# Conceptual Model of Tropically Weathered and Fractured Crystalline Bedrock and its Implications for In Situ Chemical Oxidation

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## Abstract

In tropical areas, specific chemical weathering conditions (including high temperature, high precipitation, and low pH) typically result in extensive saprolite ferralsols over crystalline rocks. The main subject of this paper is a project in Sao Paulo (Brazil), with the site located on a hilltop and underlain by saprolite and fractured granitic bedrock. Both units are impacted with chloroethenes. The conceptual site model suggests that plume migration occurred through pores and open fractures found in the saprolite. The saprolite has a thickness up to 40 meters and a ground water level at approximately 20 meters below ground surface. Constant head injection tests demonstrated high anisotropy in the saprolite, with directions in accordance with the main fracture sets identified in the underlying rock. Pumping and injection tests confirmed hydraulic connectivity between both units. During a pump test hydraulic responses were detected in bedrock monitoring wells up to 400 meters distant (variations downwards and upwards). Vertical and angled wells were installed in the bedrock to intercept all fracture sets that include subhorizontal and subvertical structures. The measured average fracture density was 0.17 fractures per linear drilled meter and 0.21 fractures per cubic meter. Average bulk hydraulic conductivity was calculated as $10^{-5}$ cm/s for the saprolite and $10^{-7}$ cm/s for the bedrock. Based on these findings and a low soil oxidant demand, chemical oxidation was applied as part of a two-step process: 1) distribution of oxidant through pores and fractures of the saprolite; and 2) allowing oxidant to migrate vertically into the underlying bedrock through subvertical fractures. Approximately 30,000 Kg of potassium permanganate was injected into the saprolite, and preliminary results showed a 82% decrease in the chloroethene mass in saprolite ground water and a decrease of up to 47% in bedrock ground water. The distribution and migration of the permanganate confirmed expected preferential pathways related to the fracture sets. The results indicate that in situ chemical oxidation is an effective remediation technology for this type of complex geological setting when applied after appropriate characterization.

## Introduction

A limited amount of fractured and weathered bedrock characterization and remediation projects in tropical zones have been documented but these are expected to become more common as environmental, legal, and economical pressures increase. Weathered bedrock aquifers in tropical zones are typically more extensive than in temperate areas and represent important sources for ground water abstraction. The success and cost-effectiveness of characterization and remedial works in these areas is likely to be dependant on projects taking into account lessons learned from abroad as well as understanding the unique local conditions.

At the subject site, fractured and weathered bedrock were impacted with chloroethenes, and a number of characterization and remediation tools have been applied. The complexity and diversity of the hydrogeological environment required a robust conceptual model to design and implement the remedial works.

## Background

### *Tropical Weathered Bedrock*

Jenny (1941) identified the following four “state factors” that act over time on geological parent materials resulting in different soils: drainage, topography, climate, and vegetation processes. The different interactions of such variables, added to human interferences, can explain the large variety of recognised soil profiles types.

A key state factor for defining soil profiles and chemical properties is the water-logging regime. Poor drainage (typically related to fine soil texture, soil structures, and topographic drainage) can result in the onset of reducing physicochemical conditions. These soils typically present pale colours (after reduction of iron oxides) and are called hydromorphic or gley soils. Soils with efficient, quick drainage normally are characterised by aerobic and oxidized conditions which can result in brown and reddish soils related to abundant iron oxides.

Soils rich in oxides are characteristic of tropically weathered bedrock due to the occurrence of aggressive chemical weathering processes associated with high temperatures, high precipitation, and low pH (related to presence of humic acids). In this setting, iron and aluminum oxides accumulate while other elements and nutrients are washed down the profile. Such soils are called ferralsols in the *World Reference Base for Soil Resources* (ISSS, 1998), latosolos in Brazil, and oxisols in the USDA Soil Taxonomy. They typically present low cation retention and mineralogy characterized by high content of quartz, kaolinite, goethite, gibbsite, and/or hematite. The world-wide prevalence of ferralsols is shown in Figure 1.

