ESTIMATION OF SOIL SUPERFICIAL CONDUCTIVITY IN A ZONE OF MATURE OIL CONTAMINATION USING DC RESISTIVITY

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Abstract

At several SAGEEP conferences we presented resistivity technology for oil contamination study. Soil resistivity and groundwater salinity measurements were recalculated into petrophysical parameters: clay content, porosity and cation exchange capacity. For uncontaminated sandy-clay soil these parameters are close to real ones. For contaminated soil these parameters are apparent ones, but can be used as good contamination indicators. The real cause of petrophysical anomalies is an increase of superficial conductivity greater than electrolytic conductivity change in pore space of contaminated soil, as it was found by Abdel Aal et al. (2004) with spectral IP method. We suppose that DC resistivity also can give information about superficial conductivity, which is the main cause of resistivity and petrophysical anomalies at contaminated sites.

Superficial conductivity for soil is estimated on clay content (calculated on soil resistivity), groundwater salinity and clay conductivity. Clay conductivity depends on pore water salinity and cation exchange capacity of clay. Anomalous clay content reflects an increase of internal surface area whereas anomalous cation exchange capacity reflects an increase of surface charges at the mineral grain - electrolyte interface.

Practical examples of superficial conductivity estimation at oil contaminated sites are demonstrated and compared with resistivity and petrophysical anomalies.

Introduction

Contamination study with application of geoelectrical methods is now recognized and applied in many countries. But some aspects of such study are now in research and development stage. Several models of electrical properties' changes of contaminated soils were developed and published (Sauck, 1998, Atekwana et al., 2001, 2003, Abdel Aal et al., 2004). Abdel Aal et al. (2004) with the help of spectral IP method in laboratory investigated changes of superficial and electrolytic conductivity of soil in biodegradation process. Authors concluded that an increase of superficial conductivity is the main factor of soil conductivity changes due to biodegradation in contaminated zones. Shevnin et al. (2004, 2005) studied soil resistivity changes in contaminated zones using vertical electrical sounding (VES) method with recalculation of soil resistivity (taking into account groundwater salinity) into petrophysical parameters: clay content, porosity and cation exchange capacity. Comparing the results of these studies we found similarity in superficial conductivity and petrophysical parameters' anomalies in mature contaminated sites. That allowed developing algorithm of superficial conductivity determination using clay content and CEC values of contaminated soil. The only difference between two approaches that for direct estimation of superficial conductivity the spectral IP measurements are needed, whereas for calculation of this parameter on petrophysical data we can use only resistivity measurements.

Changes of soil properties due to mature oil contamination

In the table 1 there is a list of changes in chemical, physical (including electrical) and biological parameters of contaminated soils, collected from publications of Sauck (1998), Atekwana et al., (2001, 2003), Abdel Aal et al., (2004); Modin et al., (1997); Shevnin et al., (2004, 2005).

Table 1.: Changes of soil properties due to mature oil contamination.

Soil Property	Changes in mature contamination zone	Soil Property	Changes in mature contamination zone
Bacterial population	Increase	Soil resistivity	Decrease
Nutrients	Decrease	Water resistivity	Decrease
Total dissolved salts	Increase	Electrolytic conductivity in pores	Increase
Contaminants density	Increase	Superficial conductivity in pores	Increase
Biofilms	Increase	Clay content (apparent)	Increase
Surfactants	Increase	Porosity (apparent)	Increase or decrease
		Cation exchange capacity (apparent)	Increase

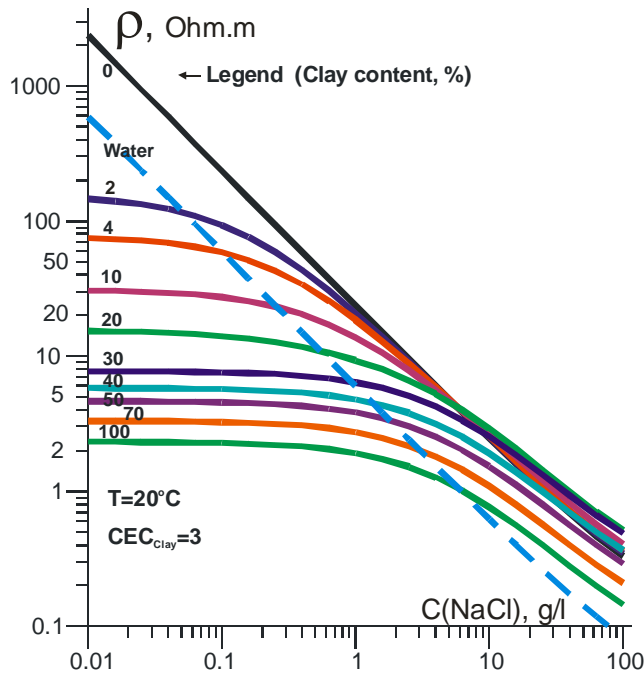*An idea of clay content estimation on soil resistivity and water salinity*

