Application of Electrokinetic Remediation Combined with Pumping for Metal Remediation in a Low Hydraulic Conductivity Area (Pilot Test).

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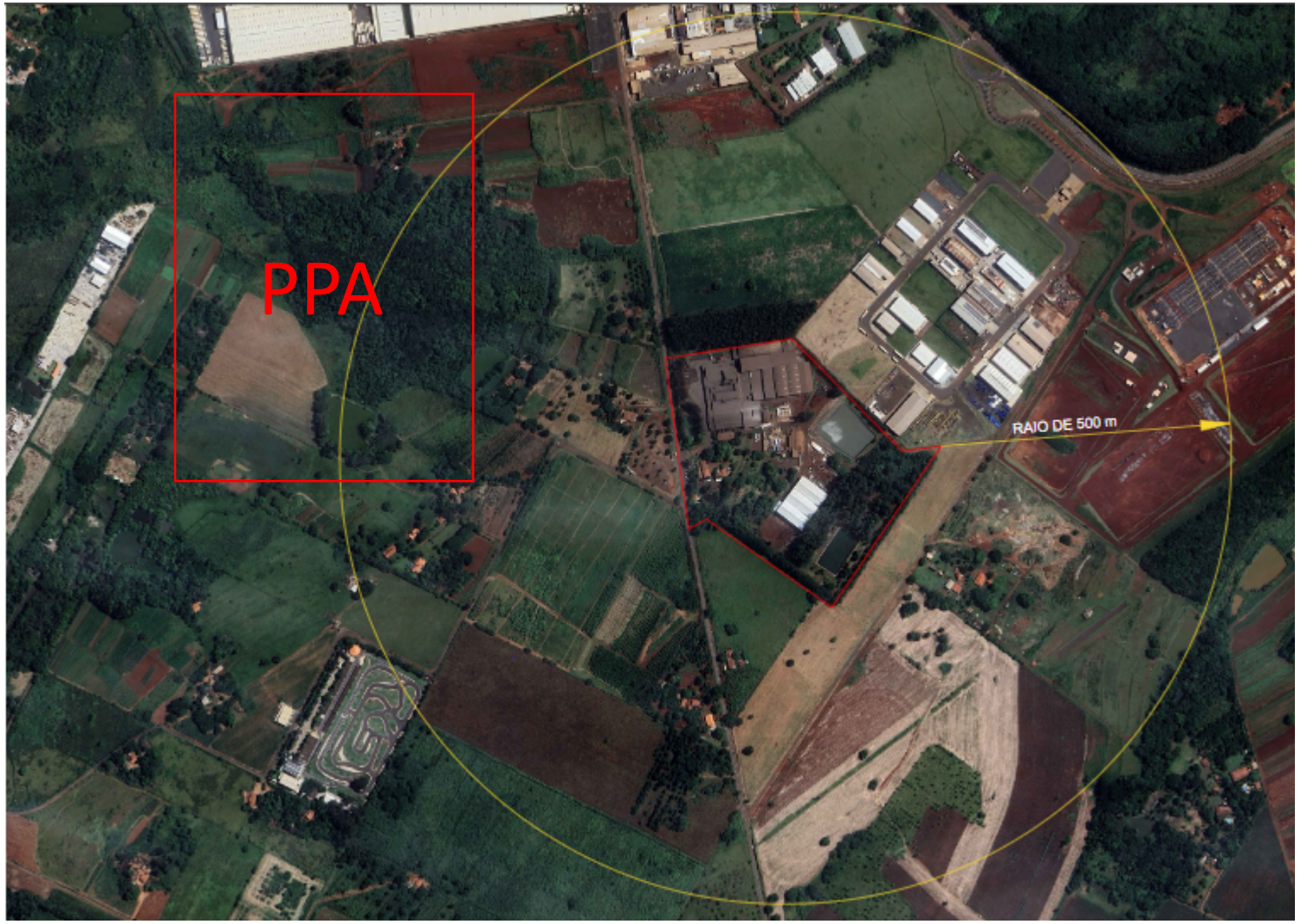
Background

Inorganic Fertilizer Industry

Surrounded by rural properties and an environmental protection area (PPA)

Countryside of São Paulo State



Background

Geology

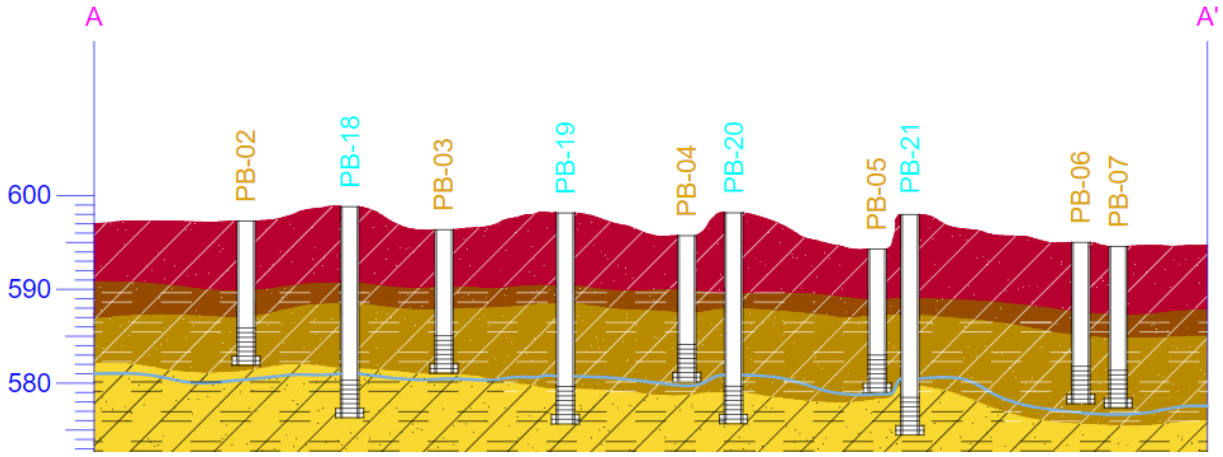
Basalt weathering soil

rocky top ~ 20 to 25 m bgs

Clayey-silty soils

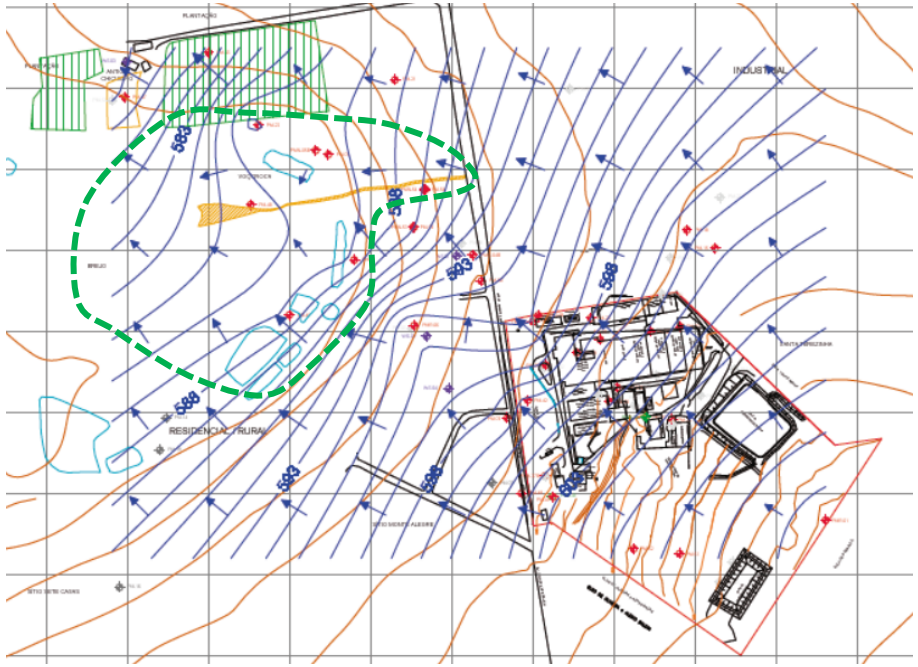
Hydraulic conductivity range: 10-5 to 10-6 cm/s

GW flows to the nearby river (about 250 m NO)



Substances used in the industry (main constituents of raw materials and products):

- Acids (sulfuric, nitric and boric)
- Salts (chlorides, carbonates, borates and sulfates)
- sodium hydroxide, phosphates, cyanide
- Iron, lead, zinc, cadmium, arsenic, chromium, silver , selenium, fluorides, molybdenum, barium, copper, manganese and nickel.



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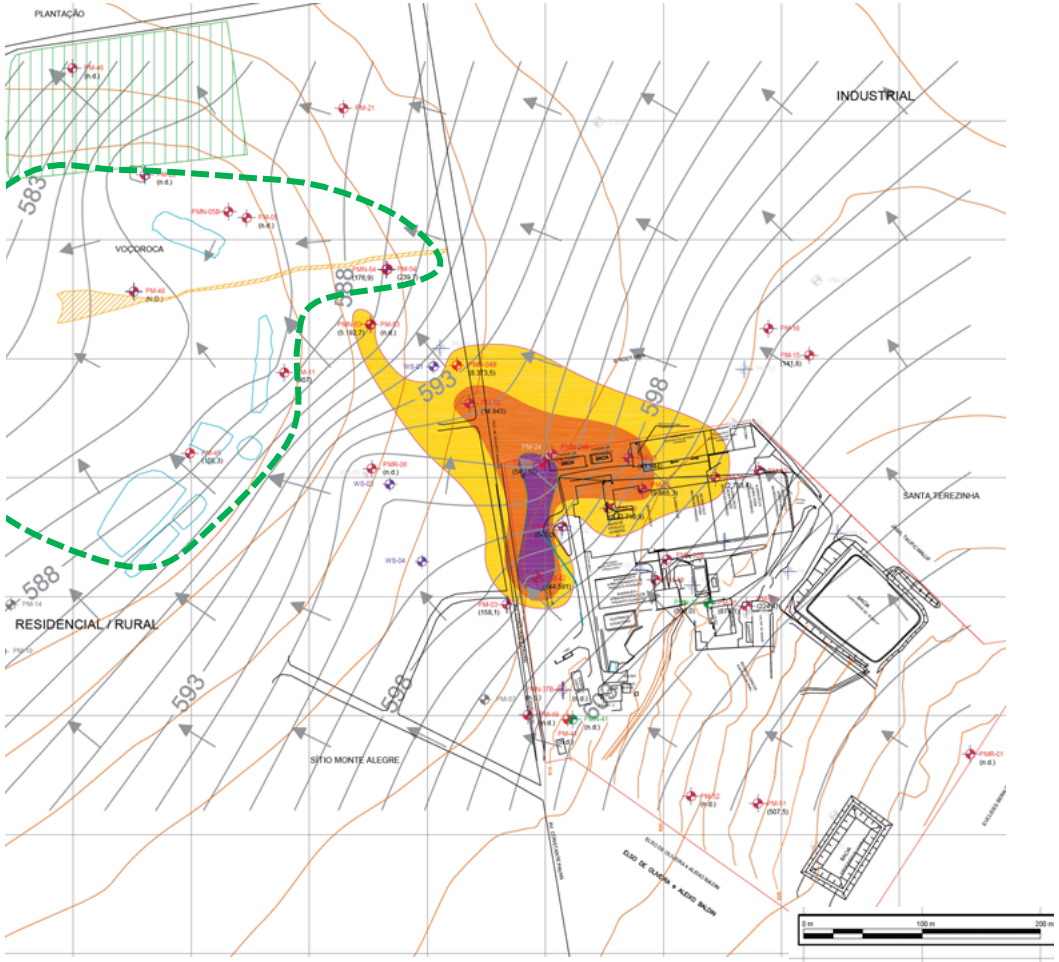


