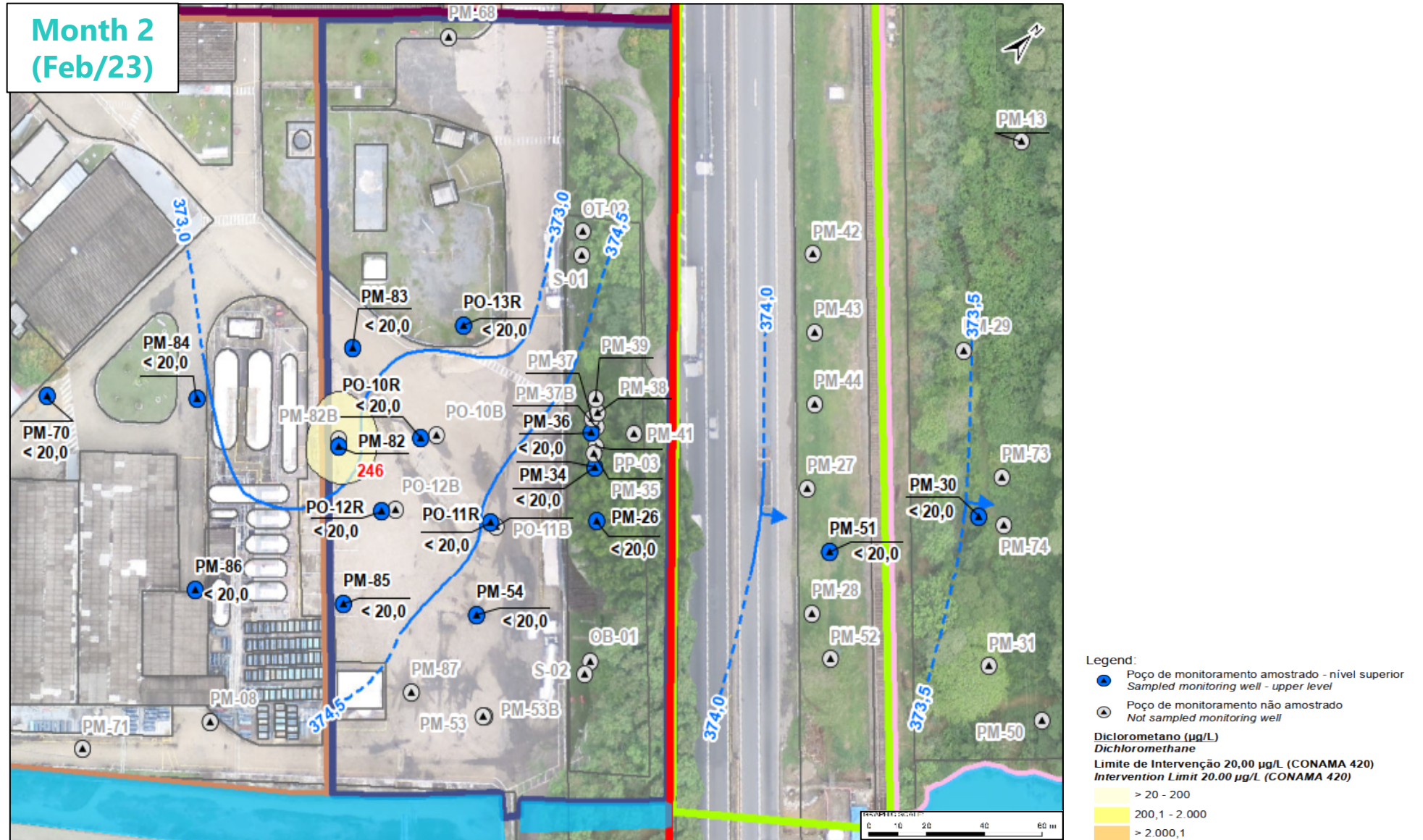
Upper Aquifer Level



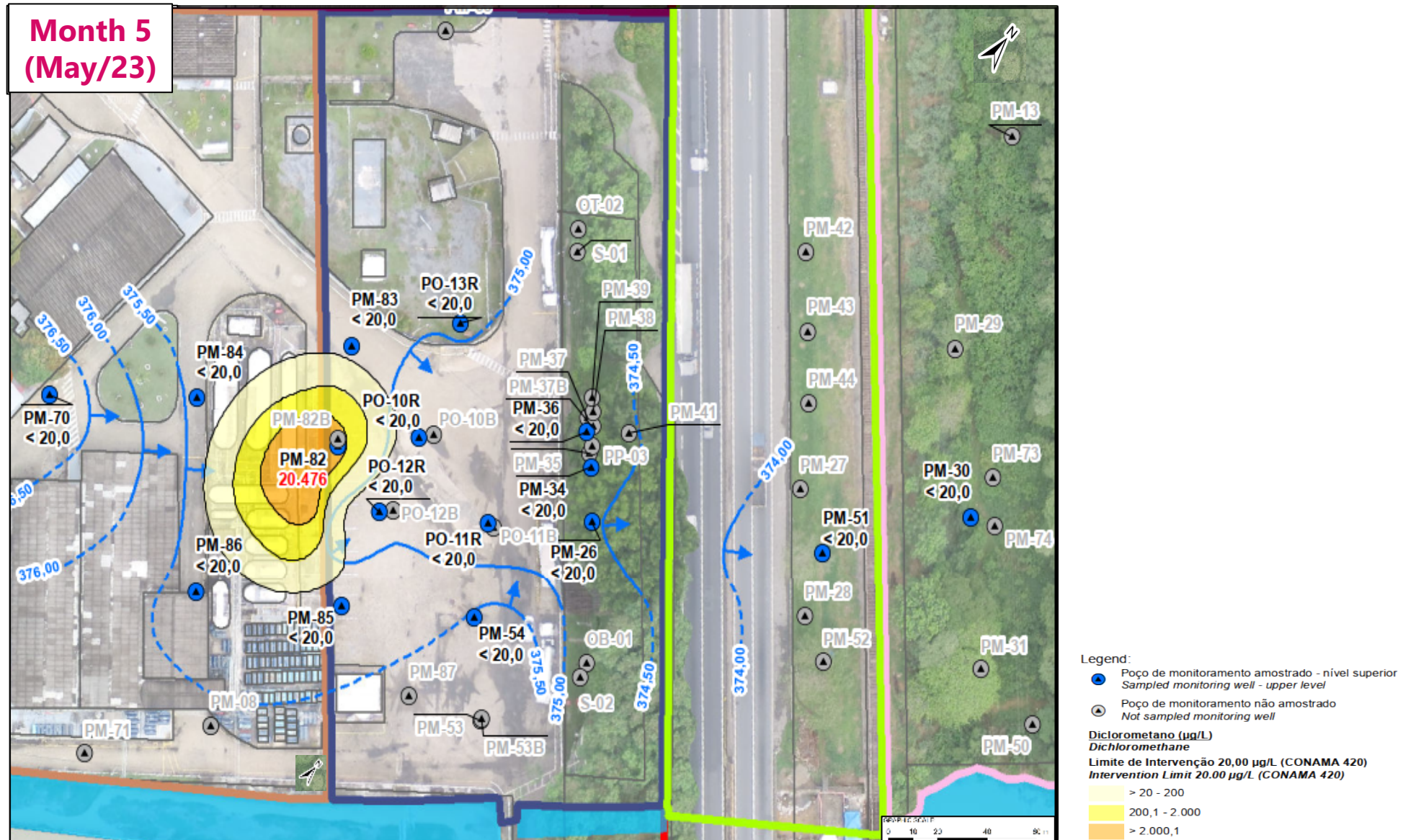
Chlorinated Methanes – Dichloromethane (DCM) – Upper Aquifer Level