Figure 1.: Theoretical graphs of soil resistivity versus water salinity for different values of clay content. Dash line is for water resistivity.
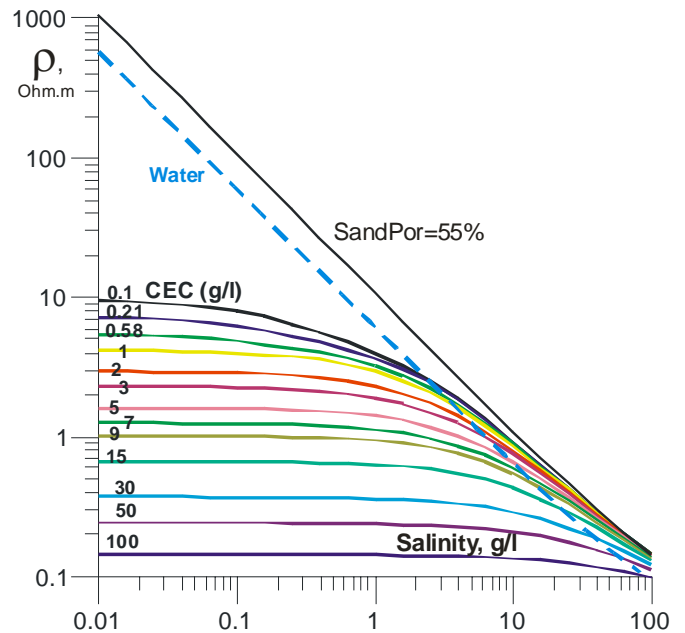
Figure 2.: Theoretical graphs of soil resistivity versus water salinity for pure sand and pure clay with 55% of porosity and different clay CEC.

Soil porosity for sand - clay mixture is in interval 0.16 - 0.55 for the case of fig.1. Sand porosity is in this case 0.25, clay porosity - 0.55. When clay content is equal to sand porosity all pores of sand are

filled with clay, soil porosity is minimal and equal 0.16. Grains of sand and clay particles have very high resistivity in comparison with pore water resistivity. Line for sand in figure 1 is situated above and in parallel of water line and distance between these lines depends on sand porosity. Clay porosity is higher than sand porosity. That is why the line for pure clay is closer to water line (at high salinity). But the line for clay is parallel to water line only for high water salinity. For fresh water clay resistivity line is not parallel to water line and is below water line. This is result of the influence of electric double layer (EDL) in clay pores. Intermediate soil lines between pure sand and pure clay are between sand and clay for fresh water and distributed in accordance with soil porosity for high water salinity. That is why soil line for minimal porosity (0.16 for clay content 20%) is above all lines at salinity more than 5 g/l when the EDL influence is negligible. The difference between sand line and any line with some clay content shows the EDL influence on soil conductivity. The more is clay content the higher is EDL influence.

Using figure 1 we can estimate clay content in soil if we know soil resistivity and groundwater salinity (at full saturation). In reality sand line position depends on sand porosity and clay line position depends on cation exchange capacity (CEC) of clay. That is why more accurate clay content estimation we can obtain if we know sand component porosity and clay component CEC value, or if we use computer program which can estimate all above mentioned parameters.

In figure 2 the line for sand resistivity with porosity 55% equal a pure clay porosity is shown. This line can be considered also as line for clay without EDL and CEC influence. The difference between sand and clay lines depends on EDL influence and also on CEC values of clay. The main idea of figure 2 is to demonstrate only influence of different CEC values.

Estimation of petrophysical parameters on resistivity data

At SAGEEP conferences we presented resistivity technology for oil contamination study (Shevnin et al., 2004, 2005). Soil resistivity and groundwater salinity measurements were recalculated into petrophysical parameters: clay content, porosity and cation exchange capacity.

The advantage of using petrophysical parameters

- For uncontaminated soil petrophysical parameters (clay content, porosity and cation exchange capacity) estimated on resistivity are close to true petrophysical parameters, found with traditional methods in laboratory.
- For contaminated soils we receive anomalous parameters, but these parameters help to localize contamination.
- Joint usage of resistivity and petrophysical parameters helps receiving more detailed characterization of non-contaminated and contaminated soils.
- Petrophysical parameters have more separation ability to resolve clean and contaminated soil.

