# TECHNOLOGY EVALUATION REPORT FOR BIOREMEDIATION IN REPSOL YPF, NEUQUÉN, ARGENTINA.

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#### Abstract

The soil restoration works performed since 1999 in a gas and oil field of Repsol YPF in Neuquén, Argentina, consisted in three stages: contaminated site assessment, in-situ and exsitu biological treatment of soils and disposition in sites destined to re-vegetation. In the first stage, the assessment of the site is done obtaining geological, hydrological and climatic data. Also, soil and contaminant characteristics are determined using a proper sampling system. The fate of the soil is defined with the collected data. It means that can be treated in place or excavated and treated in a place prepared for this purpose. The second stage consists in the selection of the treatment technique and the design of the process. The most used system for organic compounds removal in this work was Mechanic Removal Aerated Biopiles Technique, which is based on the stimulation of autochthonous microbial species that perform the hydrocarbon contaminants degradation process. In this case, instead of using large treatment areas as in the traditional land-farming process, a treatment in depth is done, which consist in the removal of piles up to two and a half meters high that accelerates the degradation process. These piles are supplied of the proper conditions for the bacterial development such as Oxygen (through removal), Nitrogen, Phosphorous (adding fertilizers) and moisture. The temperature rises up to 30°C or more spontaneously beyond environmental temperature, which makes the technique applicable for very cold climes. Another characteristic of this treatment system is the retention of moisture, which makes almost unnecessary the addition of water, important factor for arid and semiarid zones. The evolution of the process is measured through the analytical determination of total hydrocarbons and microbial counting. In salted soils, a chemical treatment is done which consists in the addition of a chemical improver adequate to the zone followed by a further wash of the soil until the salt concentration is under the allowed limits for plants. When the Total Petroleum Hydrocarbons concentration falls below 10000 ppm, biological treatment is finished an the third stage takes place, which adopts practically two forms: in the case that the treated soil is in its original place, the soil is scarified and the natural re-vegetation process is verified and controlled. In the case of the ex situ treatment, it is disposed in sites destined for re-vegetation. The bioremediated soil is set in layers of no more than 0.20 m of thickness and then it is scarified. A periodic analytical control is done to evaluate the restoration and re-vegetation process. A volume of more than 70000 cubic meters have been treated since 1999 up today.

#### Methodology

Ex situ treatment is performed in treatment units ranging from 500 to 6000 m<sup>3</sup> (field experiments A, B, C and D). The sampling of each unit is following a W pattern. In all of the cases the treatment unit is divided into a number of control units with a volume of up to 1000 m<sup>3</sup>, obtaining two samples of each one, one at 0,5 m and the another one at 1.8-2.0 m, depending of the height of the pile. In situ treatment experiments (field experiments E and F) were performed by the addition of nutrients and oxygen (removal) to the soil. The process control includes the total hydrocarbon determination of petroleum (TPH) by method EPA 418.1, heavy metals, nutrients (Nitrogen and Phosphorous), pH and count of aerobic hydrocarbon degrading microorganisms

#### **Results and discussion**

First stage: Contaminated site assessment

The climate of this zone is framed in the Semi-arid climate of Plateau. The region is characterized by a low rate precipitation, which is accentuated from the West to the East. Average temperature range from  $21.2 \degree$  C for the month of January, 6.2 to -5,5 ° C for the months of June and July, with an annual average temperature of  $13.5 \degree$  C.

The characteristics of hydrocarbon to degrade are as follows:

• In field experiments A, B, E and F, the hydrocarbon approximately displays as main component hydrocarbon cuts corresponding to 66 % of gasoline and 34 % of diesel.



Figure 1. Hydrocarbon profile of contaminant in soil (field experiments A, B, E and F).

• In the field experiments C and D the hydrocarbon presents as main hydrocarbon cut 12% of gasoline, 32% of kerosene and 51% of diesel.



Figure 2. Hydrocarbon profile of contaminant in soil (field experiments C and D)

Soil characteristics are:

	Texture of the soil
А	Silty sand
В	Sandy silt
С	Sand
D	Loamy sand
E	Sandy silt
F	Sand

Table 1. Soil texture.

