

EFFECTS OF SOLUTION AND SOIL CHEMISTRY ON THE DISTRIBUTION OF OIL RESIDUAL IN PATAGONIAN SOIL

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Abstract— The distribution coefficient of oil residuals between water and the soil under equilibrium conditions is, in the case of Patagonian soils, strongly dependent on the clay contents and humidity of the soil. Other variables such as, the soil salinity and the environmental exposure conditions, also affect the interactions between the phases. The oil residuals are generally accompanied by water spills, that are extracted together with the oil and which, frequently, have high salinity. These salts stay on soils during long times and finally they became part of the soil. The resulting oil aqueous concentrations and the soil-water distribution ratio (K_d) may be strongly influenced by these factors. Based on experimental data of several parameters determined in different regional field samplings, a semi-empiric model was developed that allows prediction of the K_d dependence with the exposure time, the salinity of the equilibrium aqueous concentration and the clay contents of the soil. The Monte Carlo simulation was used in this work. Distribution values of soil conductivity, clays content, and assumed fixed values of the age of the oil spill were used in the model. A set of calculated values of K_d was obtained and the results show a distribution that was probabilistically analyzed. The K_d values increase with increasing age of spill and soil salinity and decrease when the salinity of the initial aqueous concentration is greater than the soil salinity. The determined parameters are useful for modeling of the environmental impact on polluted soils and for the design of remediation techniques.

Keywords— Oil Residuals, Distribution Coefficient, Salinity effect, Semi-empiric Model, Monte Carlo Simulation.

I. INTRODUCTION

The behavior of the compounds in aqueous phase is of critical importance in environmental studies, because solute transport and transformations processes are known to occur predominantly in water (Lane and Loehr, 1992; Manan, 1996). Bioavailability of oil components in contaminated soils is an important regulating factor for biodegradation rates. At lower concentrations, the

bioavailability was controlled by desorption/diffusion processes in water (De Jonge *et al.*, 1997).

Sorption to natural solids is an underlying process affecting the transport, degradation, and biological activity of organic compounds in the environment (Pignatello and Baoshan, 1996). The overall sorption capacity is influenced by the nature of the soil organic matter, the mineral composition, the soil moisture content, and the presence of solvent. In dry soils, sorption of nonpolar organics in dry soils is dominated by adsorption onto mineral surfaces, particularly clays (Karimi-Loftabad *et al.*, 1996; Nudelman *et al.*, 2000).

The simplest and most common method for mathematically expressing the distribution of an organic chemical between soil surfaces and water, is the sorption or distribution coefficient (K_d). Several researchers have found that if K_d is normalized on the basis of the soil's organic matter or organic carbon content, much of the variation observed among K_d 's over different soils can be eliminated (Dragun, 1998). That there are differences in the sorption of organic compounds on different fractions of organic matter is known (Luthy *et al.*, 1998). Others researchers have found that the extent of adsorption of nonionic organic chemicals onto soil particles surfaces is well-correlated with two empirical measurements of the organic chemical hydrophobicity: the water solubility and the octanol-water partition coefficient (Carmo, 2000; Xia, 2001). These available predictive expressions of K_d do not take into account the "salt" effect, the change of the adsorption coefficient due to a change in the salt content the water. The dependence of adsorption on salt content was approximated with a derivative of the Setschenow equation (Dragun, 1998).

The oil residuals, in exploration and production areas, are generally accompanied by water spill which is extracted together with the oil and, frequently, has similar salinity to sea water. These salts stay on soils during long times and they became part of the soil. Removal of salts from oil and salt contaminated soils before undertaking bioremediation may reduce the time required for bioremediation (Rhykerd, 1995).

The purpose of the present study was to examine the salinity effect on the estimation of the distribution coefficient of oil residuals, due to spills of different ages.

With the determined parameters, a semi-empiric model was developed to estimate K_d . The Montecarlo method was used to study the parametric sensitivity of K_d with respect to the contact time, clay content and salinity content.

II. METHODS

A. Sample Characteristics

Contaminated soil samples, product of oil spills in six different locations in the surroundings of Comodoro Rivadavia's city, were obtained. The oil spills are of different ages and environmental exposure conditions, and from different crude oil sources. In all cases, except for the samples 1 and 6, fertilization of the affected areas was carried out to improve the general conditions of the land. Table 1 summarizes some properties of the samples.

All samples were extracted from the surface, except in the case of sample 1 that was extracted from a depth of 20 cm to evaluate the most aged residuals. The contamination reached that depth, since on the same land more recent oil residuals were overturned. Therefore, the age of the old sample is approximate. The contaminated soils were air-dried, ground, and sieved with a 1.7 mm sieve. The total hydrocarbon determination was carried out by Soxhlet continuous extraction with methylene chloride for 24 h to 48 h, depending on the sample. After distillation of the methylene chloride, the oil concentration was analyzed using UV-Visible spectrophotometry (Nudelman et al., 2002).