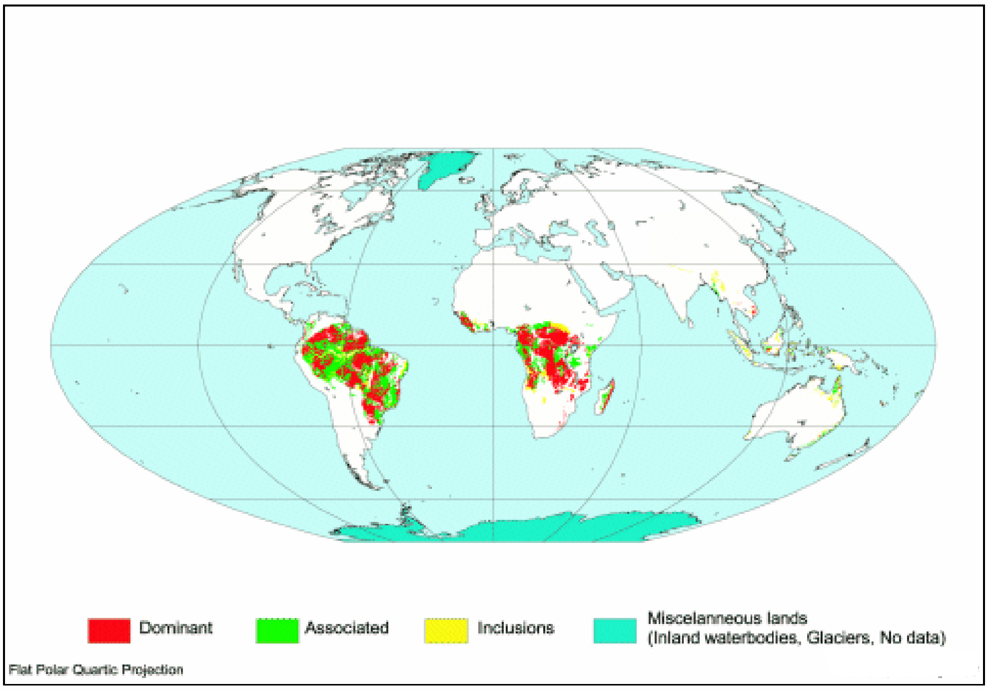

*Figure 1. World-wide Ferralsols Distribution (Driessen et al, 2001)*

Another common characteristic of tropical areas is that, under stable tectonic and environmental conditions, soils typically accumulate in situ over long time periods (up to $10^6$ years according to Alloway, 2005) diminishing the relevance of contemporary conditions (Taylor & Howard, 2000). This is possible due to the predominance of chemical weathering processes and the additional protection against erosion (stripping) that is offered by dense vegetation and stable microstructures (Figueiredo et al, 2004). This allows the formation of an extensive weathered bedrock profile (also named saprolite), many times reaching 50 meters thick (Pede, 2004). Weathering gradually decreases in depth but the higher and most consistent values for transmissivity and hydraulic conductivity of the weathered and non weathered units tends to be found near the transition zone, enhanced by the presence of highly productive isostatic decompression fractures (Taylor & Howard, 2000). Hydraulic conductivity K is typically $10^{-5}$cm/sec at shallower zones, $10^{-2}$cm/sec at the transition zone and commonly lower and more variable in the bedrock, as discussed by Pede (2004). Therefore widespread ground water abstraction has been able to occur from tropically weathered bedrock aquifers, typically with low yield pumps (<20m$^3$/day) in rural areas of South America, Africa and Asia (Taylor & Howard, 2000).

## *In Situ Chemical Oxidation*

Several cases of in situ chemical oxidation (ISCO) applications have been documented, commonly to remediate chlorinated ethenes in overburden aquifers. ISCO has also been applied to fractured bedrock aquifers, where the need for intensive and appropriate characterization of this complex media have been noted (Pac et al 2004). In these aquifers, distribution and migration of contaminants and oxidants are highly dependent on the matrix porosity and fracture characteristics. In Brazil, the first ISCO application with permanganate happened in 2005 and was closely followed by the local environmental agency, CETESB (Eskes et al 2006).

The mass of oxidant required for remediation of an impacted area is dependent on the contaminant characteristics but also on the soil oxidant demand (SOD).

Reduced metals, sulphates, and organic carbon material that may occur naturally in soil can compete with the contaminant for the oxidant. A sufficiently high SOD can render ISCO infeasible at a site. Therefore this parameter, defined through laboratory tests, must be effectively analysed before the start of ISCO remedial works.

Since 2004 several SOD tests have been conducted in Brazil and the results have been consistently low. Eskes et al (2005) presented SOD results, mostly below 0.5 g $KMnO4$/kg soil, for samples taken at different locations in Sao Paulo state, with lithologies including weathered crystalline bedrock, sedimentary rocks, and unconsolidated deposits.

## Methodology

### *Characterization*

The characterization of the subject site's impacted saprolite and fractured bedrock was performed using several intrusive and non-intrusive techniques, as suggested by the "fractured bedrock toolbox" approach (Fiacco et al, 2004). Activities included photo lineament analysis; surface geophysics; outcrop analysis; installation of vertical saprolite and bedrock monitoring wells; installation of inclined bedrock monitoring wells; analysis of soil, rock, ground water and surface water samples; borehole geophysical logging (optical and acoustic televiewing); tracer injection tests (bromide); pump tests, and constant head injection tests. Drilling techniques included hollow stem auger in the weathered bedrock and roto-percussive methods in the bedrock (with vertical wells requiring injection of water during drilling).

In order to effectively implement the project strategy and evaluate the results a multi-disciplinary team was designated and included expertise in structural geology, hydrogeology, geophysics, geochemistry, and engineering design.