pH acid alteration
Boron, cobalt, aluminum

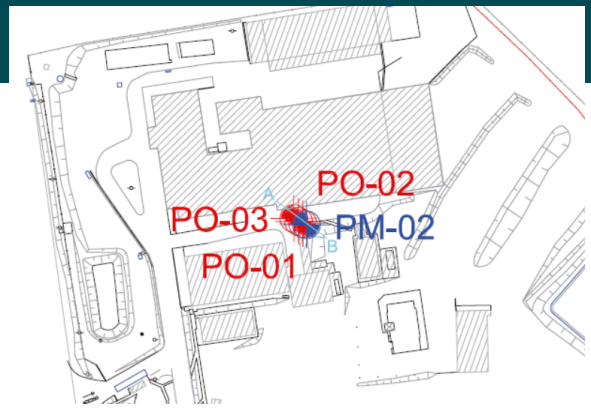
Background

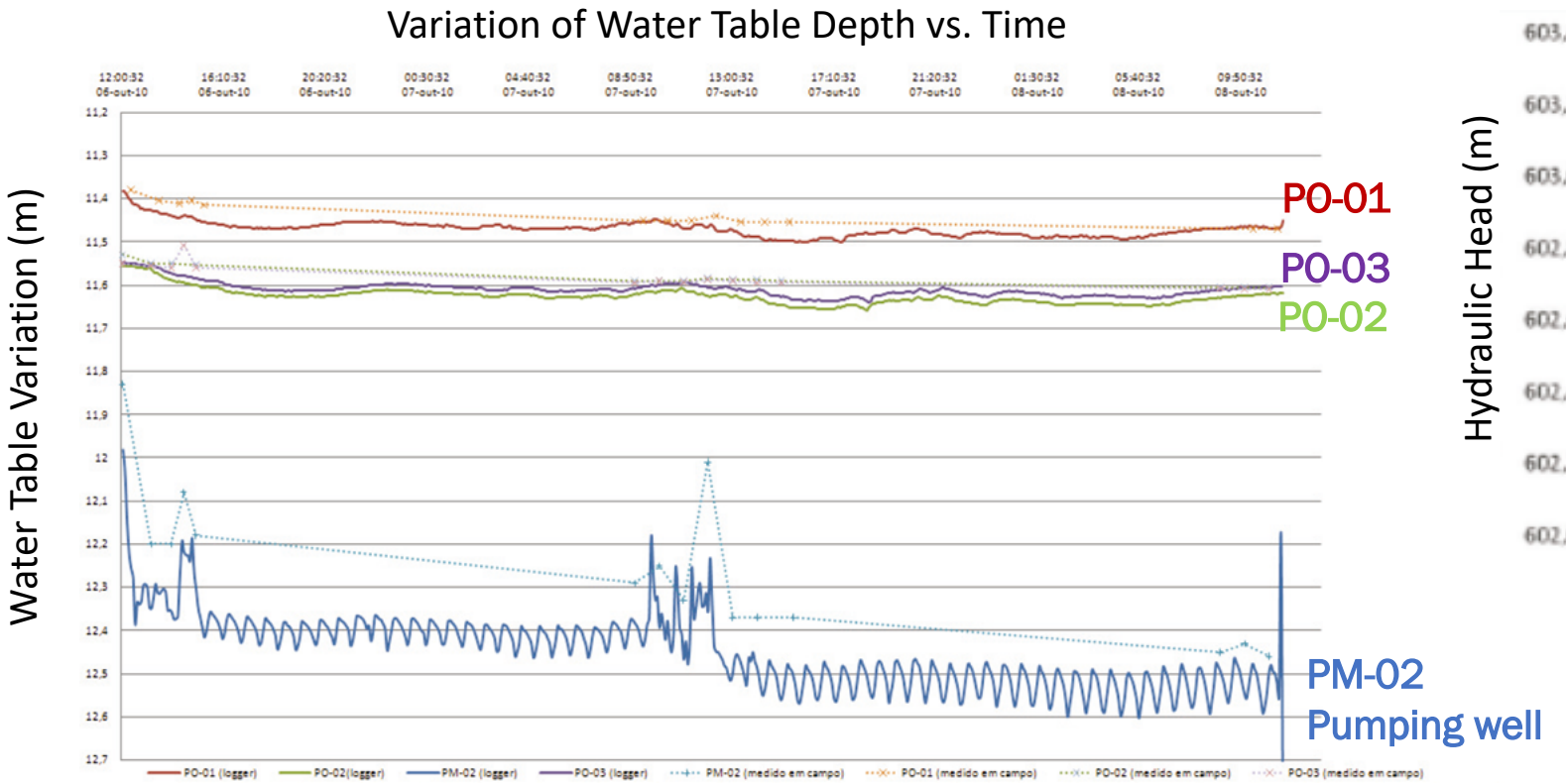
2011: pilot test for pump and treat – 48h test

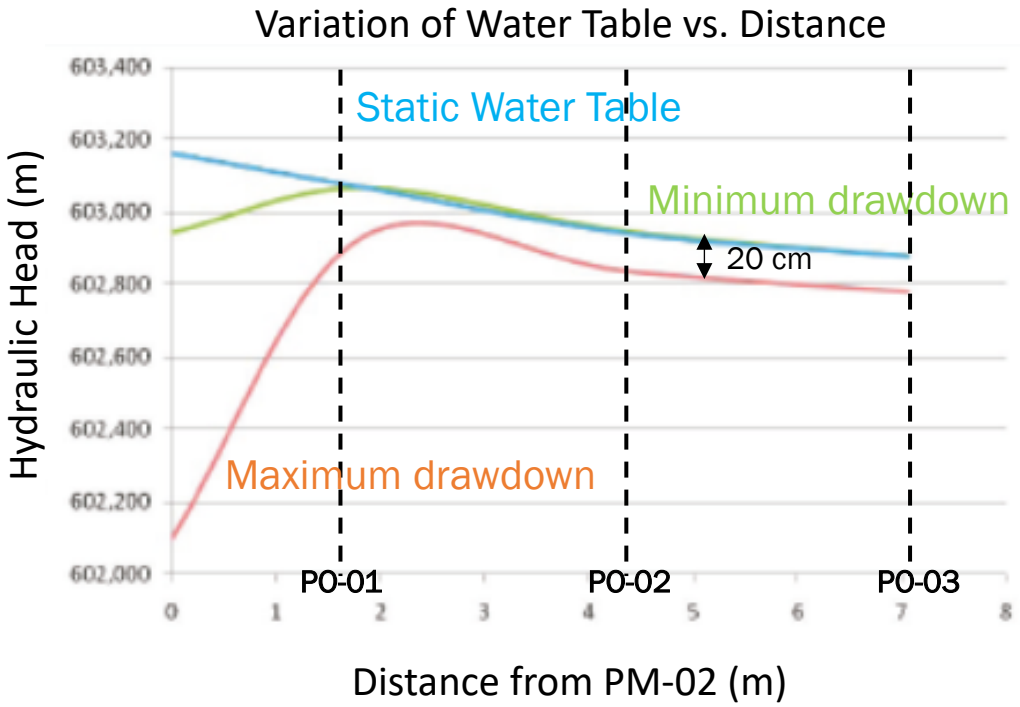
Bomb pressure ranged from 20 to 50 PSI

Flow rate ranged between 84 and 114 l/h (average of 85.67 l/h)

4,055 liters of water pumped.