Table 1. Description of oil contaminated soil samples

Sample	Oil spill age (years)	Conduc tivity ^{a,b}	Clay wt%	pH ^a	Total oil wt%	Aliph /Pol
1	20	9364	33	7.6	25.8	1.00
2	10	1633	22	7.4	16.6	1.16
3	6	646	9	8.0	8.7	1.20
4	3	618	8	7.4	8.6	0.38
5	3	387	12	7.6	9.3	0.58
6	2	426	16	6.8	16.1	0.50

^aextract 1:5 wt/wt, ^b $\mu\text{S cm}^{-1}$, 25°C.

The oil residues were analyzed by silica gel column chromatography, to separate group components (i.e. aromatic, aliphatic and polar compounds). The eluent solvents were hexane (30mL), benzene (30mL) and methanol/chloroform (1:1) (30mL). The portion remaining in the column contains the "asphaltenes" fraction (Nudelman et al., 2000).

B. Desorption Experiments

The desorption protocol was as follows. Aliquots of approximately 0.1 g of each soil sample were placed in 15 mL test tubes (at least by duplicate), 10 mL of pure water was added to each tube, making the soil solution ratio 1:100. Three experiments were carried out for each sample, two with calcium chloride and another without

it. Calcium chloride was added to each tube (1 or 2mL) to achieve a matrix of 0.01 N CaCl_2 to provide a initial ionic strength and minimize nonsettling particles (Lane and Loehr, 1992). The tubes containing the soil-solvent slurries were periodically shaken during seven days. The soil solution ratio and the total contact time were selected on the basis of previous studies. The tubes were sealed with plastic film and covered with aluminum foil to avoid light exposure and prevent photooxidation. After the required time had elapsed the supernatant solution was separated from the soil, and the solution centrifuged at 3000 rpm for 10 min. The supernatant was immediately withdrawn from each tube and the oil concentration was analyzed by using UV-Visible spectrophotometry. The oil concentration in the solid phase was determined by Soxhlet extraction and UV-Visible spectrophotometry. Desorption determinations were carried out at ambient temperature ($22\pm 3^\circ\text{C}$). The electric conductivity of the aqueous phase was measured at the beginning ($t=0$) and at the end of each experiment ($t=7$ days).

C. Theoretical Framework

The aqueous solubility of the organic compound in the presence of dissolved salts can be expressed by the Setchenow equation. (Schwarzenbach et al., 1995):

$$\log S_{w \text{ salt}} = \log S_w - K_s [\text{salt}] \quad (1)$$

where $S_{w \text{ salt}}$ is the molar solubility in the presence of salts, S_w is the molar aqueous solubility, K_s (M^{-1}) is the salting constant (which is a function of the hydrophobic surface area of the compound) and $[\text{salt}]$ is the molar concentration of dissolved salts. This relationship has been used, for example, for the calculation of aqueous solubility of organic pollutants as chloroform, lindane and vinyl chloride in sea water (Schwarzenbach *et al.*, 1995).

The dependence of adsorption on salt content was approximated with a derivative of the Setschenow equation,

$$\log (K_{d12} / K_{d11}) = K_s (I_2 - I_1) \quad (2)$$

where I_1 and I_2 are the aqueous salt concentrations, K_s is the Setschenow constant for a given salt (e.g. 0.16 L mol^{-1} for NaCl) and K_d is the adsorption coefficient (Dragun, 1998).

Eq. (2) is strictly valid only for a single solute, however, in this work the applicability of the equation is tested considering the oil residual as only one solute. The scope of the equation. will be also examined to evaluate the variation of K_d with the salinity. The aqueous concentration and the distribution coefficients, in this case are global values, and therefore they account for the interactions among the components in the mixture and for the overall interactions of each of them with the mineral matrix.

III. RESULTS AND DISCUSSION

The electric conductivity of the aqueous phase, C , is

a good measure of the total ionic strength (the ionic exchange characteristic of the soil plus the added calcium chloride). A relationship of the type of Eq. (2) can be formulated between C and K_d ,

$$\ln(K_d/K_d^0) = a(C - C^0) \quad (3)$$

where C is the electric conductivity of the aqueous phase ($\mu\text{S cm}^{-1}$), C^0 is the electric conductivity of the aqueous phase without Cl_2Ca , K_d (L kg^{-1}) is the distribution coefficient observed with C , K_d^0 is the distribution coefficient observed with C^0 and "a" ($\mu\text{S}^{-1}\text{cm}$) is the slope of the straight line. Fig. 1 shows the plotted data, which empirical correlation is given by Eq. (3). A similar relationship between Eqs. (2) and (3) is observed.