Mature oil contamination changes soil petrophysical parameters in such a way as it looks like an increase of clay content together with CEC of clay. We call this effect - quasi-clay. In table 2 there are some examples of quasi-clay appearance.

Table 2.: Clay content, estimated from VES resistivity and water salinity for some contaminated sites.

Site name	Background values, %	Anomalous values, %	Ratio
Paredon-31	40	100	2.5
Km-42	2	6	3
Km-124 Layer 1	20	50	2.5
Km-124 Layer 2	2.5	18	7.2
Km-124 Layer 3	2.5	22	8.8
Mecatepec	25	100	4

Comparison of two contamination indicators: clay content and superficial conductivity
- Sometimes it is difficult to explain that increase of clay content in contaminated zone isn't real, it is quasi-clay effect, created by biodegradation processes. Clay content is well known geological term. There is no real increase of clay content in contaminated site.
- Superficial (interfacial) conductivity is the term not so well known, and its usage is more close to real geoelectrical situation than usage of clay content.
- Quasi-clay is intermediate term related to both clay content and superficial conductivity.

Table 3.: Comparison between our approach and results of Abdel Aal et al. (2004)

Our approach	Abdel Aal et al., 2004 approach
DC resistivity method measures only real resistivity, which conductivity is the combination of electrolytic and superficial conductivities.	Spectral IP (SIP) method measures real and imagine conductivity component. Real component is a sum of electrolytic and superficial conductivities.
Clay mainly has superficial conductivity, which depends on the area between solid and liquid and also on EDL and CEC (electrical charges). In contaminated soil (including sandy soil) quasi-clay is appeared (apparent increase of clay content), due to physical - chemical changes caused by biodegradation. Increase of quasi-clay is followed by increase of CEC (like increase of surface and charges).	The relative increase of interfacial (or superficial) conductivity above electrolytic conductivity was found in experiment with SIP method. Interfacial electrical properties were modified due to microbial activity. An increase of surface area exerts a primary control on interfacial electrical properties. An additional factor is enhanced mineral weathering, which releases ions into solution increasing water conductivity.

What method or parameter is the best to detect contamination?

In this work we consider and compare several ideas: Resistivity and Induced Polarization methods, determination petrophysical parameters from resistivity, determination superficial conductivity (or resistivity) from clay content and CEC. Induced polarization is further development of resistivity method. It measures several parameters, including resistivity. But IP instruments cost more; IP field measurements are more complicated. We suppose that resistivity method with determination of petrophysical parameters can give valuable information. That is why we are trying to compare these two methods. The next question is comparison of different parameters estimated on resistivity: clay content, porosity, CEC, superficial resistivity. Below we are trying to estimate their separation index or resolution between clean and contaminated soil (figure 9).

Figure 3.: A – sand model; B – central part of sand model with biofilms on the surface of sand grains; C – model with biofilms on the surface of sand grains and inside pore space; D – model with oil emulsion in pore space, caused by surfactants.

Some models of contamination in pores

With the help of figure 3 we compare some possible models explaining quasi-clay and superficial conductivity increase in case of mature contamination.

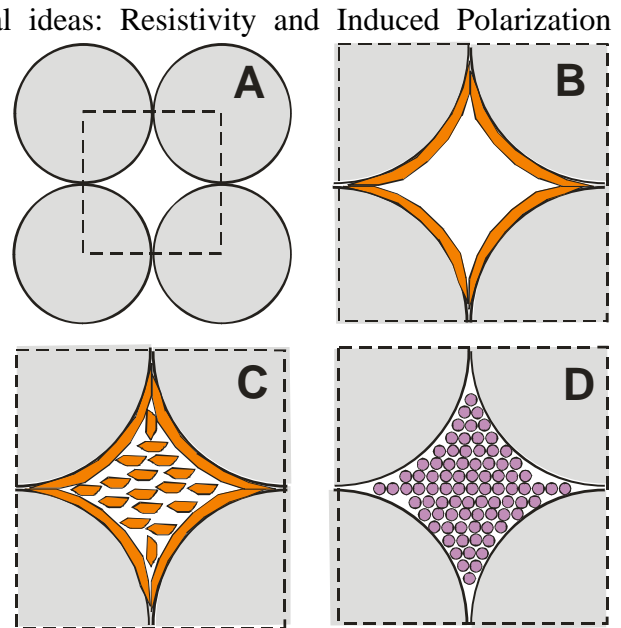If biofilms, which are products of biodegradations, are distributed on mineral grains

surface as in figure 3, B, then small biofilm thickness in comparison with capillary diameter can not noticeably change capillary conductivity. To obtain noticeable effect, biofilms should be distributed on mineral grains and in capillary volume (Fig.3, C). In this case the influence of EDL on all surfaces (grains and biofilms) would be noticeable. Another model (Fig.3, D) shows capillary path filled with oil products, separated into small drops under the influence of surfactants, produced by bacteria (Atekwana et al., 2001). Each drop has high resistivity, but spaces between them are very thin and influence of EDL is high. Is it possible that real situation can include combination of models C and D. The principal difference between models B and C (or D) is in pore radius and the grade of EDL influence.