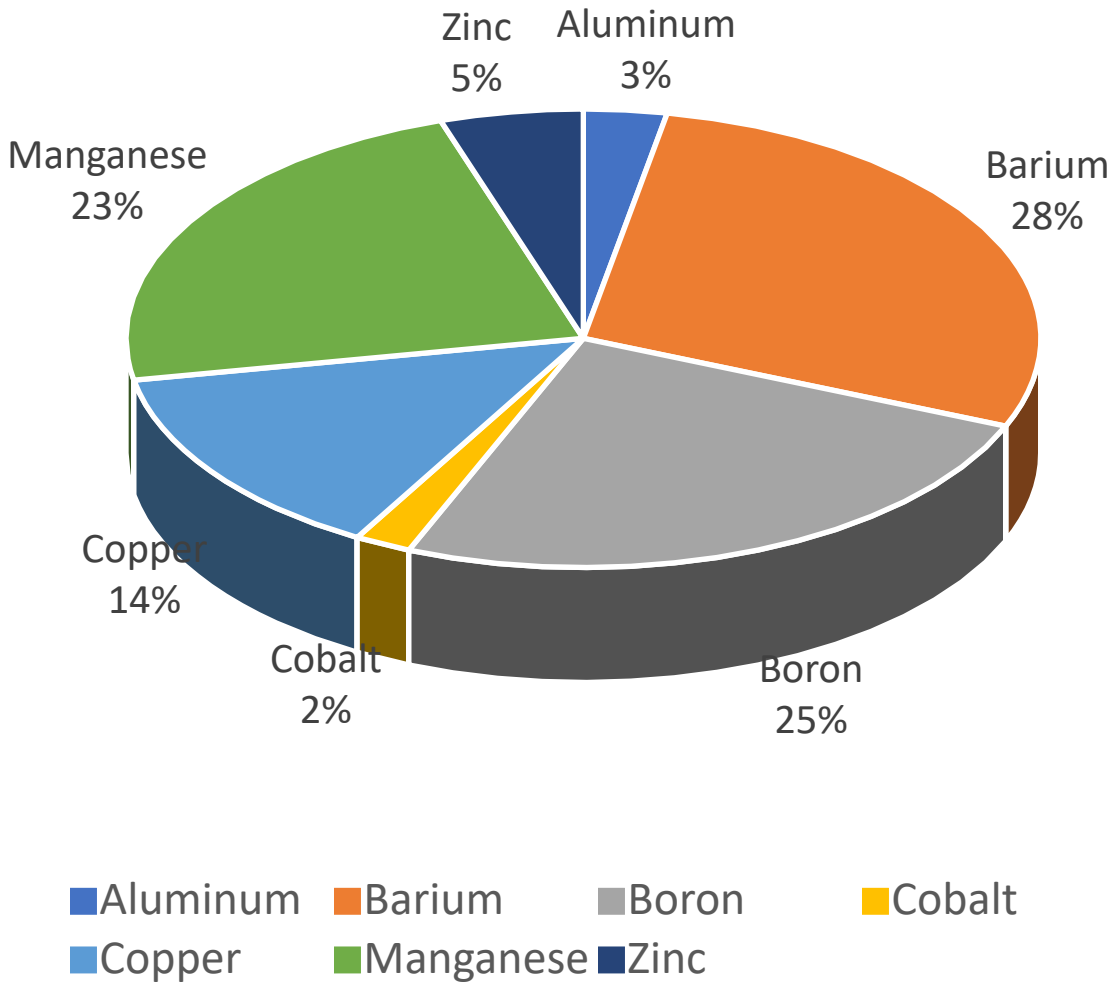




Background

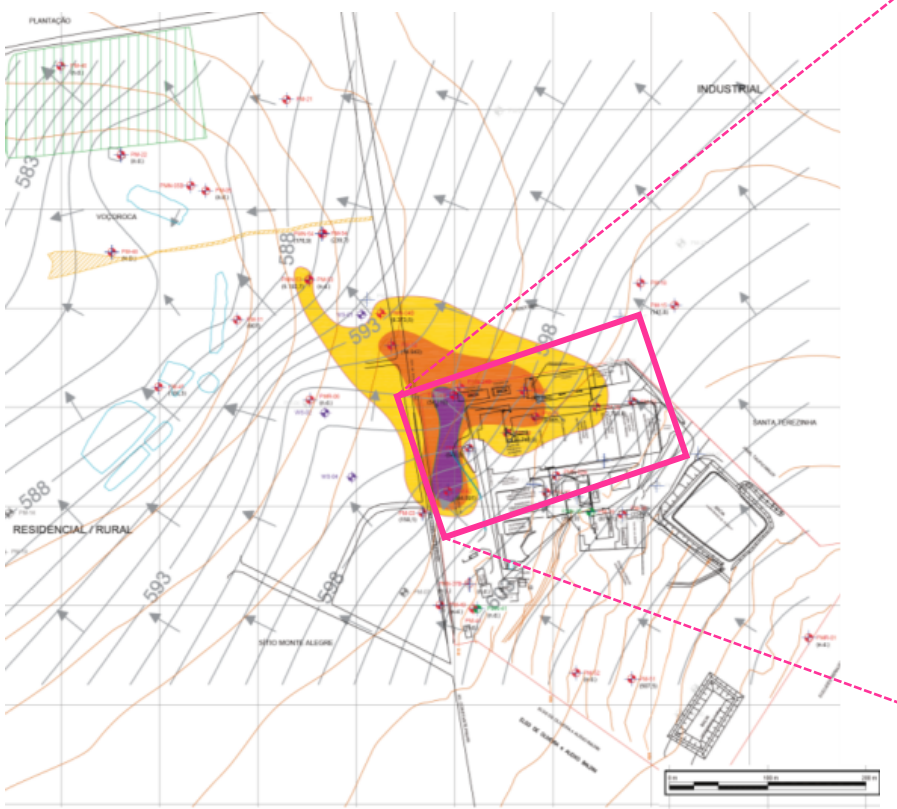
2011: pilot test for pump and treat – 48h test

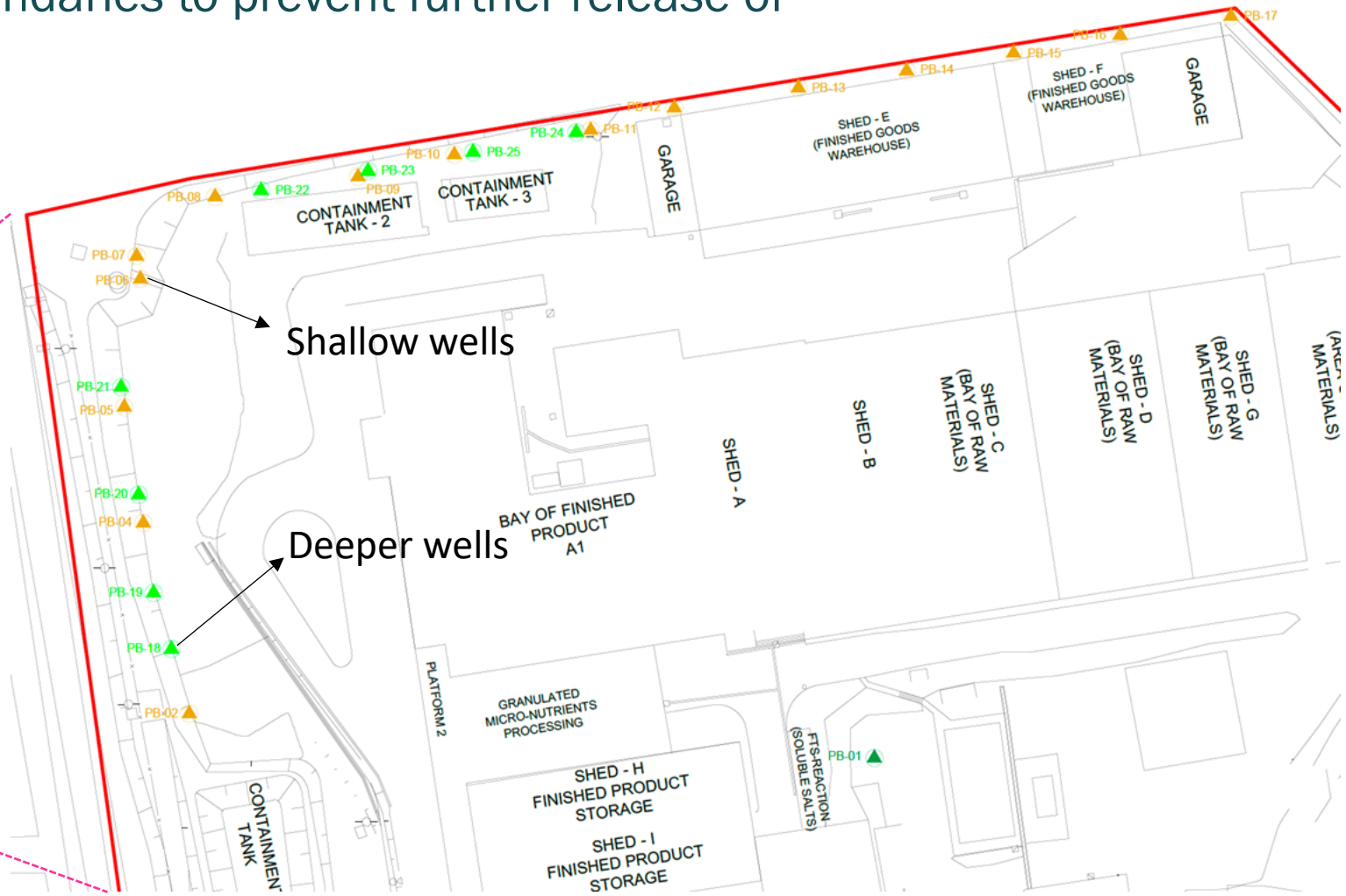
Dissolved metal	Removed mass (mg)
Aluminum	470.35
Barium	4,541.33
Boron	4,002.05
Cobalt	320.33
Copper	2,217.95
Manganese	3,665.50
Zinc	810.95
TOTAL	**16.02 g**



Background

Results supported the position and distance of pumping wells to install a hydraulic barrier at the area's boundaries to prevent further release of contaminants.





Background

Hydraulic barrier has no results to treat the main mass contaminant centers.

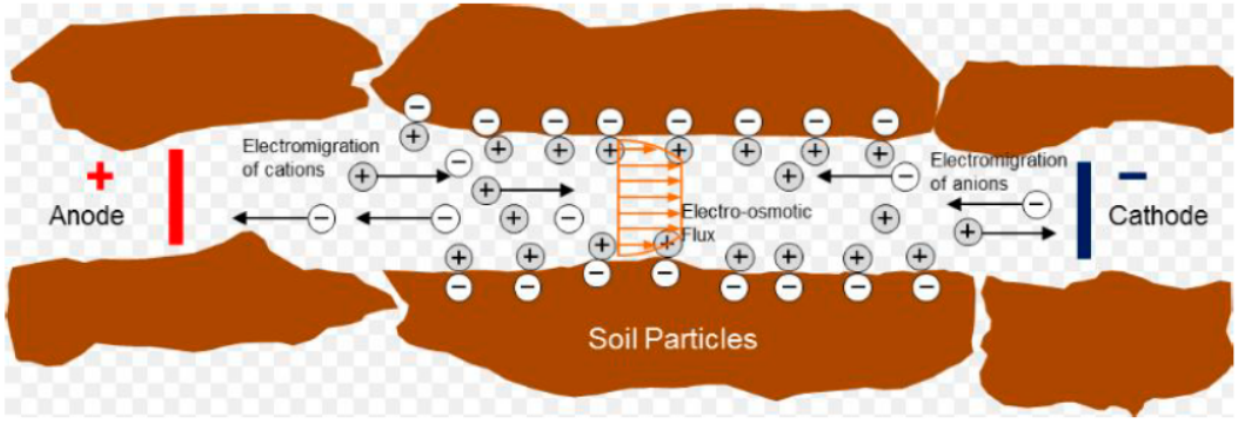
2023

Company decided to conduct a pilot test to evaluate the application of **combined electrokinetic remediation and pumping techniques.**

Electrokinetics

Technique that has been more extensively studied since the 2000s.

It involves applying an electric potential in a porous medium (saturated or not) to facilitate the physico-chemical transport of ions or charged particles towards the electrode regions (Acar et al., 1995; Ramalho, 2008).



Cameselle, 2013.

Applications:

- Alone with extraction;
- Combined with amendments (control).

Limited studies conducted on tropical clay soils.

Applicability depends on:

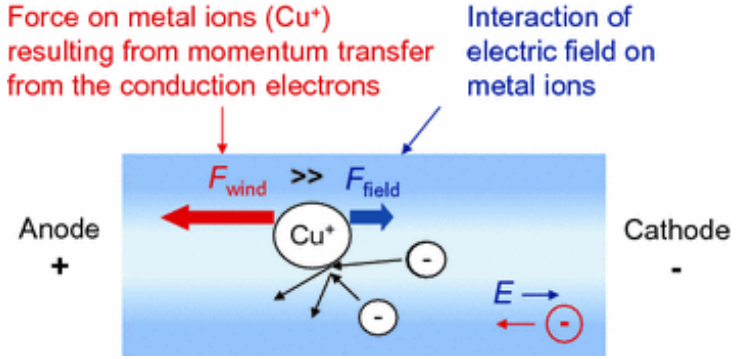
- Presence of moisture;
- Sufficient ions → enable the conduction of electrical energy, thereby reducing the soil's electrical resistance.

Clay soils may offer greater potential for the application of the technique, as they commonly contain more exchangeable ions.