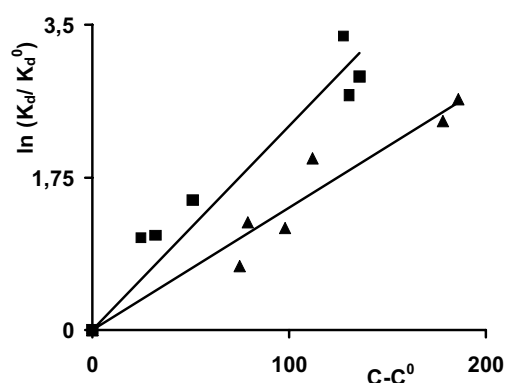


Fig. 1. $\ln(K_d/K_d^0)$ as a function of $(C - C^0)$, samples 1-3 (triangles) and samples 4-6 (squares). C and C^0 are the electric conductivities of the aqueous phases, with and without Cl_2Ca , respectively.

Samples 1-6 can be gathered in two groups: those with a ratio of Aliph/Pol (Aliphatic Groups/Polar Groups) near to 1 (samples 1-3) and those with ratios Aliph/Pol near to 0.5 (samples 4-6). The ratios are showed in Table 1. According to the model, an increase of sorption is observed when the ionic strength of the aqueous phase increases. The observed increase of K_d with the ionic strength agrees with the distributive behavior of the nonionic compounds depending on the changes in salinity (Young, 1992; Dragun, 1998). The slope of the straight line "a", is $(1.33 \pm 0.05) 10^{-2} \mu\text{S}^{-1}\text{cm}$, for residuals with ratios Aliph/Pol near to 1 (samples 1-3), and $(1.92 \pm 0.26) 10^{-2} \mu\text{S}^{-1}\text{cm}$ for ratios Aliph/Pol near to 0.5 (samples 4-6). The regression values are $r^2 \geq 0.923$ in both cases. As it is observed for samples 1-3, an increase of the ratio Aliph/Pol is expected with age because these residuals have a higher hydrophobic behavior due to the loss of polar components with time. The increase of the slope "a" for samples 4-6 implies a high salinity effect on K_d , in agreement with the relative increase of polar compounds when the age decreases.

Prediction of the K_d Dependence

A semi-empiric model was developed that allows prediction of K_d as a function of the exposure time, the

salinity of the equilibrium aqueous concentration and the soil clays content. The last variable was included because previous studies showed an important dependence of K_d with the clays soil content (Karimi et al., 1996), e.g. $K_d (\text{L kg}^{-1}) = 8.26 + 3.04 10^{-2} \% \text{clay}$, for dry soils, where $\% \text{clay}$ are the soil clay contents ($\% \text{wt/wt}$). It is a correlation of experimental data obtained in organic phase (Nudelman et al., 2000).

The relationship (straight line) between the calculated (with the model) and the measured values (experimental data) of $\ln K_d$, has a slope equal to 0.994 ($r^2 = 0.884$). This slope indicates that $\ln K_d$ can be estimated with an error $< 6\%$. Although the correlation coefficient is poor, it can be considered that a good adjustment has been achieved, taking into account the diversity in the environmental conditions, and the sources and history of the residuals.

Table 2. Simulations for assumed distributions of C_i , clays soil contents and C_s

Variable, distribution	Simulation				
	1	2	3	4	5
C_i , normal	X=300 $\sigma=60$	X=300 $\sigma=60$	X=300 $\sigma=60$	X=300 $\sigma=60$	X=500 $\sigma=50$
Clay, normal	X=50 $\sigma=15$	X=50 $\sigma=15$	X=10 $\sigma=5$	X=85 $\sigma=5$	X=50 $\sigma=15$
	X=600 $\sigma=100$	X=2500 $\sigma=80$	X=600 $\sigma=100$	X=600 $\sigma=100$	X=600 $\sigma=100$

X = mean, σ = standard deviation

To evaluate the sensitivity of the model to variations in the main factors involved in the prediction of K_d , the Monte Carlo simulation was used. Data of soil electric conductivity C_s , clays soil content ($\% \text{wt/wt}$) and initial electric conductivity of the aqueous phase C_i were generated, according to the distributions assumed in the Table 2 (five different simulations). Each simulation described in this paper was the result of 100 repetitions. With the object to evaluate low, medium and high spill age, C , K_d^0 and K_d have been calculated for oil residuals with spill age equal to 2, 10 and 20 years.