Second Stage: Biological treatment

Ex situ Treatment (A, B, C and D)

Ex- situ treatment were performed in four units distributed in a radius of 100 km. Once the contaminated soil was deposited in the treatment unit, piles were built and then sampled and analyzed to collect preliminary data for the fertilization to initiate the biological treatment. During the removal of the piles (weekly, biweekly or monthly) the incorporation of nutrients were made. In the case of field experiment A, hydrocarbon average degradation was 81% in seven months of treatment.



Figure 3. Change of the Total Hydrocarbon concentration in the field experiment A

In the field experiment B the removal of the soil was made every two weeks and the average degradation was 80% in eleven months of treatment.



Figure 4. Change of the Total Hydrocarbon concentration in the field experiment B.

Field experiment C begins with a hydrocarbon concentration smaller than in the previous units being the type of polluting agent of greater molecular weight. In this case an average degradation of 49% in nine months of treatment is obtained. The removal was made monthly.



Figure 5. Change of the Total Hydrocarbon concentration in the field experiment C.

The degradation obtained in field experiment D was of 62% in ten months of treatment considering the same characteristics of the polluting agent than in C, removing with a biweekly frequency.



Figure 6. Change of the Total Hydrocarbon concentration in the field experiment D.

### In situ treatment

The first in situ experiment had a surface of  $60000 \text{ m}^2$ , reason why it was divided in five zones for monitoring and control. The soil was treated up to a depth of 1,50 m.



Figure 7. Site map of the site of treatment in situ.

The profile of the land in this zone is made up of nonconsolidated sediments. Underlying sandy gravel of fluvial origin to fine grounds like slime and fine sands of aeolian and torrential origin. In this case it was only fertilized with triple calcium phosphate. Nitrogen was not added to avoid possible leached to ground water. The removal was made monthly obtaining a degradation of 71% in nine months of treatment.



*Figure 8. Change of the Total Hydrocarbon concentration in the in situ treatment.* 

The second case of ex situ treatment had an area of  $10000 \text{ m}^2$  and the soil was impacted as a depth of 0,5 m.



The existence of an underlying layer of compact ground to the contaminated profile, allowed to make a treatment in situ, incorporating urea and diamonic phosphate like sources of Nitrogen and Phosphorus. The site was removed monthly obtaining a degradation of 65% in five months of treatment.



Figure 11. Change in the Total Hydrocarbon concentration

It is to emphasize that in both cases of in situ treatment the Total Hydrocarbon concentration was diminished below 0,6 %.

## Third Stage

In the case that the soil was treated ex situ, it comes arranging in sites destined to re-vegetation. The biorremediated soil was placed in layers of a thickness no greater than 0,20 m and then scarified. A periodic analytical control was made to evaluate the process of restoration of the ground and the re-vegetation process.

Date	TPH (g/kg)
01/12/1999	8.4
17/01/2000	6.5
10/10/2001	3.5

 Table 2. Concentration of Total Hydrocarbons in re-vegetation

 process (ex situ treatment)



Figure 12. View of the ex situ re-vegetated site.

For the case of in situ treatment, the superficial layer of the ground (0,30 m) was scarified to facilitate the vegetation process.



Figure 13. View of the ground after concluding the treatment.



Figure 14. View of the recovered soil.

Date	TPH
	(g/kg)
05/11/2002	4.7
04/09/2003	1,7

 

 Table 3. Total Hydrocarbon Concentration in re-vegetation process (in situ treatment)

## CONCLUSIONS

The soils contaminated with hydrocarbons in this oil field are framed within a management system that involves the remediation of the impacted site, the treatment of the contaminated ground, its final disposition and the recovery of the remediated site.

The technology used (Biopiles Aerated by Mechanical Removal) for the treatment of these soils is very versatile since it responds to different characteristics of soil and polluting agent. This biological alternative solves the problem of the treatment of great volumes of moderately contaminated soil.

The methodology of treatment used in this work, consisting of three stages (assessment, biological treatment and revegetation) allows to obtain soils with Total Hydrocarbon concentrations below 5000 ppm in a reasonable period of time at competitive costs respect to other technical alternatives. It is necessary to mention that this methodology is only applicable to contaminated soil with heavy metals concentration lower than the allowed by the legislation.

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