### *Remediation*

Based on the field and laboratory results, it was decided to inject potassium permanganate directly into the saprolite via injection wells, near the contact zone with the underlying fractured rock. The aim was to initiate a two-step process: 1) distribute the oxidant horizontally through the more permeable saprolite using applied hydraulic pressure and 2) allow the oxidant to migrate vertically from the saprolite into the bedrock through sub vertical and diagonal fracture sets using a naturally occurring hydraulic gradient that favoured downward flow. The first application included injection of 30 tons of potassium permanganate into the source area and part of the plume. In parallel with the ISCO injection, a soil vapour extraction (SVE) system was installed in localized areas to target the unsaturated zone. The effectiveness of the ISCO application was assessed via ground water monitoring. Additional injection works in specific areas are ongoing, and will be followed by further monitoring.

## Site Description and Regional Geological Setting

The subject site is an industrial property where chlorinated solvents were stored and used throughout the last three decades. It is located in Sao Paulo, Brazil, on a hilltop (approximately 800m above sea level) with medium to steep sides leading to densely vegetated valleys and creeks (commonly in NE-SW direction). Annual precipitation rate is approximately 1400mm and summer is the rainy season. Rock outcrops are scarce at the site and in the surroundings area and are mostly related to major human interventions such as motorway digs.

The regional geology is characterized by the Ribeira Belt, an extensive Neo-Proterozoic fold belt with a predominant ENE-WSW direction (CPRM 1999). The site is located in the central portion of the Belt between the Taxaquara and Cubatao Shear Zones, a geological region named the Embu Domain. Towards the east this Domain is covered by the Sao Paulo Basin.

The Embu Domain predominantly comprises crystalline rocks of variable levels of metamorphism and intrusions of tectonic and post-tectonic granitoids. The study area inserts itself in a block comprising schists, migmatites, and intrusive granitoids. It is limited to the north by the Taxaquara Shear Zone and to the south by Caucaia do Alto Shear Zone (Hasui 1973). These shear zones show a general E-W to ENE-WSW orientation and are up to 300 meters thick. They formed intensive ductile and cataclastic metamorphic structures that are commonly planar and subvertical.

The tectonic evolution embodied diverse episodes of brittle deformation. At the end of the Proterozoic, big shear zones were formed (e.g. Caucaia and Taxaquara). New major brittle deformations related to the opening of the Atlantic Ocean occurred during the Mesozoic. This event applied extensive force on the pre-existing structures, culminating in the Paleogene formation of the Continental Rift of Southeastern Brazil (Riccomini 1989). More recent ruptures have acted on the previous brittle structures, with predominance of reactivation along ENE-WSW normal and NNW-SSE right-lateral strike-slip faults. Tectonic and decompression (i.e. isostatic uplift) pressure release related sub horizontal joints are also commonly present.

Locally, the presence of brittle structures (mostly faults or shear zones, CPRM 1999) has created deformed and foliated granitoids that resemble gneissic rocks (with foliation typically dipping towards NNW).

## Results

### *Site Geological Profile and Analytical Results*

Due to naturally steep sloping topography, the site was leveled with fill material composed of 1 to 13 meters of reddish sandy clay and, in portions of the base, organic clay. Beneath the fill material, up to 35 meters of weathered granitic rock (saprolite), with a clayey-silty composition that becomes sandier in the deeper saturated zone was recorded. Several characteristics of the underlying unweathered bedrock were identified in the weathered material (see Figure 2), such as open fractured zones, foliation, and preserved minerals (e.g. mica, quartz, and feldspar). Open fractures were identified in the weathered rock material (mostly at higher depths) with low, medium, and high dip angles. Below the water table, which varies from 15 to 30m bgs (meters below ground surface), the saprolite color changes from reddish to gray, probably as a result of changes in the oxidation condition. The water-saturated saprolite zone is typically 6 meters thick but reaches 15 meters locally. The saprolite average matrix porosity was measured as 38%, and decreases in depth. Analysis of bedrock cores in nearby and other sites indicate that matrix porosity in the bedrock is approximately 3% at shallower depths (near the weathering transition zone) and decreases with depth to approximately 1%. The bedrock is composed of a foliated granite rock that is heterogeneous (in terms of foliation, mineral size, and vein presence) and sparsely fractured. Hydraulic heads in the saprolite are consistently higher than in the bedrock aquifer, where ground water is typically found from 35 to

50m bgs. Consequently, the vertical gradient favors downward flow, while the horizontal gradient favors discharge of both units into the local creeks.