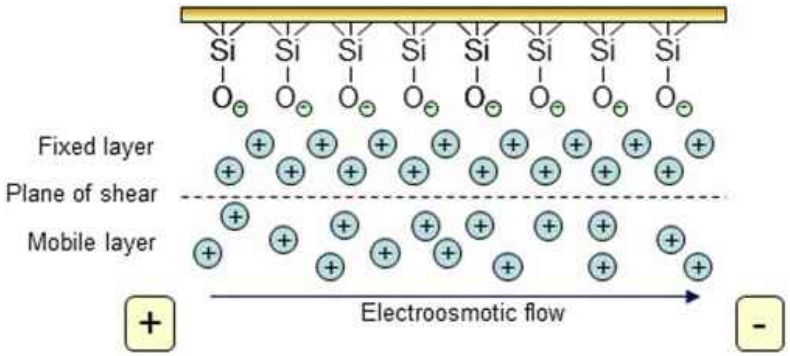
Electrokinetics

Transport and migration occur through three main processes:

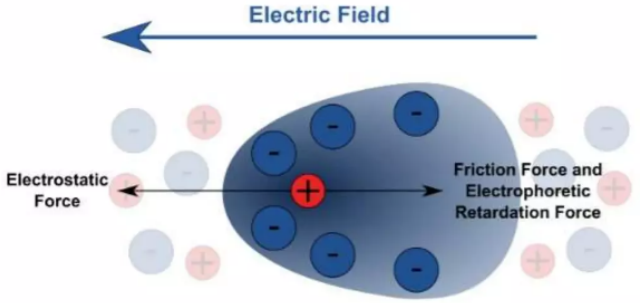
- Electromigration: This is the primary mechanism for the migration of ionic contaminants, driven by the attraction exerted by an electrode of opposite charge. The migration speed and mobility are specific to each element or ion, along with the availability and concentration of the element.



- Electroosmosis: This is the movement of pore water towards the cathode when the soil surface charge is negative and has adsorbed cations, driven by the potential difference (PD). During this movement, which also includes the migration of H^+ ions, water and any dissolved, uncharged solutes migrate as well.



- Electrophoresis: This is the transport of electrically charged particles under the influence of an electric field. For a particle to move in the electric field, it must carry a charge, meaning it has an excess or deficiency of electrons, resulting in a free electrostatic charge.

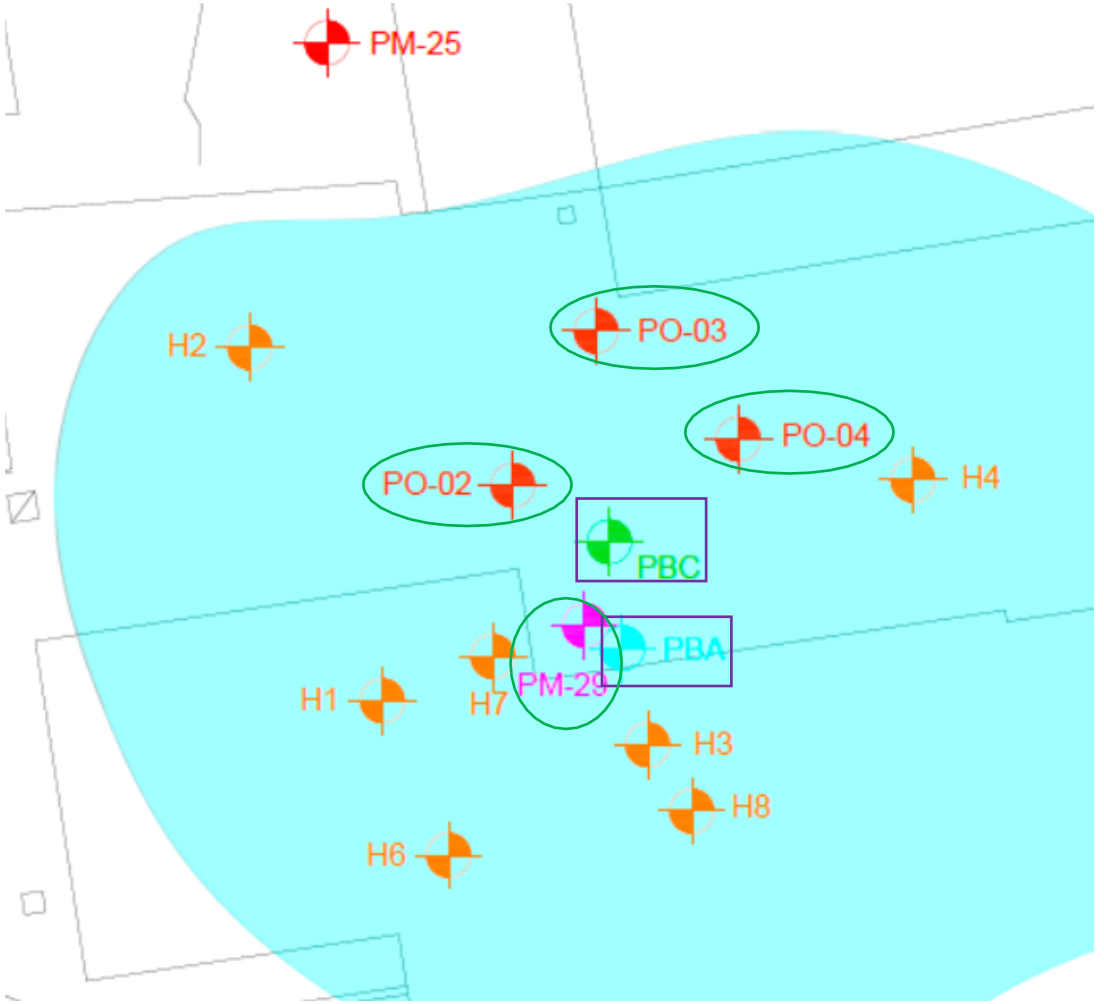


Pilot Test Premises

Wells for electrode insertion and pumping (cathode and anode)

Observation well

H1 to H8 Wells for rod insertion (electric current evaluation)



Objectives:

- Pumping test to determine the radius of influence;
- Pumping test associated with electrokinetics applying low voltage (30V);
- Pumping test associated with electrokinetics applying high voltage (220V)

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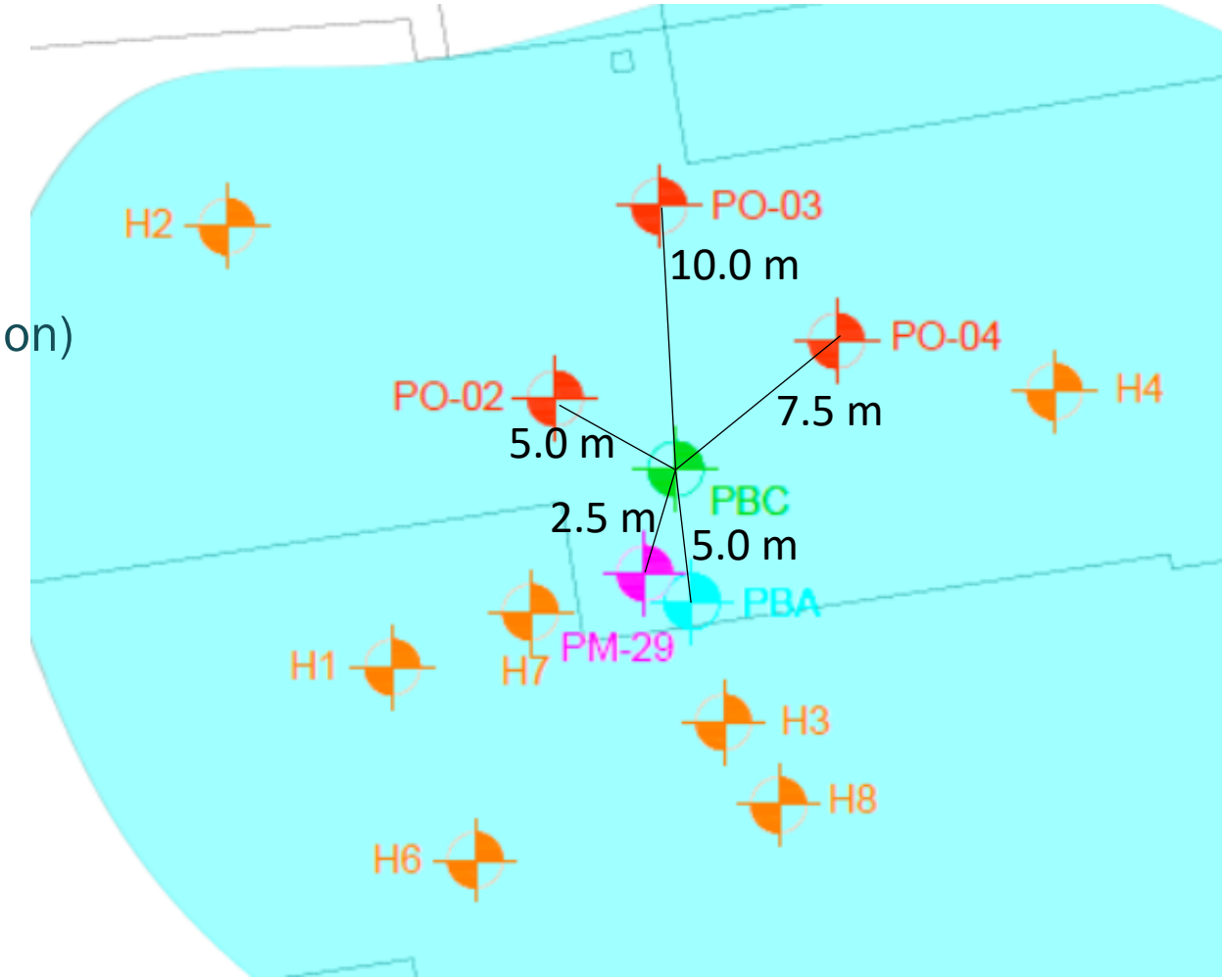

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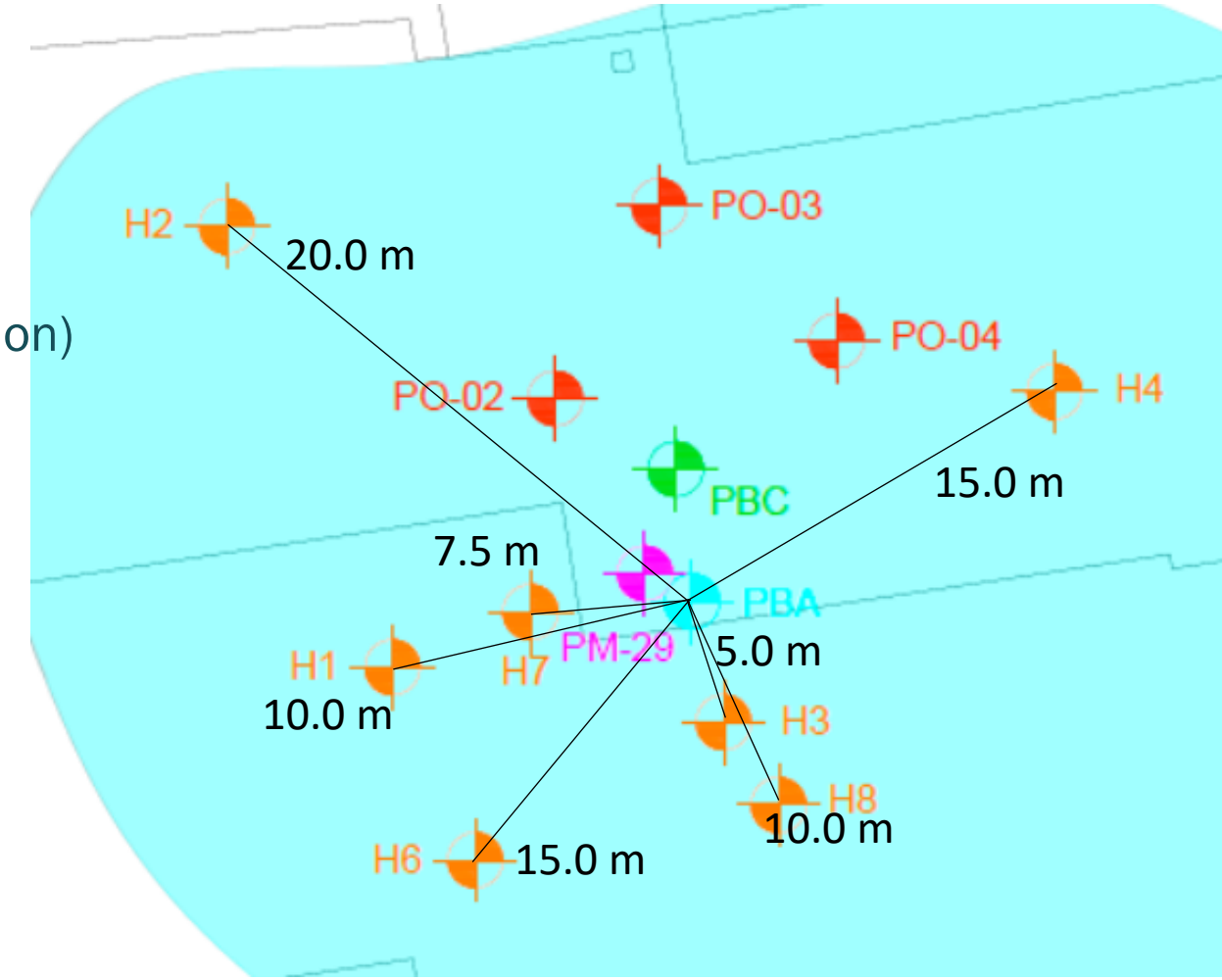