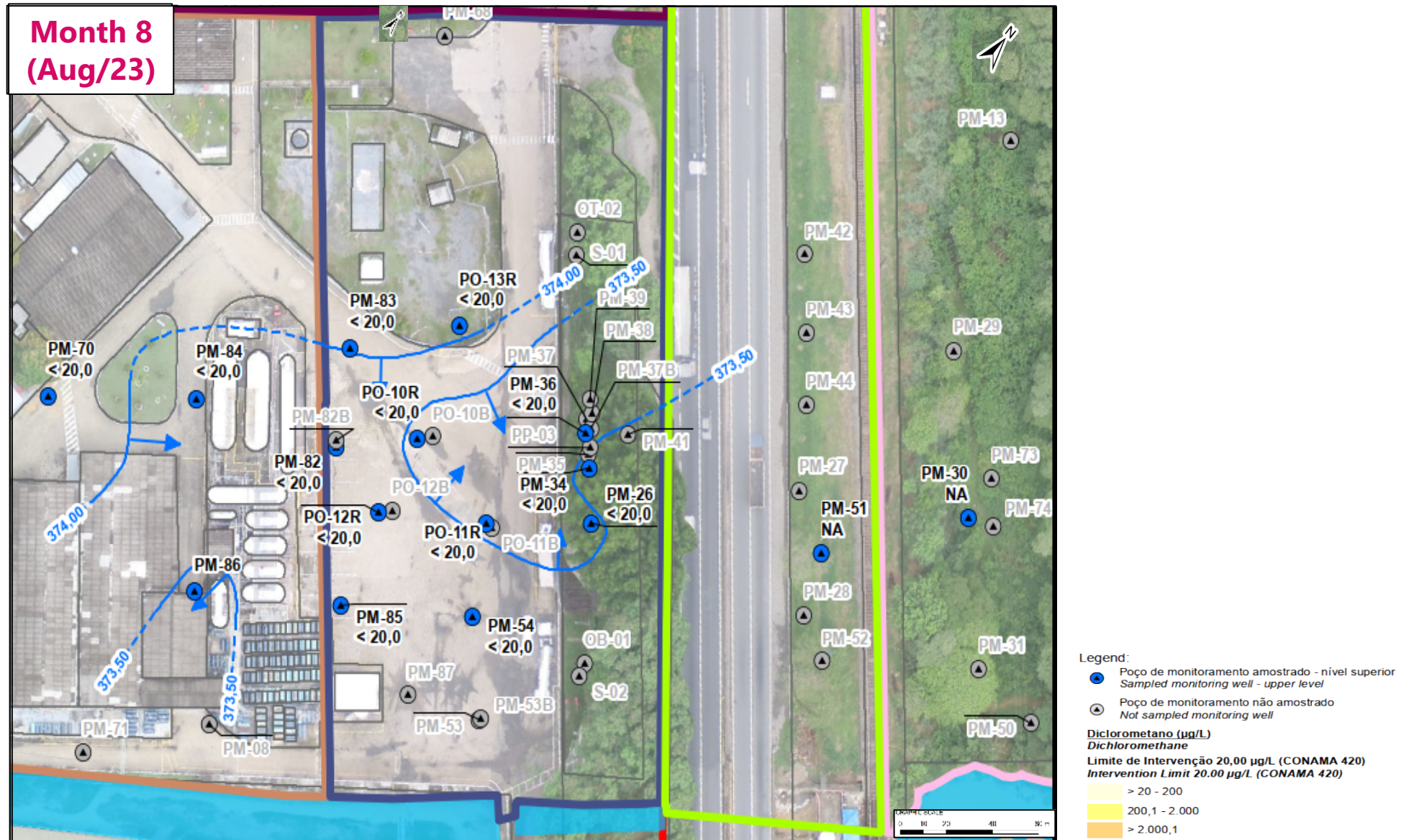
Chlorinated Methanes – Dichloromethane (DCM) – Upper Aquifer Level