*Figure 2. Weathered Bedrock at 20m bgs Presenting Fracture with Oxides*

Analytical results for soil and ground water indicated that both the saprolite and the underlying fractured aquifer have been impacted with chloroethenes. The plume in the saprolite was delineated over an area of approximately 36000 $m^2$. The bedrock unit exhibited lower concentrations but higher percentage of degradation products than the saprolite (see example in Table 1).

| Nested Wells | PCE (ug/L) | TCE (ug/L) | 1,1 DCE (ug/L) | CIS-1,2 DCE (ug/L) |
|---|---|---|---|---|
| MW-19 (saprolite) | 16171 (50%) | 10163 (32%) | 5500 (17%) | 410 (1%) |
| OW-06 (bedrock) | 186 (6%) | 920 (28%) | 2200 (66%) | 31 (1%) |

*Table 1. Nested Wells VOC Concentration and Mass Percentage before Remediation*

Soil samples and PID measurements were taken during drilling in the weathered bedrock and indicated higher VOC concentrations near the open fractures than in the soil matrix (indicating that fractures act as preferential pathways).

Saprolite and ground water samples were collected from the site and submitted for a series of laboratory tests. The soil oxidant demand for potassium permanganate ($KMnO_4$) from 12 samples varied between 0.13 and 0.54 g $KMnO_4$/Kg soil. Within the saturated zone, soils from shallower depths presented lower iron content (approximately 10.000mg/kg) than samples from deeper zones (approximately 50.000mg/kg). However, the iron content did not correlate to the range of SOD results, suggesting that this iron is not readily available for oxidation. Furthermore, the formation exhibited low total organic carbon content (typically 0.05%).

### *Geophysics in Vertical and Inclined Boreholes*

Vertical and inclined drilling in the bedrock was conducted to allow geophysical measurements (acoustic borehole and oriented optical televiewers) followed by monitoring well installation. The direction and dip of each inclined borehole was defined in order to intercept and characterise existing geological structures throughout the site (particularly the open fractures which potentially transmit ground water flow). Afterwards, the identification and analyses of structures served as the basis for selecting the filter section of each monitoring well. A total of 293m of bedrock (97m vertically) were drilled and analysed with a total of fifty open fractures identified, as summarized in a stereogram (Figure 3). Three groups of fractures were defined: Family 1 subhorizontal; Family 2 dipping WNW with medium angle (N280/36); and Family 3 dipping NNW higher angle (N338/66). Table 2 summarizes the findings and indicates significant differences for each borehole and type of well. As expected more medium angle fractures were identified with inclined boreholes, however these boreholes also presented less low and high angle fractures. This possibly is because of the heterogeneity in distribution of these fractures and the location within lineaments of the vertical wells (however differences in drilling methods were noted). Anyhow, the overall average fracture density was found to be low (0.17 fractures per linear drilled meter and 0.21 fractures per aquifer cubic meter).

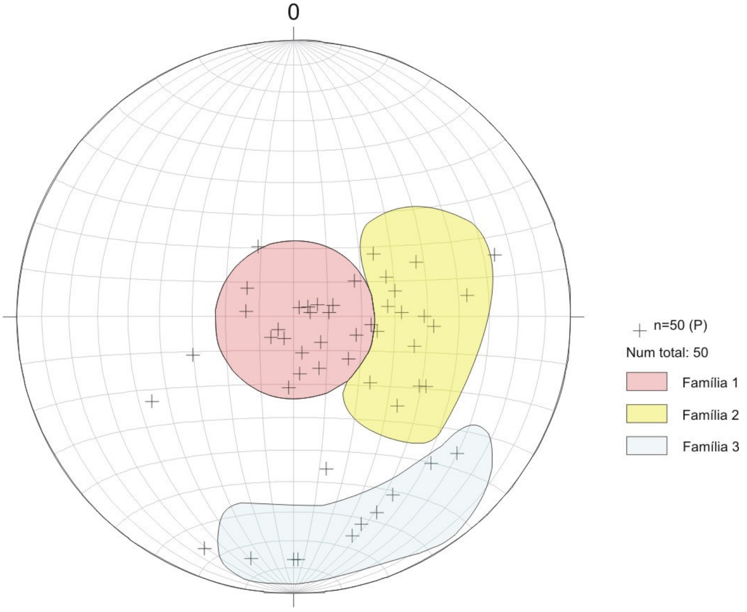

*Figure 3. Open fractures (Lower Hemisphere Projection)*

| Well (direction) | Family 1<br>(low angle) | Family 2<br>(WNW medium) | Family 3<br>(NWN high) | Total Amount of Open Fracturas |
|---|---|---|---|---|
| OW-01 (vertical) | 5 | 0 | 0 | 5 |
| OW-02 (vertical) | 4 | 0 | 3 | 7 |
| OW-03 (vertical) | 4 | 0 | 0 | 4 |
| OW-04 (vertical) | 0 | 1 | 1 | 2 |
| *Adjusted Density for vertical boreholes (frac./m$^3$)* | 0.134 | 0.025 | 0.076 | 0.236 |
| OW -05 (N210º; 60º) | 0 | 1 | 2 | 3 |
| OW -06 (N125º; 60º) | 3 | 6 | 0 | 9 |
| OW -07 (N165º; 60º) | 0 | 2 | 4 | 6 |
| OW -08 (N090º; 60º) | 5 | 2 | 0 | 7 |
| OW -09 (N120º; 60º) | 0 | 0 | 0 | 0 |
| OW -10 (N160º; 60º) | 1 | 3 | 3 | 7 |
| *Adjusted Density for inclined boreholes (frac./m$^3$)* | 0.052 | 0.087 | 0.057 | 0.196 |
| *Total Fractures* | 22 | 17 | 11 | 50 |
| *Total Adjusted Density (frac./m$^3$)* | 0,081 | 0,068 | 0,061 | 0,21 |
| *Adjusted Density %* | 38,75% | 32,18% | 29,08% | 100% |