Dependence of electrical conductivity (σ) of NaCl aquatic solution from a distance up to capillary wall.

Figure 4 shows the change of water conductivity in EDL. Conductivity in EDL for fresh water increases until 30 times (Fig.4, line for salinity 0.059 g/l). When all capillaries are fine, soil conductivity depends greatly on conductivity in EDL of capillaries. In case of wide capillaries EDL does not influence on soil conductivity.

Looking on fig. 2 we can conclude that sand and clay resistivities are equal at the same porosity at high salinity and different at low salinity due to superficial conductivity. Soil superficial conductivity depends on clay content in soil (or quasi-clay for contaminated soil), on cation exchange capacity and groundwater salinity. If we know these parameters we can determine superficial conductivity.

Superficial conductivity of soil is conductivity of the solution in clay (or quasi-clay) pores multiplied to clay content in soil. To estimate conductivity of water solution in clay pores, we need to use clay conductivity and divide it to clay porosity. We calculate clay conductivity theoretically like function of pore water salinity and cation exchange capacity (according to algorithm of Ryjov) (Ryjov and Sudoplatov, 1990).
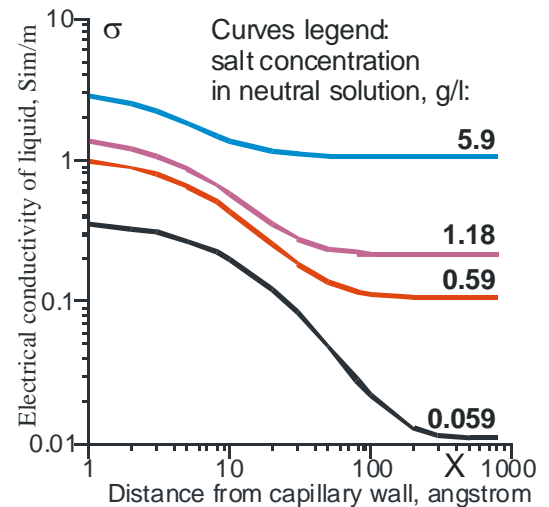

Figure 4.: Change of conductivity in electric double layer as function of the distance from the solid phase. (1 angstrom = 10^{-10} m, 100 Å=1 mkm), capillary radius for clay is 1-10 A, for sand - > 100 mkm.

In figure 2 dependence of clay resistivity versus water salinity is shown for different values of clay CEC. Using these data we can find dependence between clay conductivity and CEC for every salinity value to use it for clay conductivity determination. For practical application we use resistivity instead of conductivity.

Three steps of superficial resistivity calculation:

1. Calculation of $\rho_{Clay}(f(CEC, Salin.))$ using data presented in figure 2.

For example X=ln(CEC) and Y=ln(ρ_{Clay}): $\ln Y = a - b*X - c*X^2$ (1), where a, b, c – approximating coefficients, different for each salinity (see example in figure 5).
Equation for salinity 0.01g/l:
Y = 1.384397357 - 0.4938222434 * X - 0.05359104356 * pow (X, 2);   (1, A)
Equation for salinity 0.1g/l:
Y = 1.32372928 - 0.4454906043 * X - 0.06208606125 * pow (X, 2);   (1, B)
Equation for salinity 1 g/l:
Y = 1.051064232 - 0.3276935254 * X - 0.07539715295 * pow (X, 2).   (1, C)

$$\rho_{Clay} = \exp(Y) . \qquad (2)$$

2. Resistivity of the solution in clay pores is multiplication of clay resistivity on clay porosity

$$\rho_{W,Clay} = \theta_{Clay} \cdot \rho_{Clay}(f(CEC, Salin.)) \qquad (3)$$

3. Superficial resistivity is resistivity of the solution in clay pores divided on clay content.

$$\rho_{SC} = \frac{\rho_{W,Clay}}{C_{Clay}} = \frac{\theta_{Clay}}{C_{Clay}} \cdot \rho_{Clay}(f(CEC, Salin.)) \qquad (4)$$

Using these formulas we calculated superficial resistivity for several contaminated sites and compared new maps with maps of soil resistivity and petrophysical parameters.