Chlorinated Methanes – Dichloromethane (DCM) – Upper Aquifer Level



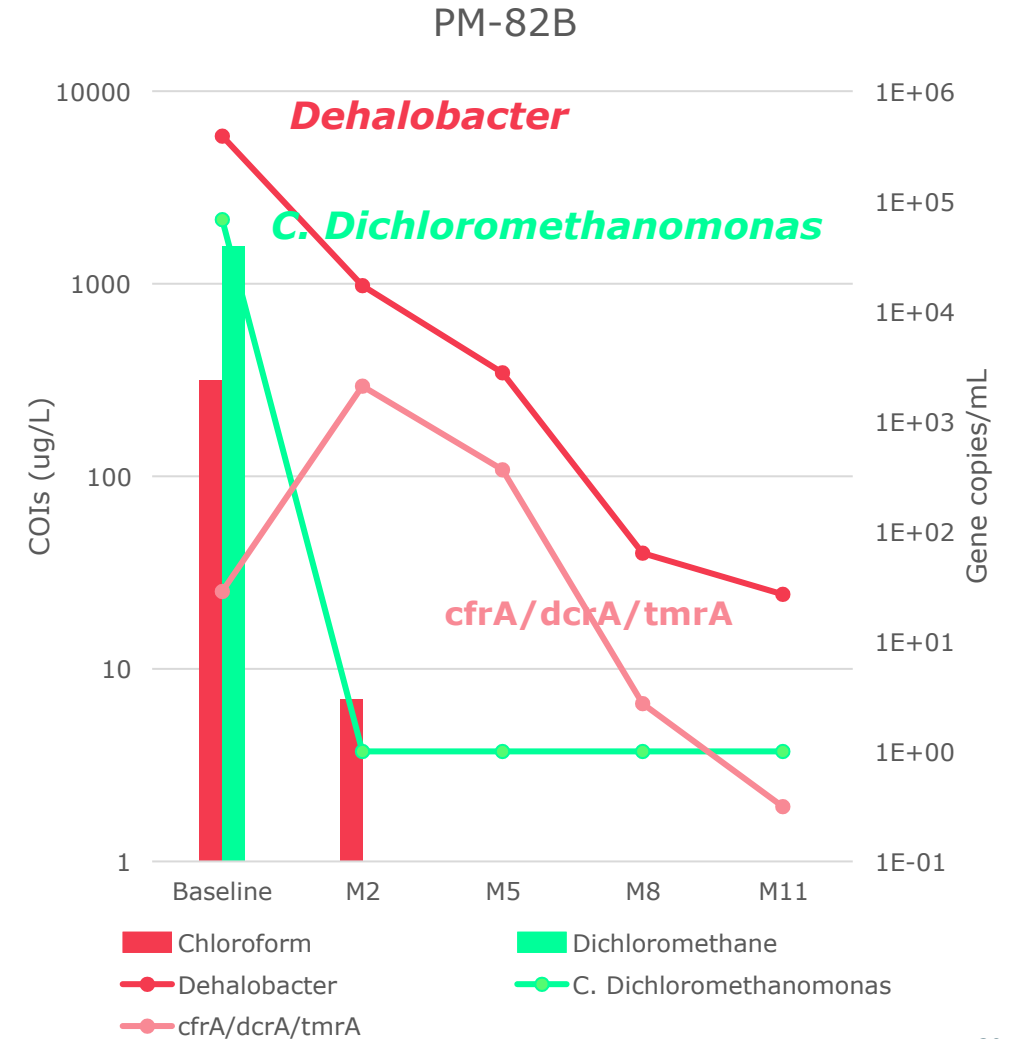