*Table 2. Findings for Vertical and Inclined Boreholes Bedrock*

*Pump Test*

A 96-hour pumping test was performed on an on-site former abstraction well (200 meters deep, bedrock from 40 m bgs). The pump was installed at a depth of approximately 175 m, and the pumping rate was constant, at approximately 3,0 m³/h, totalling 250 $m^3$ of pumped ground water. Prior, during and after the test, water levels were measured with transducers and manually in bedrock and saprolite wells. Figure 4 presents the graphed water level responses for the main bedrock monitoring wells, which indicate a high level of heterogeneity and strong connection between the abstraction well with downgradient wells up to 400 meters away. In Figure 4, wells showing similar types of hydraulic responses are grouped together. Interestingly, the most distant observation well showed the best interconnection with fractures encountered in the pumping well. This well, OW-3, and nearby OW-2 exhibited drawdown almost immediately after the start of pumping and began to show recovery within an hour or two of the cessation of pumping.

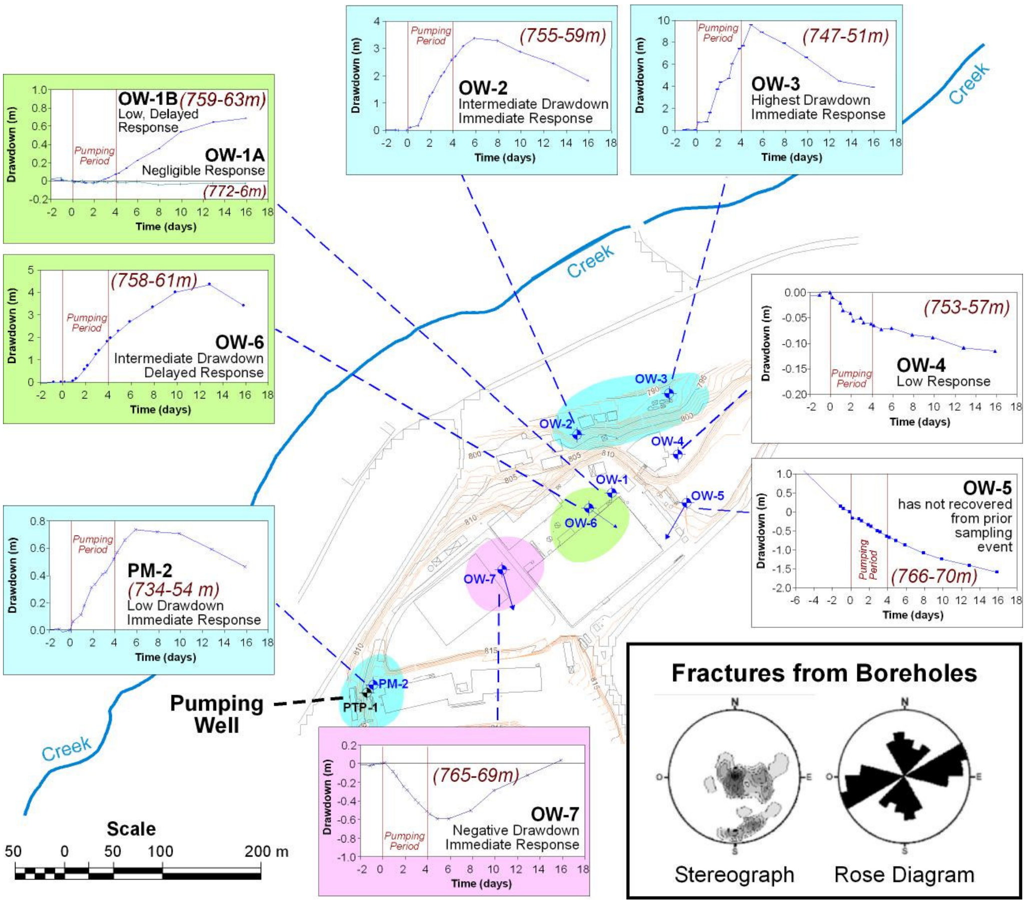

*Figure 4. Pumping Test Results, Showing Responses at Bedrock Monitoring Wells*

Between OW-3/OW-2 and the pumping well are two wells, OW-1B and OW-6, which showed a delayed response to the pumping. These wells contain fractures which are interconnected to those in the pumping well, but with lower transmissivity than those in OW-2 and OW-3. Monitoring data from well OW-7 presented unusual behavior, with ground water increasing during and in clear correlation with the pump test. This was considered an instance of the “Noordbergum effect” due to three-dimensional deformations of the pore space that occur ahead of the transmittal of hydraulic effects of pumping (Hsieh, 1996). This effect occurs in low hydraulic conductivity media within a heterogeneous flow system. Typically, the Noordbergum effect is associated with deformable media such as clays and may, in this instance, be related to the bottom of the weathering zone.