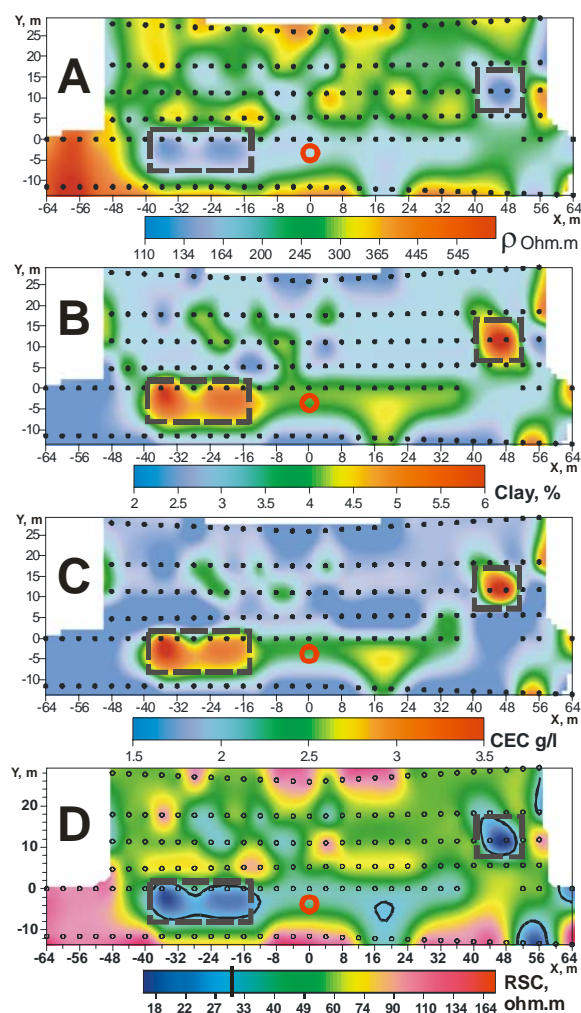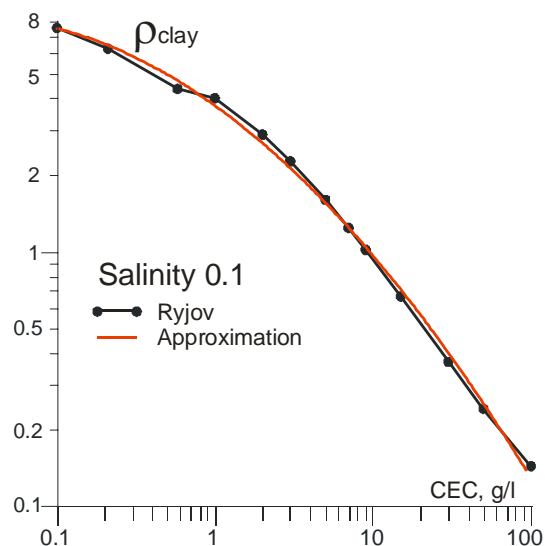## Practical examples of superficial conductivity

Figure 5.: Approximation of interrelation between clay resistivity and cation exchange capacity for definite salinity.

(resistivity) determination.

In each contaminated site we performed vertical electrical sounding measurements along profiles on multi-electrodes technology. Profiles were placed in studied area in such a way to have possibility to draw resistivity maps. Each profile data we interpreted using Res2DInv program (Loke and Barker, 1995) and then with the help of X2IPI and IPI software (Bobachev, 1994, 2003) we converted the data into data cube to present interpretation results as vertical cross-sections and maps for different depths. Normally maps have higher resolution to find fine anomalies from contamination (Shevnin et al., 2005). Interpreted resistivity data we recalculated into petrophysical parameters: clay-content, porosity, cation exchange capacity, taking into account groundwater salinity of the study area.

In figure 6 we present a series of maps for sandy aquifer of the site km 42 in Tabasco, Mexico. Survey was performed 9 months after the oil products leakage. Resistivity anomalies caused by contamination are weak, while petrophysical anomalies are more definite and have more contrast. Mean value of sand resistivity (saturated by water with resistivity 110 Ohm.m) is 280 Ohm.m. Superficial resistivity (RSC) estimated for the sand layer is in interval from 15 to 170 Ohm.m. In contaminated zone quasi-clay content is 5-6% in comparison with clean zone with 2-3% of clay.