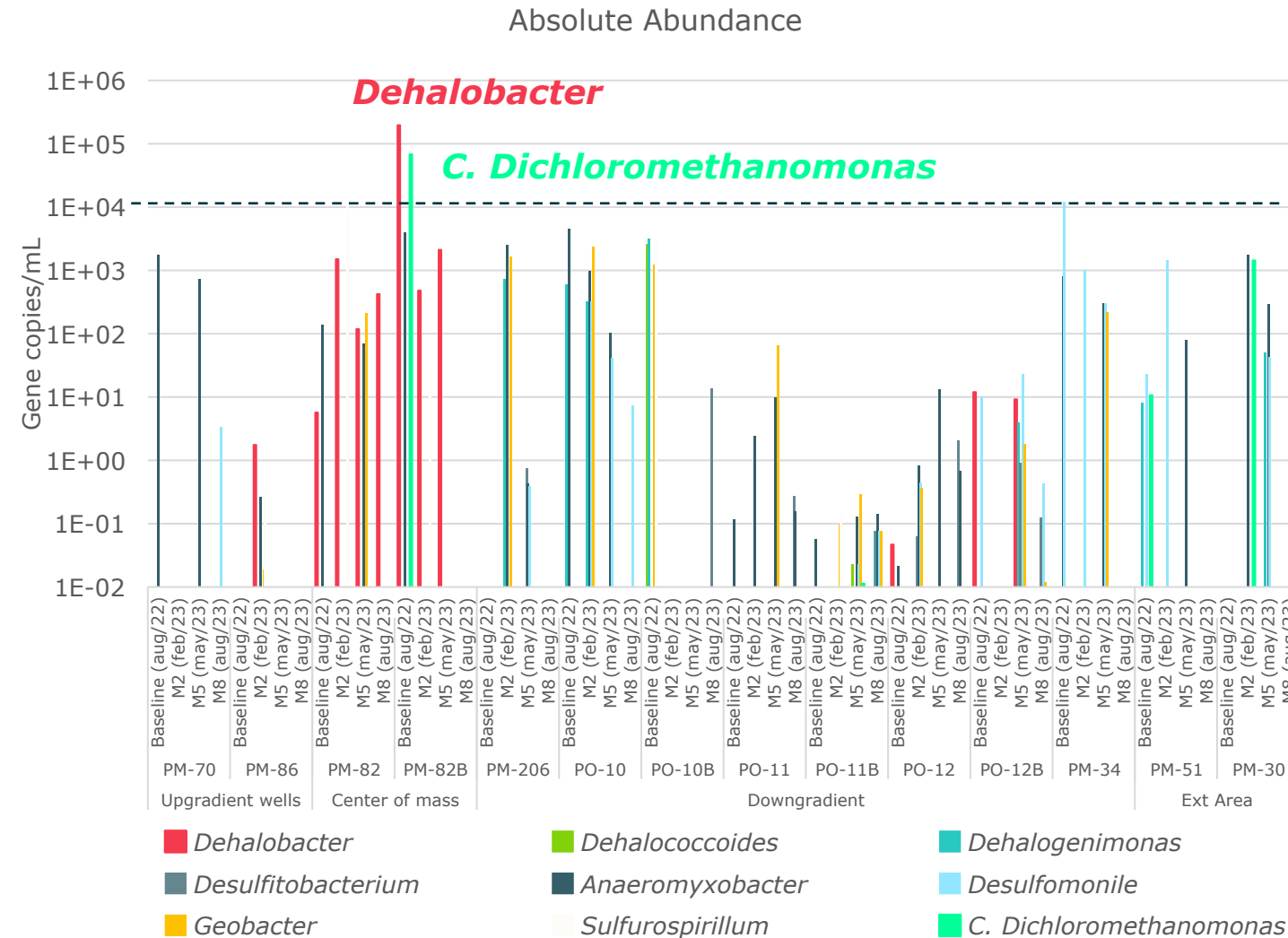
Chlorinated Methanes – Dichloromethane (DCM) – Upper Aquifer Level