### *Injection Test*

A gravity fed constant head injection test was performed in the saprolite and presented final injection rates of approximately 200 L/hour. Figure 5 shows the head rise contours in the saprolite wells after a 72-hour injection. The zone of influence of the injection showed strong anisotropy that correlates with the main fracture sets in the underlying rock aquifer and the orientation (NE-SW) of the strongest hydraulic response that was observed during the bedrock pumping test (see Figure 4). Hydraulic response was also noticed in adjacent bedrock wells.

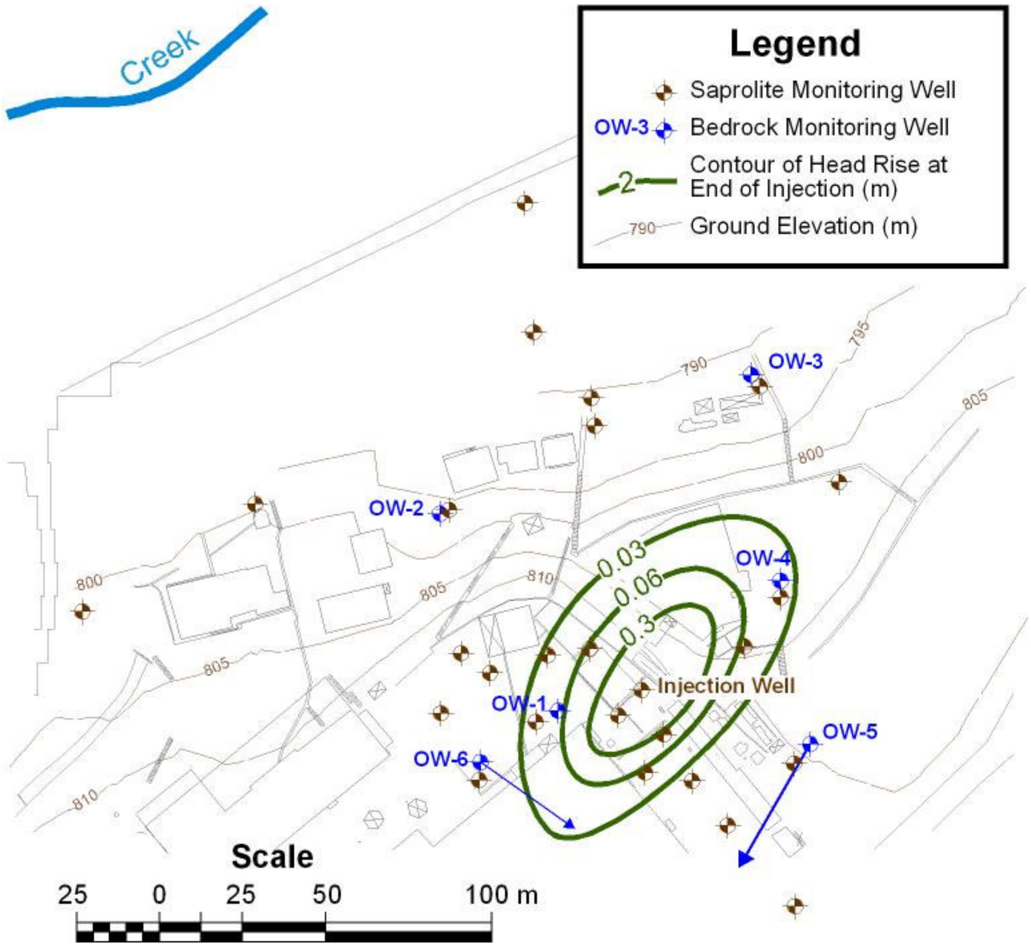

*Figure 5. Head Rise after 72-Hour Injection Test*

*Conceptual Model*

The site conceptual site model is summarized in Figure 6. It suggests that plume migration occurred horizontally and vertically through pores and fractures in the extensive ferralsol saprolite. Low to high angle fractures become more common in depth and connect this unit to the fractured granite bedrock (where matrix porosity becomes less significant with depth). High precipitation rates and presence of vegetation enhance natural oxidizing and slightly acid conditions in the weathered bedrock (predominantly in shallower zones and in open fractures that act as preferential pathways for infiltrating water and contaminants). Density of fractures in the bedrock was calculated as 0.21 fractures per meter, with significant preferential pathways in WSW-ENE direction (related to extensive structures) and, to less extent, NNW-SSE direction (related to strike-slip structures) and within horizontal structures (related to isostatic uplift). WSW-ENE and NNW-SSE lineaments were identified near the plume area (in correlation with the plume and permanganate distribution). A pump test in the bedrock and an injection test in the saprolite indicated high connectivity between zones in WSW-ENE direction (up to 400 meters distance during the pump test). Average bulk hydraulic conductivity was calculated with several hydraulic tests as $10^{-5}$ cm/s for the saprolite (lower in the clayey shallower zones) and $10^{-7}$ cm/s for the bedrock.