In figure 7, B we presented additional map of

Figure 6.: Maps of resistivity (A), clay content (B), CEC (C) and superficial resistivity RSC (D) of sandy aquifer for the site km. 42.

normalized superficial resistivity. This parameter was estimated on the next formula:

$$Norm\_RSC = (RSC - BGV)/BGV \qquad (5)$$

BGV means background value of superficial resistivity. There isn't clear procedure to estimate background value. We used BGV=30 Ohm.m. Normalized superficial resistivity shows the total interval (between maximum and minimum, -0.9 - +2.6 in the case of fig.7, C) and probably should be useful at comparison of data for different contaminated site. On the histogram of normalized superficial resistivity (figure 7, C) the gray rectangular marks values interval for contaminated zone.

In figure 8 several maps for the first layer (0-1 m) in the site km124 in Tabasco, Mexico are presented. Soil resistivity changes from 30 to 330 Ohm.m. Superficial resistivity (RSC) of the same layer changes from 0.4 to 40 Ohm.m.

Outlines of contaminated zone are very similar for resistivity, clay content and superficial resistivity. For localization of contamination all 4 parameters are similar, but for explanation, as we think, superficial resistivity or quasi-clay concept is better.
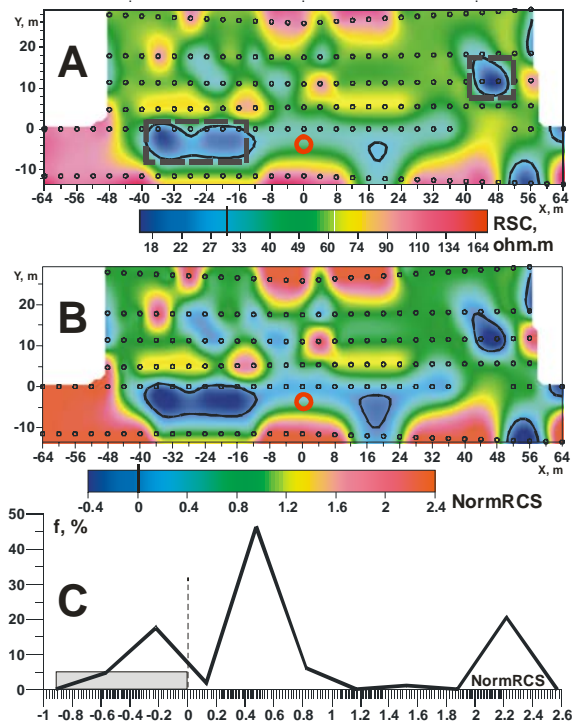

Figure 7.: Maps of RSC (A), normalized RSC (B) and histogram of normalized RSC (C).
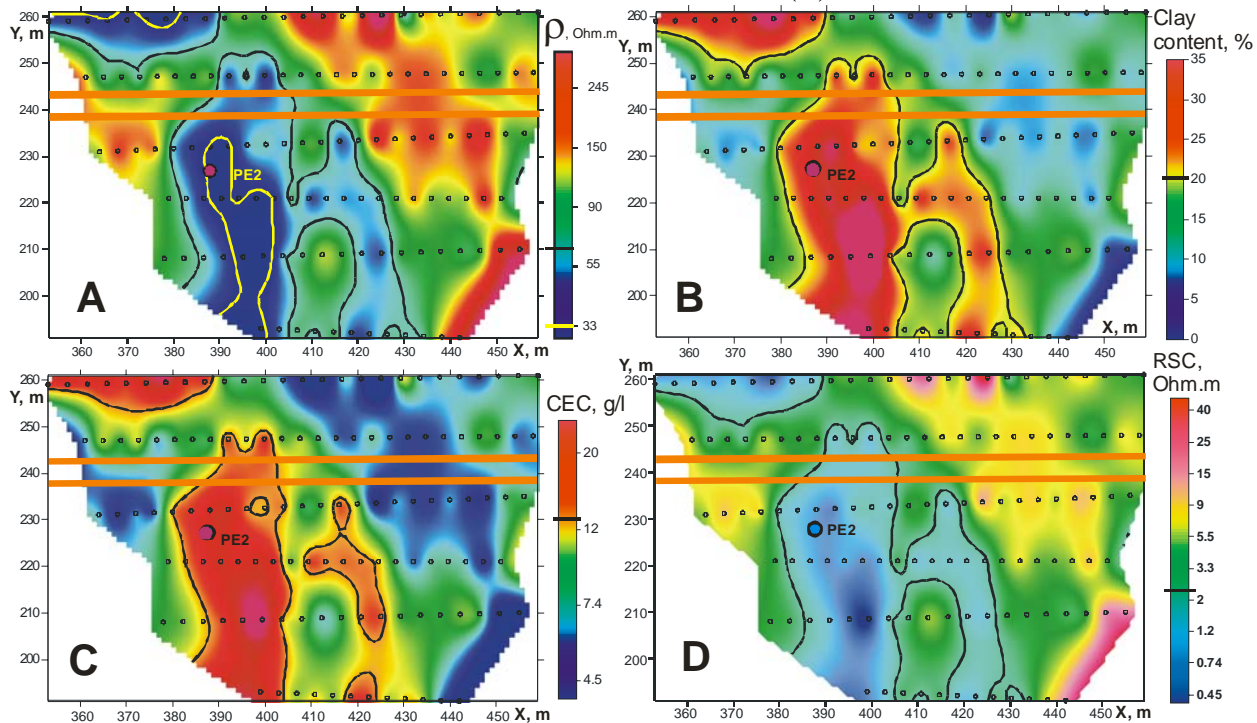