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Pumping Test Development and Results

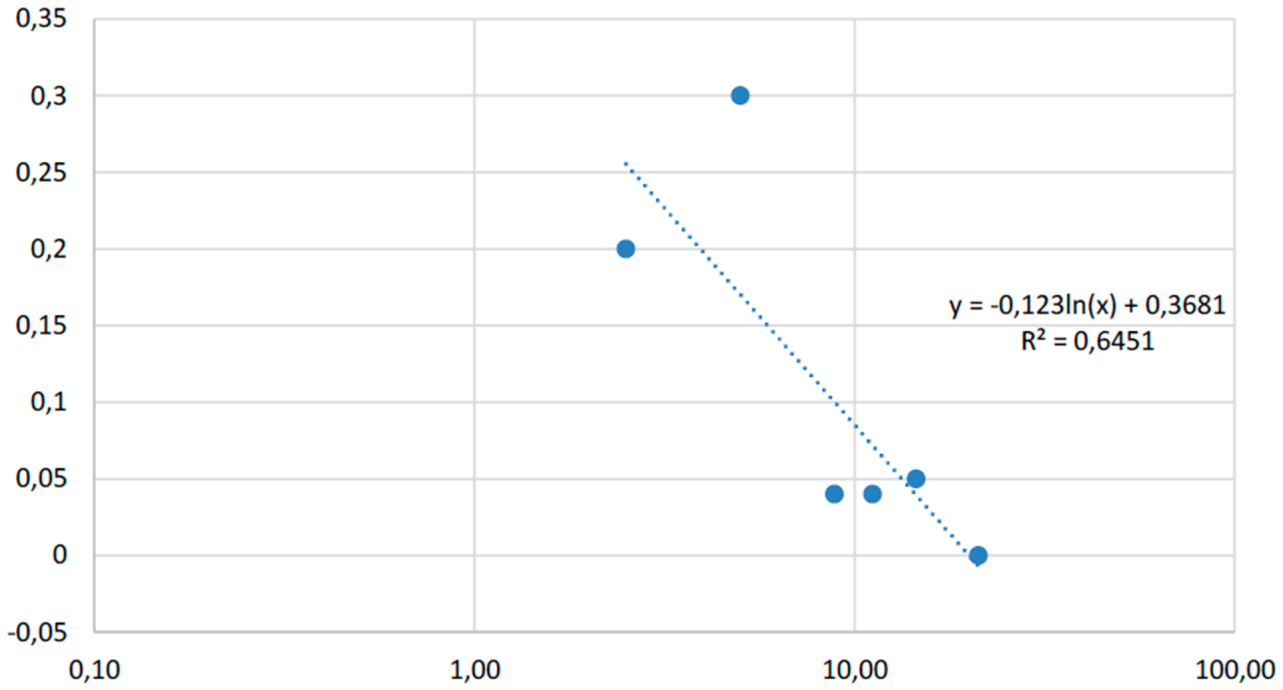
Pumping test (PBA)

- 8.5h test
- 570 L pumped
- Average flow rate: 67 L/h

Well	Distance to PBA (m)	Average Drawdown (m)
PBC	5.0	0.3
PM-29	2.5	0.2
H-8	10.0	0.07
PO-03	15.0	0.05
PO-04	11.5	0.04
PO-02	9.0	0.04
H-2	20.0	0.0

Radius of influence (ROI) calculated considering the intersection point where the drawdown would be equal to 0.10m + 15% safety factor.

ROI = 7.5 m



Pilot Test Development and Results

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Electrokinetics + Pumping Test

Test Data:

- 17 days of operation with 30 V
- 23 days of operation with 220 V
- Average flow rate of 67 L/h per pumping well (PBA and PBC)

Effluent Sampling:

- Operation with 30 V: T2, T8 and T17
- Operation with 220 V: T3, T14, and T23

GW sampling of Observation Wells:

- Baseline and final.

Data	Stage 1 (30 V)	Stage 2 (220 V)
Test Execution Date	05/08 to 05/24/23 (17 days)	05/24 to 06/15/23 (23 days)
Hour Meter (electrokinetics / regeneration)	325.8 h / 16.74 h	269.8 h / 10.5 h
Test Duration (by Hour Meter)	~14.5 days	~11.5 days
Current (average)	6.8 mA	37.4 mA
Medium resistance (Ω)	4.411.7	5.882.3
Resistivity (Ω/m)	$1.73x10^4$	$2.31x10^4$
Total Pumped Volume	11.417 L	13.377 L
Pumped Volume – Cathode	5.765 L	8.967 L
Pumped Volume – Anode	5.652 L	2.410 L
Cathode Flow Rate	397.58 L/d	779.7 L/d
Anode Flow Rate	389.79 L/d	209.6 L/d
Observation	-	Issues with the pump (system remained in regeneration mode)

Electrical Results

Increase did not follow the same proportion as the voltage → high resistance

High resistivity. exceeding by 2 OoM the expected range for clayey soils → 10 to 10^2 Ω/m (Orellana. 1972).

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Electrical Results

AmbScience ENGENHARIA

Evaluation of Electric Current in Wells Installed in the Test Region													
Points	Distance to PC (m)	05/24/2023				05/24/2023				06/15/2023			
		Voltage (V)	Current (mA)	Resistance (Ω)	Resistance per m (Ω/m)	**Voltage** (V)	Current (mA)	Resistance (Ω)	Resistance per m (Ω/m)	**Voltage** (V)	Current (mA)	Resistance (Ω)	Resistance per m (Ω/m)
PA-PC graphite	5	31.2	6.7	4656.7	931.3	201	38.1	5275.6	1055.1	202	38.9	5192.8	1038.6
PA-PC bar	5	31.2	10.55	2957.3	591.5	201	38	5289.5	1057.9	202	38.4	5260.4	1052.1
PO-02	5	31.2	11.15	2798.2	559.6	198	36.4	5439.6	1087.9	202	36.1	5595.6	1119.1
PO-04	7.5	31.2	10.38	3005.8	601.2	199	36.4	5467	1093.4	202	36.1	5595.6	1119.1
H4	15	31.2	10.25	3043.9	608.8	199	36.4	5467	1093.4	202	36.3	5564.7	1112.9
PO-03	10	31.2	11.3	2761.1	552.2	199	36.7	5422.3	1084.5	202	36.6	5519.1	1103.8
H2	20	31.2	11.6	2689.7	537.9	199	37.2	5349.5	1069.9	202	35.7	5658.3	1131.7
H1	10	31.2	11.42	2732	546.4	198	37	5351.4	1070.3	-	-	-	-
H7	7.5	31.2	11.86	2630.7	526.1	191	38.3	4986.9	997.4	202	37.3	5415.5	1083.1
H8	5	31.2	11.55	2701.3	540.3	196	36.8	5326.1	1065.2	202	37.1	5444.7	1088.9
H3	10	31.2	9.93	3142	628.4	200	36.4	5494.5	1098.9	202	37.1	5444.7	1088.9
H6	15	31.2	10.5	2971.4	594.3	200	36.5	5479.5	1095.9	202	37.1	5444.7	1088.9
Average	-	-	-	-	**601.5**	-	-	-	**1072.5**	-	-	-	**1093.4**

Increasing the voltage did not reduce the resistance

Most of the wells show similar values of resistance and resistance per meter. indicating low heterogeneity of soil

Lowest resistances obtained in wells located along the southeast-northwest axis → direction of groundwater flow and highest concentrations of metals.

Points	Distance to PC (m)	05/								Test			
		Voltage (V)	Current (mA)	Resistance (Ω)	Resistance per m (Ω/m)	Voltage (V)	Current (mA)	Resistance (Ω)	Resistance per m (Ω/m)	**Voltage** (V)	Current (mA)	Resistance (Ω)	Resistance per m (Ω/m)
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Monitored parameters during the pilot test