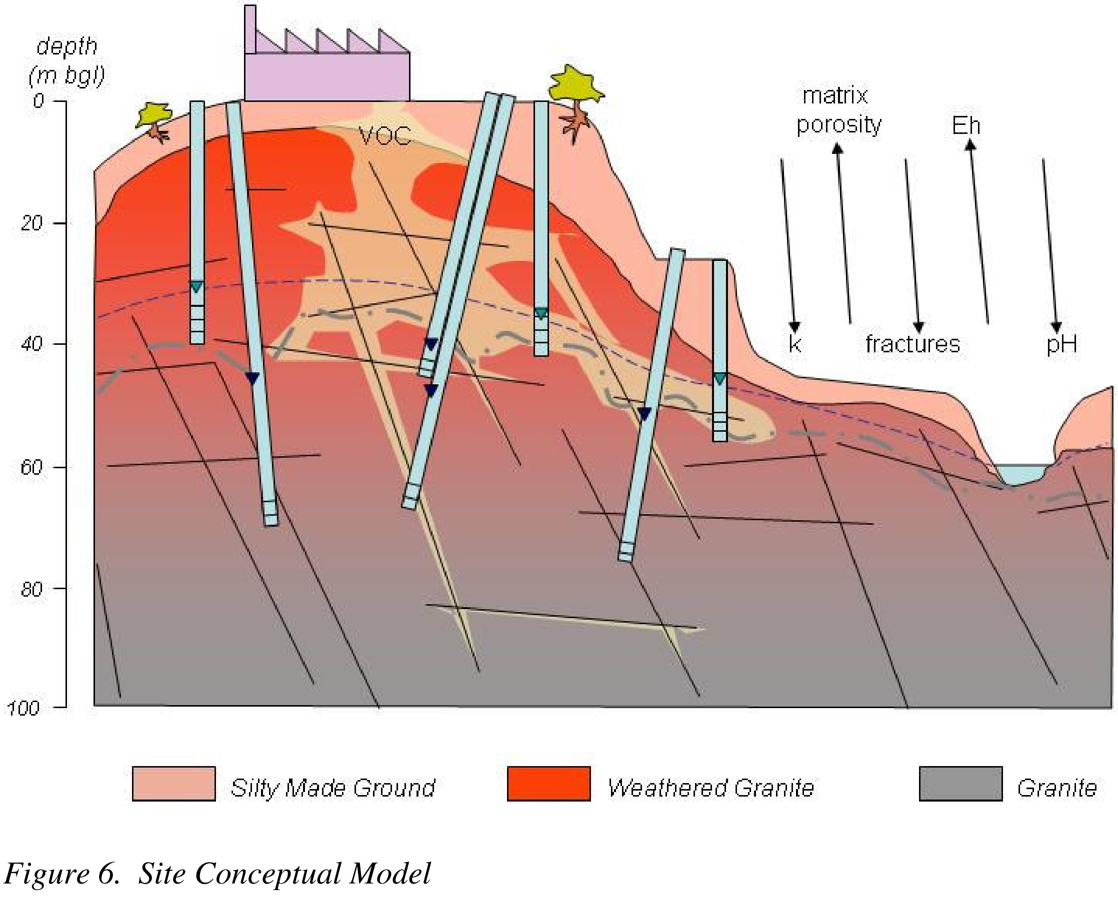

*Figure 6. Site Conceptual Model*

*Remediation Monitoring Results*

Over the course of 64 days, a total of 3,000 m$^3$ of potassium permanganate solution, with an average concentration of 10,000 m/L or 1%, was injected under pressure into 41 injection wells at the site. Figure 7 shows the maximum rise in head resulting from the injection program with the zone of maximum head mounding aligned WSW-ENE. This direction of anisotropy was also noted during ground water monitoring for permanganate and SVE activities (vacuum alignment).