Figure 8.: Maps of resistivity (A), clay content (B), CEC (C) and RSC (D) for the site 124 km in Tabasco.

Resolution between contaminated and non-contaminated soil for different parameters.

In Shevnin et al. (2005) we proposed to use separation index between clean and contaminated soil to compare different parameters, estimated on the next formula: SI=dX/stnd   (6). Where dX is the distance between distribution maximums for clean and contaminated soil and stnd – is a standard.

Using this formula for the 1st layer of the site Km 124 we found SI values (Fig. 9) for resistivity SI= 2.52, for clay content – 4.36, for porosity – 3.02, for CEC – 2.46 and for superficial resistivity RSC – 6. For RSC calculation we used clay content and CEC. Probably because of that SI for RSC has greater value in comparison with clay content and CEC. We plan to continue calculate separation index for different contaminated sites with different geological situation.

In figure 10 maps of resistivity and superficial resistivity for the site Paredon in Tabasco, Mexico are shown. Resistivity for the contamination indicator layer changes from 1 to 54 Ohm.m. Superficial resistivity of the same layer changes from 0.14 to 55 Ohm.m.

Outlines of contaminated zones are very similar for resistivity and superficial resistivity. Zone of high superficial resistivity near the oil borehole corresponds (on our opinion) to fresh contamination due to nowadays oil leakage from closed borehole.

Figure 9.: Histograms and separation between clean and contaminated soil for several parameters.

In figure 11 several maps for the third layer (2-3 m) for the site Mecatepec in Veracruz, Mexico are presented. Soil resistivity changes from 4 to 400 Ohm.m. Superficial resistivity of the same layer changes from 0.08 to 150 Ohm.m.
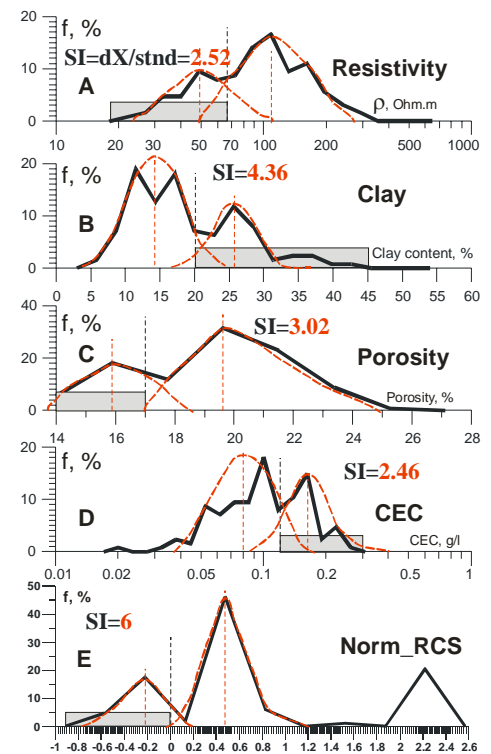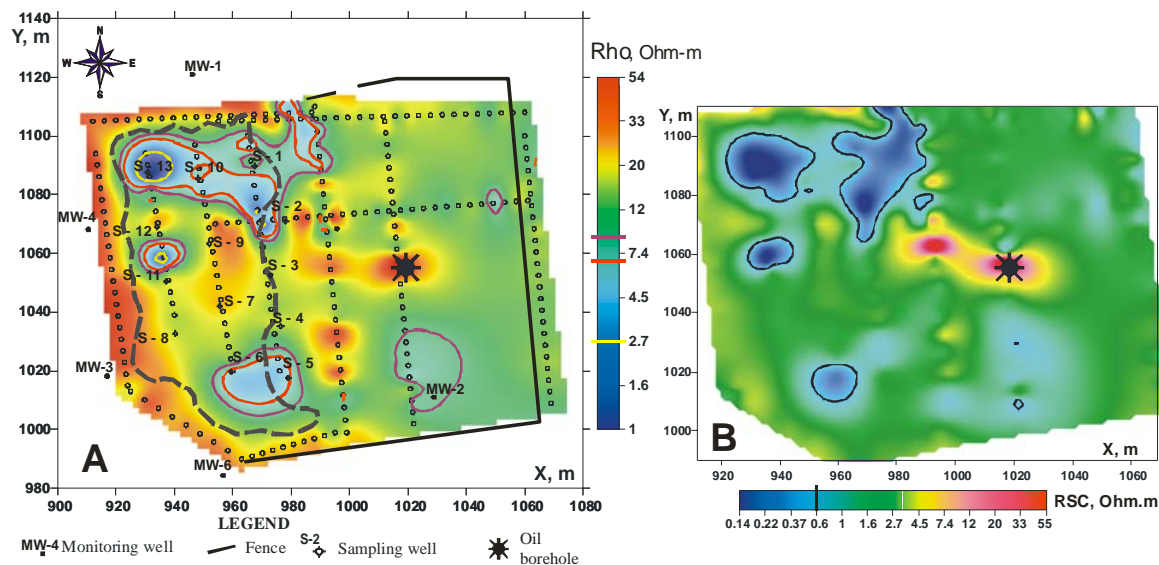