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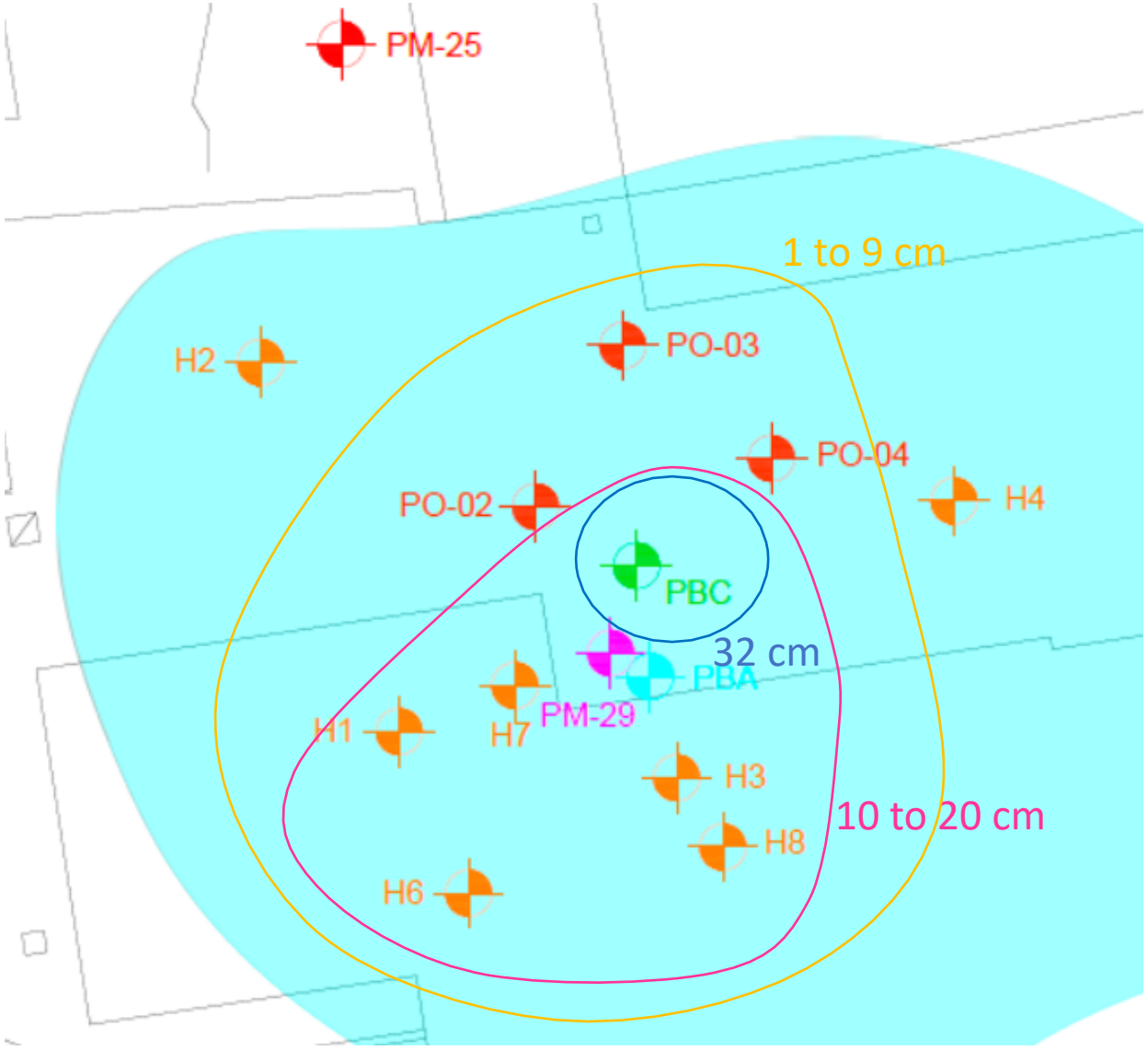
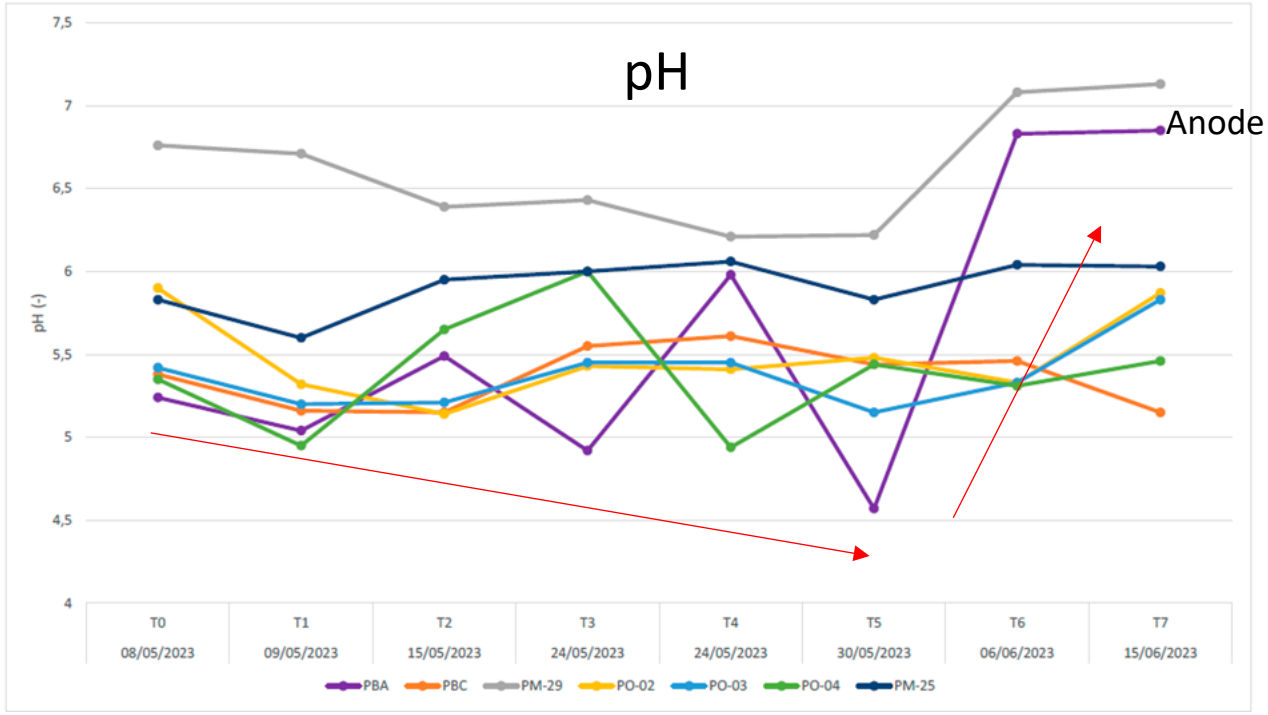
GW Level

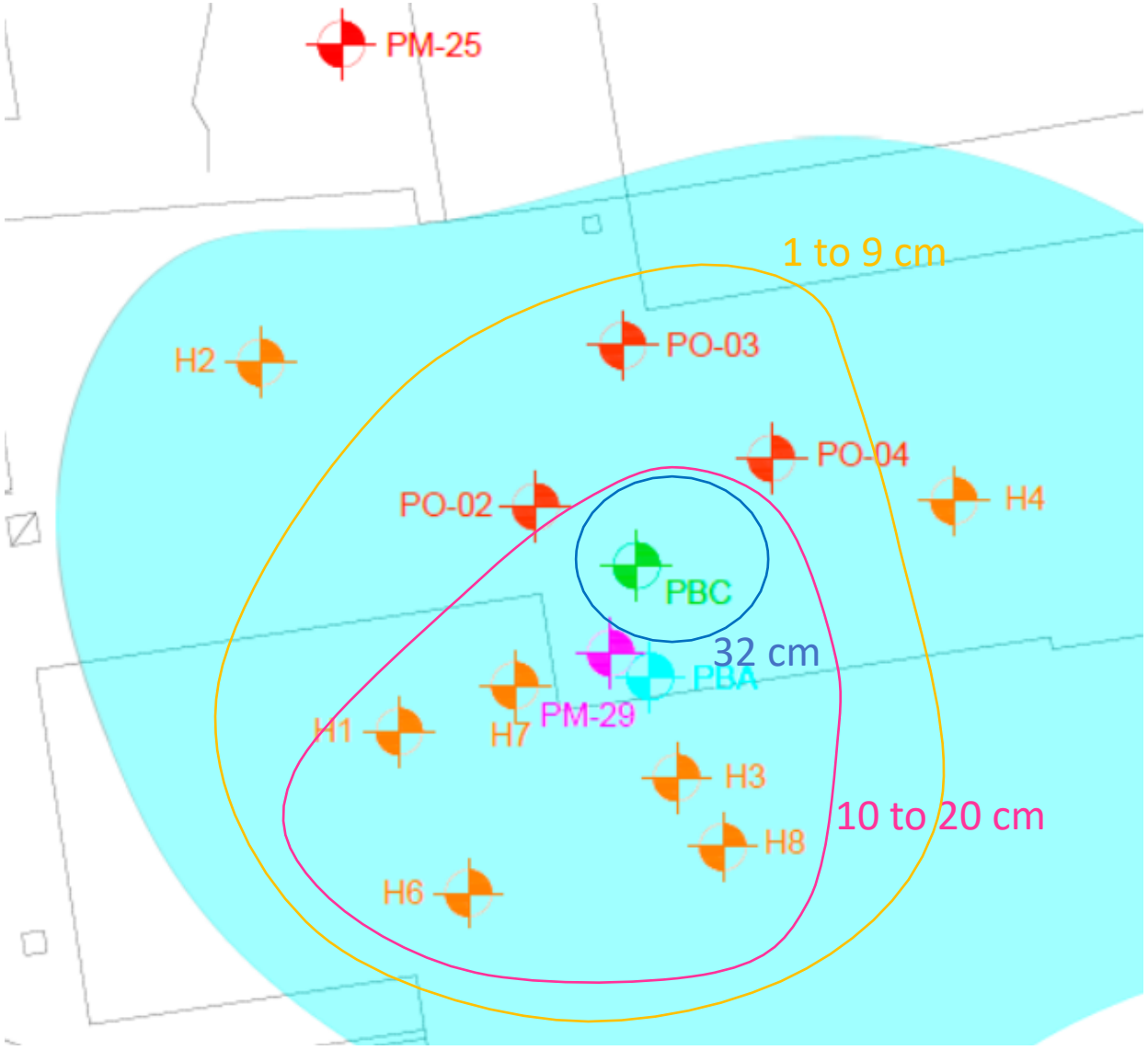


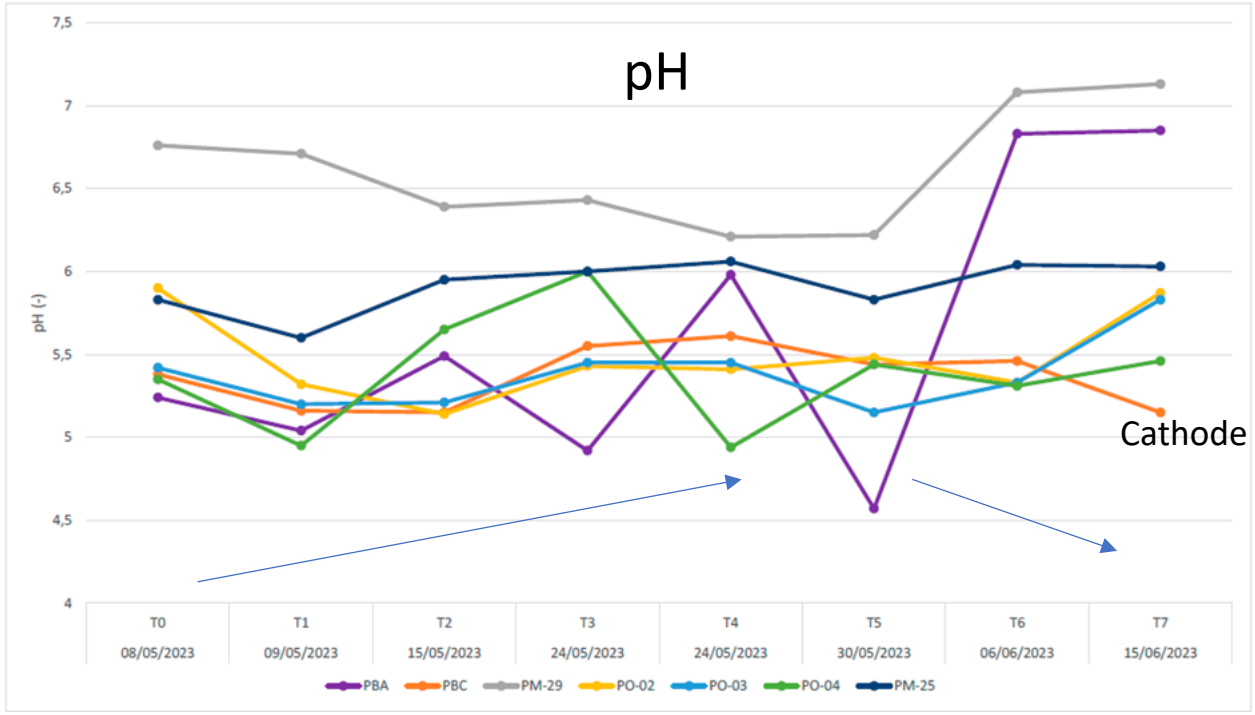


General trend towards pH values reduction in PBA (anode) → increasing at regeneration times.