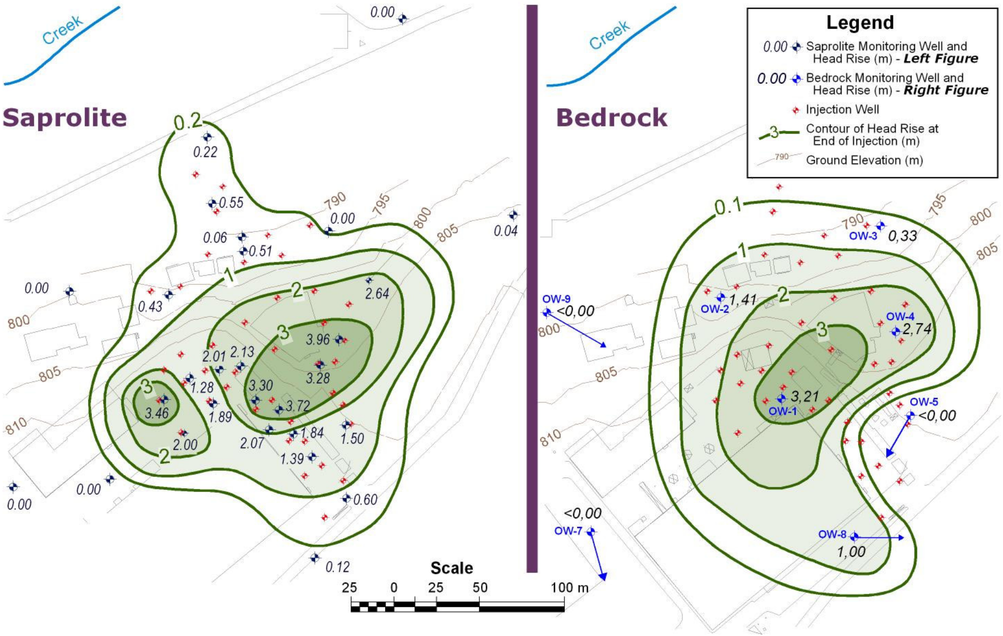

*Figure 7. Maximum Head Rise during 64-Day Permanganate Injection*

Figure 8 shows the total chloroethene concentration before and after the permanganate injection. The zone of chloroethene contamination is significantly reduced from the pre-injection state (concentrations decreased in 82% in the saprolite monitoring wells and up to 47% in bedrock monitoring wells).

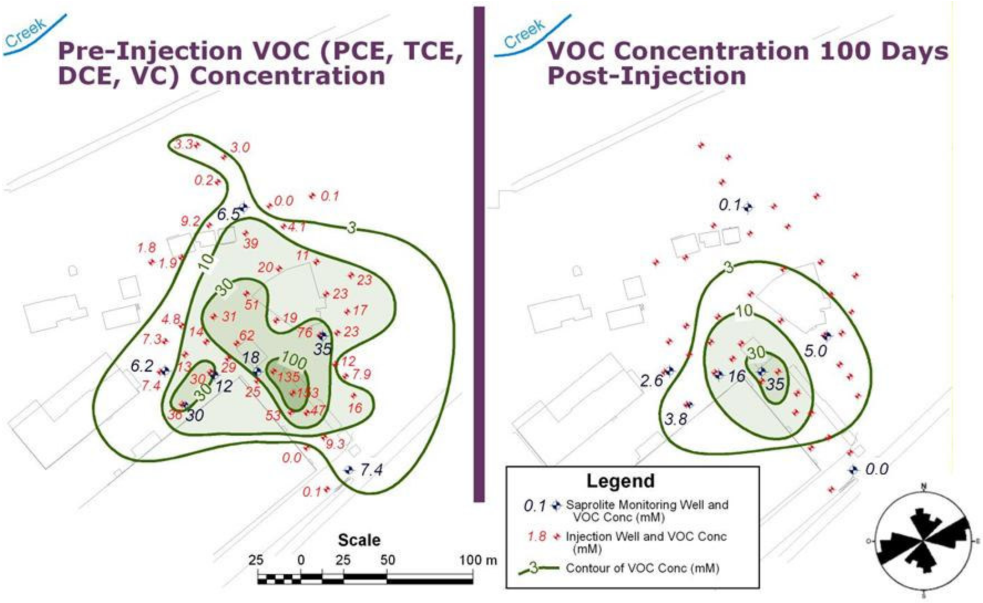

*Figure 8. VOC Concentration in Saprolite Before and After Permanganate Injection*

## Conclusions

Based on the results obtained, it is possible to draw the following conclusions regarding the site characterization and remediation:

- VOCs and Permanganate distribution in the weathered bedrock was possible through open fractures that exist in continuity with the bedrock and enhanced matrix porosity;
- The direction of main fractures were identified during characterization phase (improved with angled wells) and confirmed during ISCO and SVE works; and
- The ISCO remediation strategy was effective and had a beneficial effect it the bedrock (VOC mass reduction of 82% in the weathered bedrock and up to 47% in the bedrock).

In addition, it is possible to draw the following conclusions regarding fractured and weathered bedrock implications for ISCO:

- The hydrogeology of tropically weathered bedrock presents unique features that differ from those typically found in temperate zones (e.g. extension; physicochemical features, decompression fracturing, and permeability variation);
- The tropical intensive chemical weathering contributes for a low SOD in ferralsols; and
- ISCO remediation in fractured and weathered crystalline bedrock can be a viable option but shall be implemented in a dynamic process based on a robust conceptual model combined with intensive monitoring.

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