Chlorinated Methanes – Dichloromethane (DCM) – Upper Aquifer Level



Presence of degraders | associated functional genes x COIs



Integration of Results

- Integration of Geochemical, Analytical and Microbial Sequencing data.
- Ordination method (NMDS – nonmetric multidimensional scaling) that indicates the similarity (or distance) between samples;
- Monitoring wells grouped per location;



Conclusions and Lessons Learned

- Carbon tetrachloride (CT) and chloroform (CF) were substantially reduced after 2 injection events;
- CT was likely reduced abiotically;
- Strong evidence for the biological degradation of CF/DCM (dichloromethane) was observed;
- ISCR injection promoted shifts in microbial communities towards anaerobic genera;
- CF and DCM degraders were present at the center of mass and their concentrations decreased over time as CF/DCM plumes were shrinking;
- *Dehalobacter* and *C. Dichloromethanomonas* were key players in chlorinated methanes degradation. Reductive dehalogenases from *Dehalobacter* that act on CF were abundant as well.





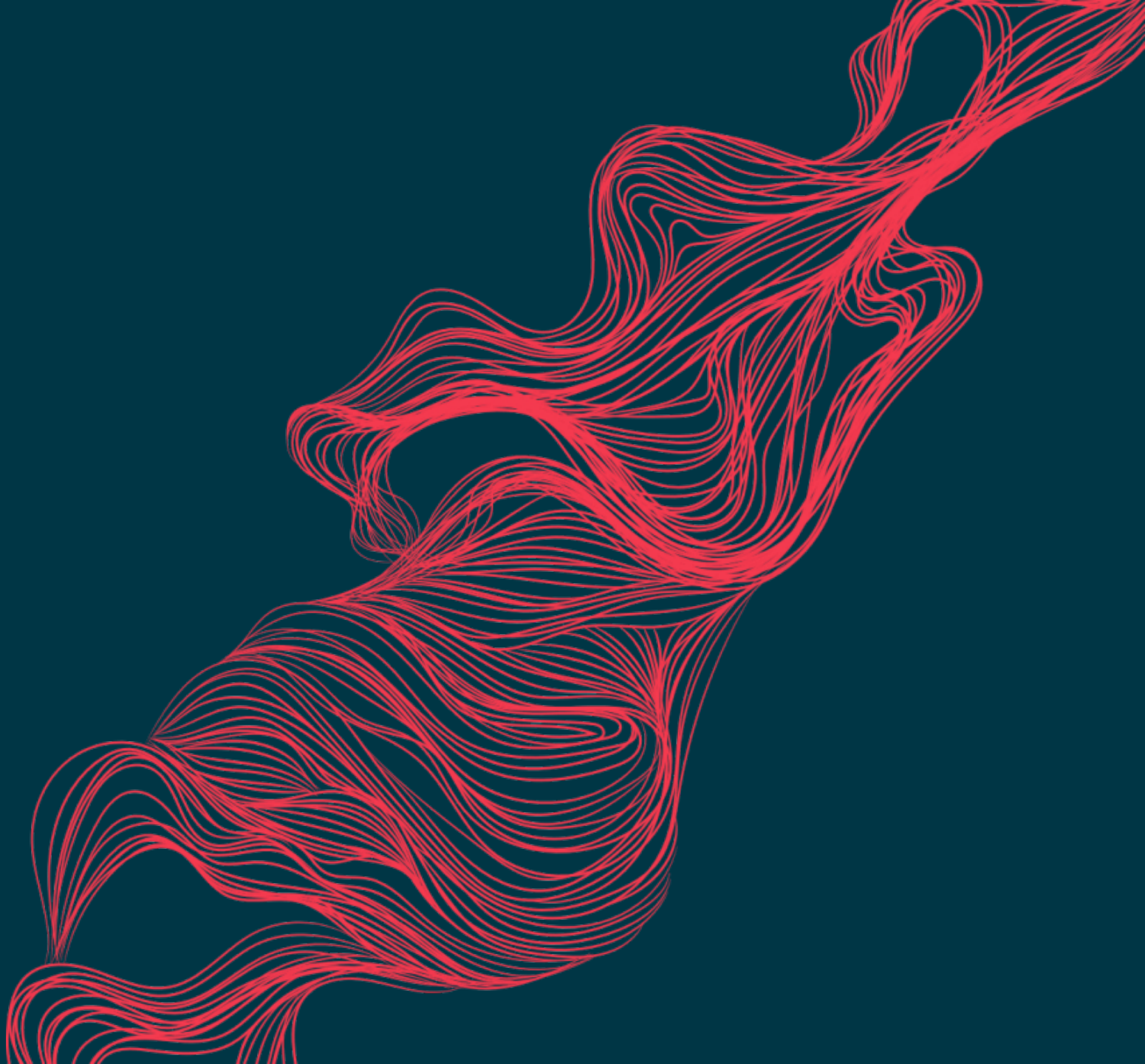
Contact Us:

Debora Ramos

+ [55] 41996334568

debora.ramos@worley.com

worley.com



Disclaimer

This presentation has been prepared by a representative of Worley.

The presentation contains the professional and personal opinions of the presenter, which are given in good faith. As such, opinions presented herein may not always necessarily reflect the position of Worley as a whole, its officers or executive.

Any forward-looking statements included in this presentation will involve subjective judgment and analysis and are subject to uncertainties, risks and contingencies—many of which are outside the control of, and may be unknown to, Worley.

Worley and all associated entities and representatives make no representation or warranty as to the accuracy, reliability or completeness of information in this document and do not take responsibility for updating any information or correcting any error or omission that may become apparent after this document has been issued.

To the extent permitted by law, Worley and its officers, employees, related bodies and agents disclaim all liability—direct, indirect or consequential (and whether or not arising out of the negligence, default or lack of care of Worley and/or any of its agents)—for any loss or damage suffered by a recipient or other persons arising out of, or in connection with, any use or reliance on this presentation or information.