Monitored parameters during the pilot test

GW Level

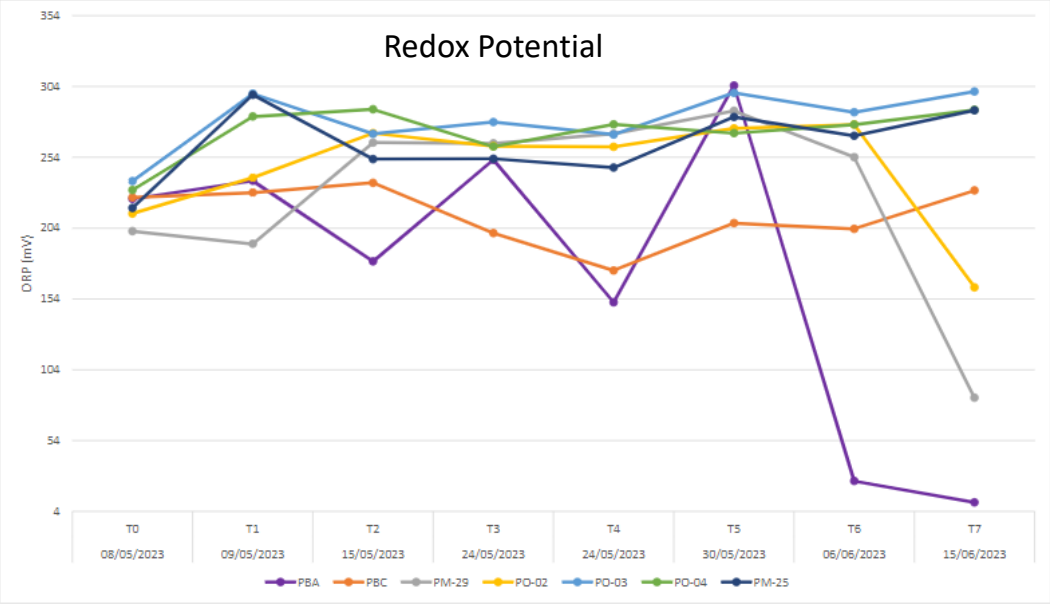




It was expected that due to the electrolysis process of water, molecules of H+ and OH- would be released, making the aquifer more acidic at the anode and more alkaline at the cathode.

In general, other wells followed PBA trends

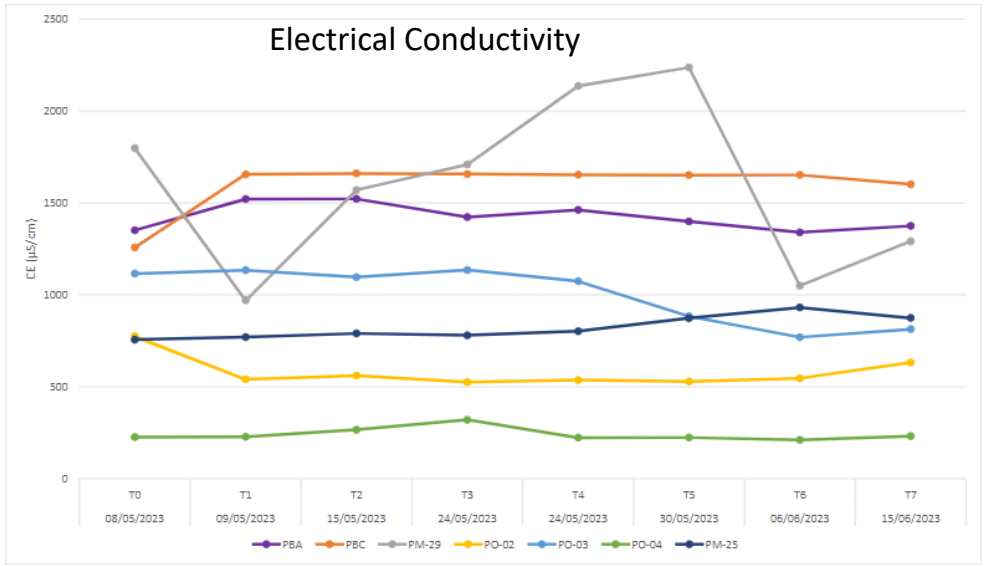
Monitored parameters during the pilot test



Anode showed an increase up to time T5, while the cathode exhibited a decrease.

At time T6, there was a shift in reactions, supporting the hypothesis that the system entered regeneration mode.

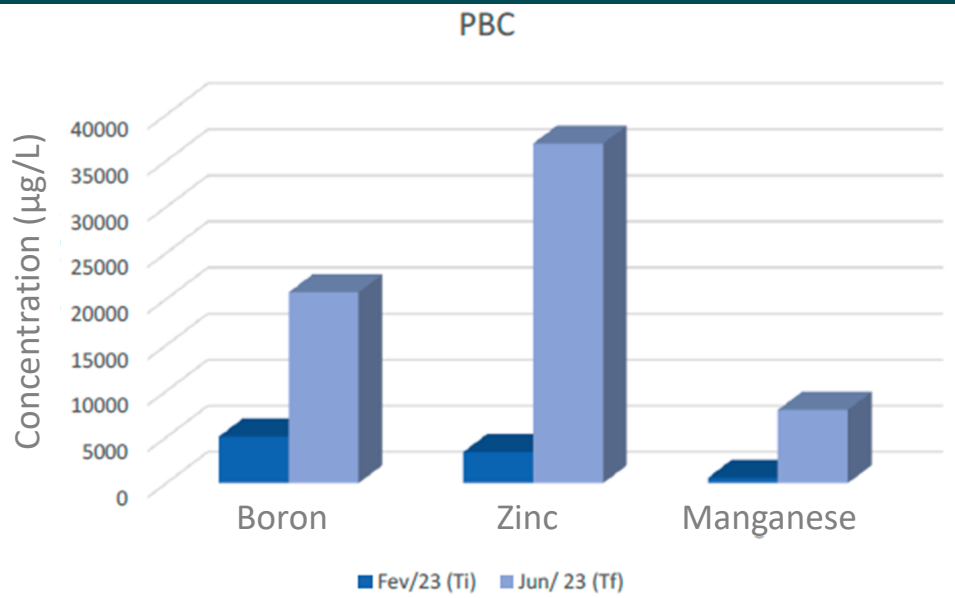
- PM-29 and PO-02 → followed the behavior of the anode
- PO-03, PO-04, and PM-25 → subtly followed the behavior of the cathode.

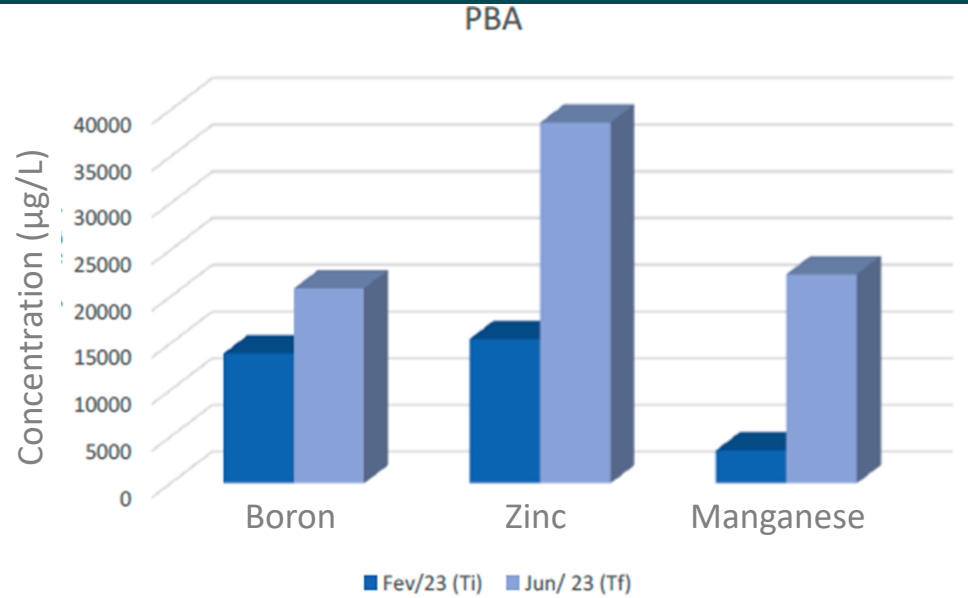


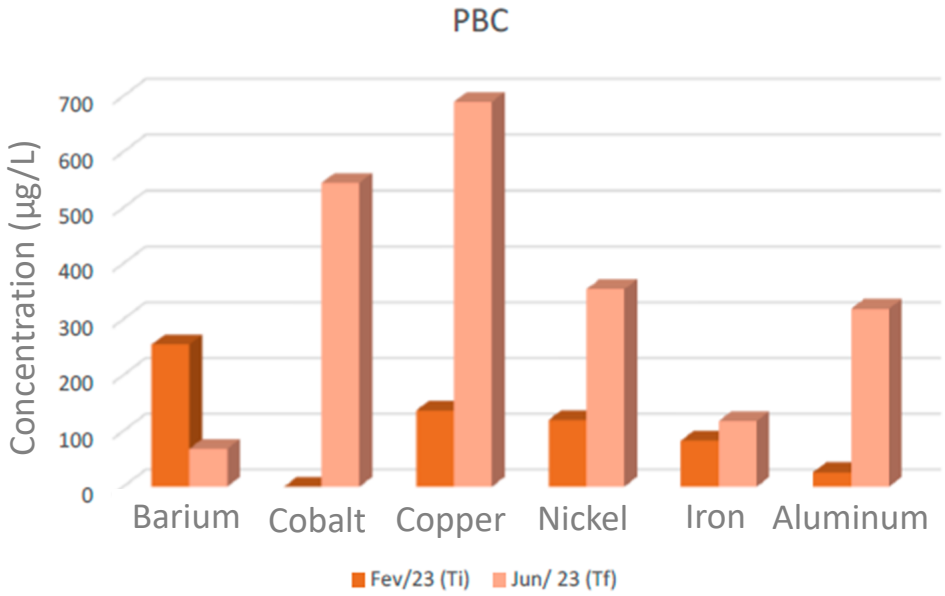
- **Anode** well: slight reduction in electrical conductivity after T2
- **Cathode**: increase starting at T1, remaining stable until T7 → may be related to the migration of cations to this pole.