Figure 10.: Maps of resistivity and RSC for the site Paredon in Tabasco.
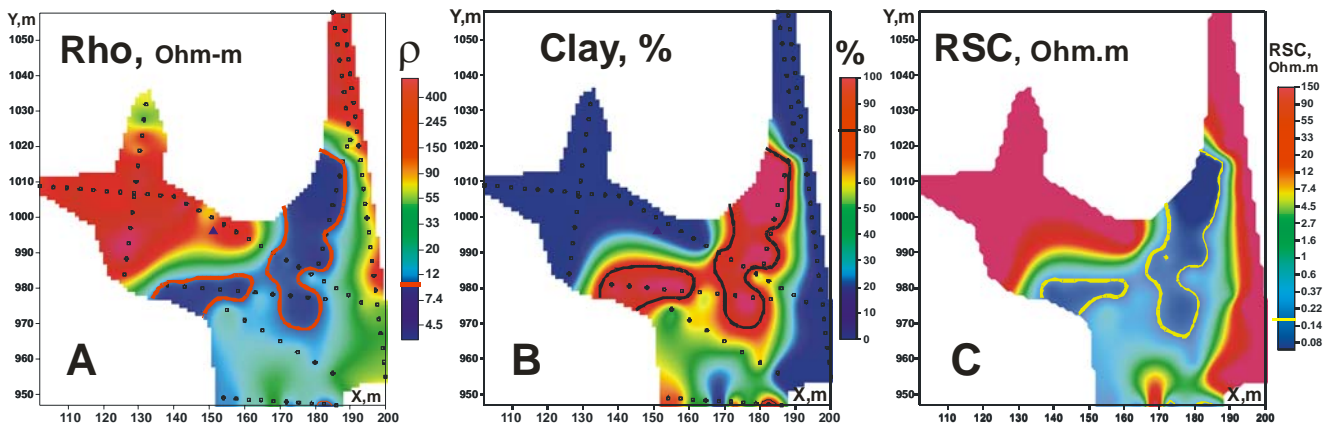
Figure 11.: Maps of resistivity (A), clay content (B) and RSC (C) for the site Mecatepec in Veracruz.

Table 4.: Comparison of ratio between resistivity and RSC values: ratio intervals and mean ratios.

Site	Interval Rho / RSC	Mean Rho / RSC
Paredon	2-30	7.5
Km 42	3-6	4.7
Km 124	10-33	22
Mecatepec	15-55	34

In table 4 values of ratio between resistivity and superficial resistivity (RSC) for different sites and their mean ratio are shown, to estimate the input of superficial resistivity created by soil lithology and biodegradation.

Conclusions

DC resistivity can give information about superficial conductivity, which is the main cause of resistivity anomalies and petrophysical anomalies at contaminated sites.

Superficial conductivity can be estimated on clay content and CEC values, received from soil resistivity and water salinity data.

Several parameters visualized as maps or cross-sections can characterize contamination of a site: resistivity, clay content, porosity, cation exchange capacity, superficial resistivity. An advantage of superficial resistivity is that it is the real cause of changes in other soil properties in contaminated area. This parameter probably has more resolution, taking into account separation index. Another possibility consists in using quasi-clay concept - that is such effect of contamination that is equivalent to the appearance of additional clay in soil. Quasi-clay allows explaining changes of soil resistivity, porosity, CEC and even changes of filtration coefficient. The disadvantage of the quasi-clay term is that real clay content does not change due to contamination.

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