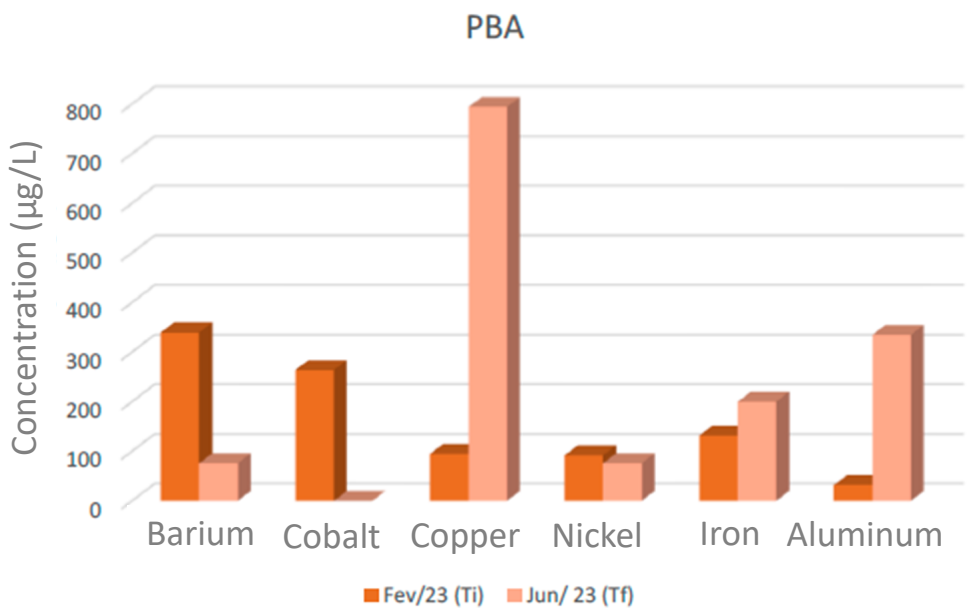
Well PM-29, located between the two poles, initially showed a reduction in electrical conductivity and then followed an upward trend, which may indicate ion migration towards the cathode region.

Results for Metals



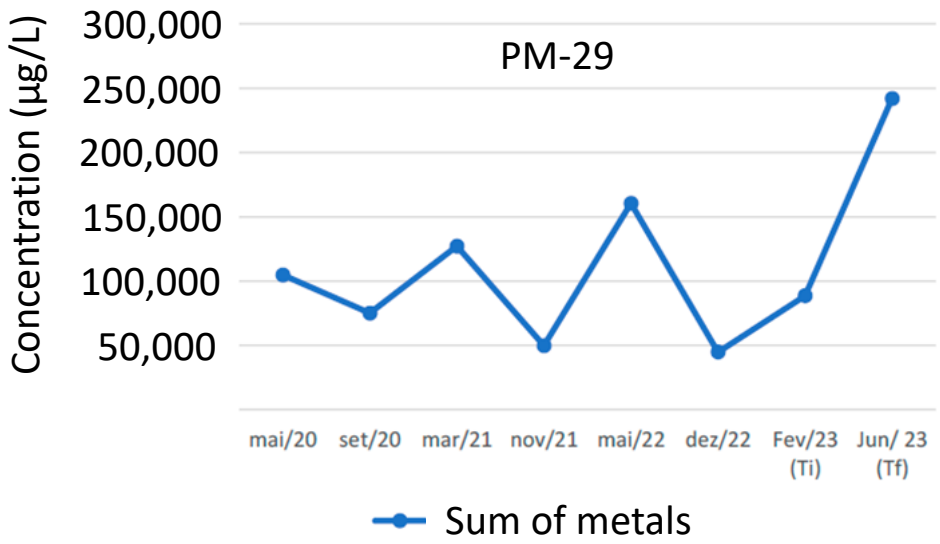






Results for Metals (Sum)

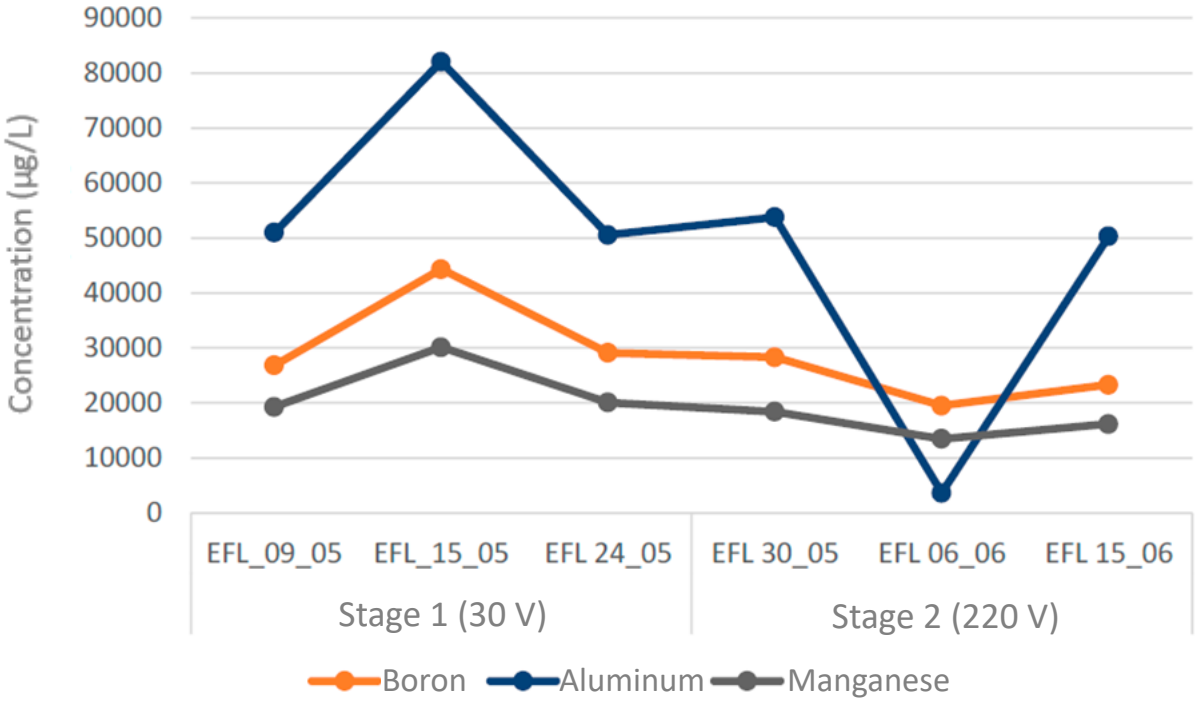
Wells	Sum of Total Metals (µg/L)			Sum of Dissolved Metals (µg/L)		
	Baseline	Final	%	Baseline	Final	%
PBA	71,236.20	102,974.00	-44.55	33,921.60	83,431.00	-145.95
PBC	15,625.70	73,483.00	-370.27	9,696.20	67,660.00	-597.8
PM-29 (2.5m – between PBs)	153,262.70	264,305.00	-72.45	88,595.70	242,065.00	-173.22
PO-02 (7.5m)	13,517.30	13,722.80	-1.52	4,897.40	9,522.20	-94.43
PO-03 (10 m)	14,450.00	21,831.00	-51.08	7,437.00	9,153.00	-23.07
PO-04 (12.5 m)	8,573.10	9,681.10	-12.92	2,942.10	2,155.60	26.73

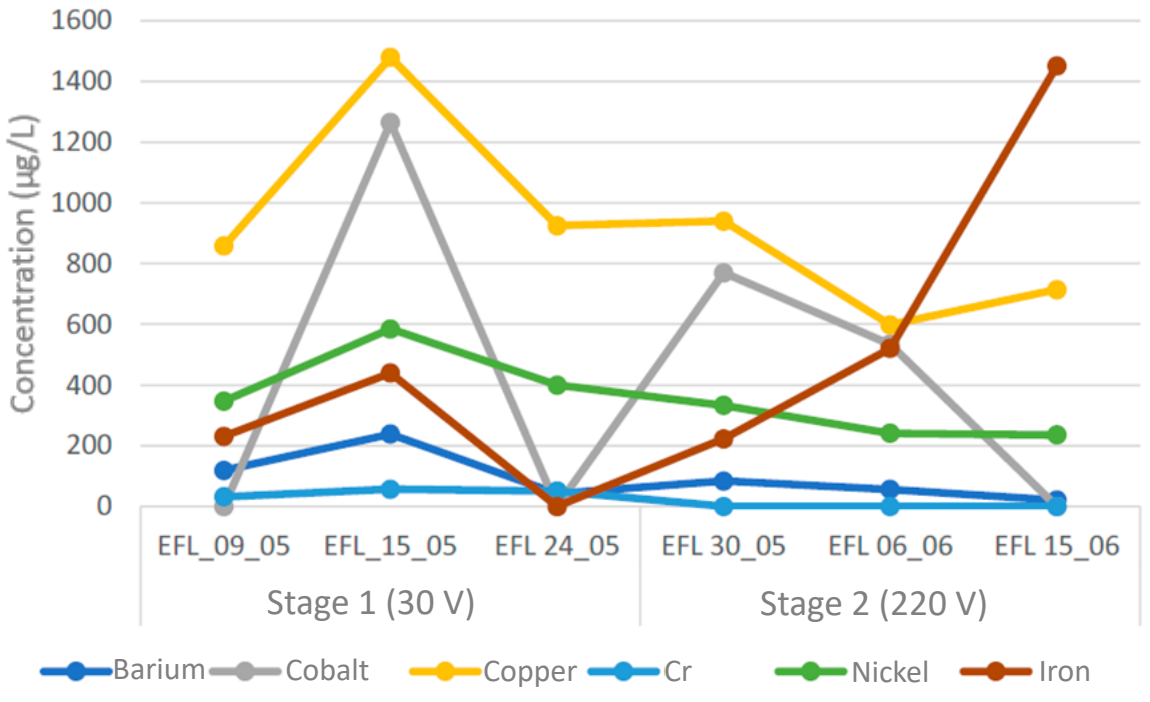


Conc. Increase

Conc. Decrease

Results for Pumping Effluents





In general, the highest concentrations occurred when a voltage of 30V was applied (except for Iron).

Problems with the pump possibly compromised the results at 220V.

The atypical behavior of iron likely reflects its mobilization from the soil, which is not a desired condition.

Mass Removal

Data	Step 1 (30 V)	Step 2 (220 V)
	Mass removed (g)	Mass removed (g)
Barium	1.52	0.7
Boron	381.48	342.9
Cobalt	4.81	5.8
Copper	12.42	11.0
Chromium	0.53	0.2
Nickel	5.07	4.3
Aluminum	698.57	481.3
Iron	2.55	3.3
Manganese	264.38	231.5
Sum	**1371.33**	**1081.05**
Total Rate (g/L)	**0.12**	**0.08**
Rate (g/day per pump well)	**94.57**	**94.0**

Data	Pumping only	Pumping + Electrokinetics (30 V)
Radius of Influence (m)	7.50	7.50
GW flow rate (L/h)	85.67	~ 17.0
Mass removal rate per pump well (mg/L)	3.95	120.0

The results allowed for the design of a full-scale remediation (currently being implemented), with each electrokinetic + pumping module expected to operate for a period of 12 to 18 months.

Thank you!

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