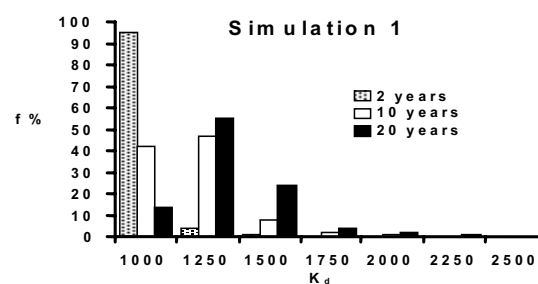


Fig. 2. Histograms showing results from Simulation 1. (f% : percentage frequency)

Simulation 1. The results are shown in the Fig. 2. The aqueous salinity is less than the soil salinity. This situation could correspond to rain water that has increased its salinity during its superficial run-off. Mean values of electric conductivity have been assumed for soil salinity, according to regional data. The values of

K_d ($L\ kg^{-1}$) are ≤ 1000 for 2 year-old residuals (95%), while only 42% and 15% present these values for 10 and 20 years-old residuals, respectively. When the age of the spill increases, the maximum frequencies shift to higher values of K_d .

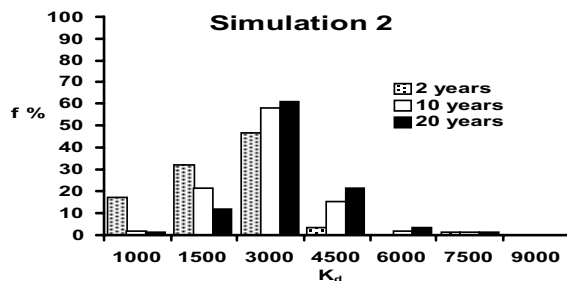


Fig. 3. Histograms showing results from Simulation 2. (f% : percentage frequency)

Simulation 2. The results are shown in the Fig. 3. A higher electric conductivity for the soil has been assumed. When the soil salinity is greater than the aqueous salinity, K_d ($L\ kg^{-1}$) increases and the maximum frequencies show at $1500 \leq K_d \leq 3000$, for all the samples. Therefore, the age of spill is a secondary factor and the values of K_d would be mainly affected by the soil salinity.

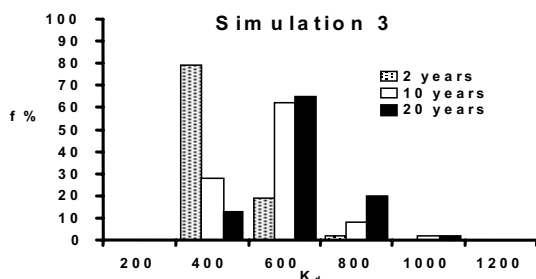


Fig. 4. Histograms showing results from Simulation 3. (f% : percentage frequency)

Simulation 3: The results are shown in the Fig. 4. In this case, the assumed mean value and standard deviation for C_s corresponds to regional sand-clay soils. It can be observed a decrease of K_d , due to the small clay soil content and a marked effect of age.

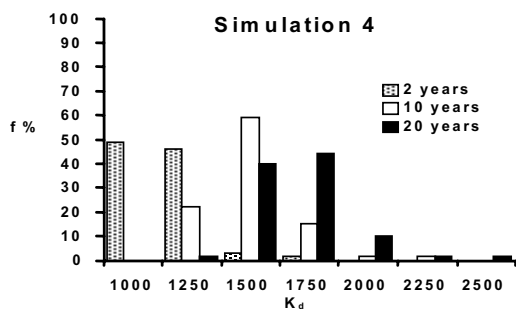


Fig. 5. Histograms showing results from Simulation 4. (f% : percentage frequency)

Simulation 4. The results are shown in the Fig. 5. It

has been assumed the C_s mean value and the standard deviation corresponding to regional clay soils. An increase in K_d , due to the high clay soil content can be observed. The distribution shows a bigger dispersion of the values as a function of the age.

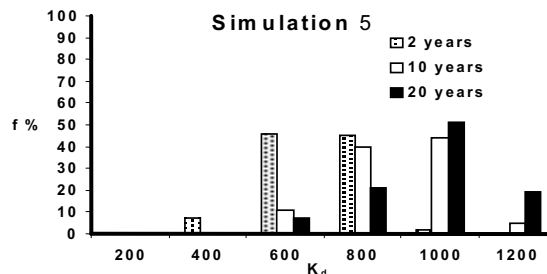


Fig. 6. Histograms showing results from Simulation 5. (f% : percentage frequency)

Simulation 5. The results are shown in the Fig. 6. For the initial aqueous phase salinity, a high mean value and standard deviation of C_i have been assumed. This situation could correspond to oil residuals that are accompanied by water spills, which are extracted together with the oil, which frequently, have salinity similar to sea water. When the initial aqueous phase salinity is greater than the soil salinity, a decrease in K_d is observed: $300 \leq K_d \leq 1200$ for all the samples.

IV. CONCLUSIONS

The increase of K_d with increasing soil salinity (simulation 2), would imply a high degree of oil sorption under these conditions. This would agree with the observation that, when the soil salinity increases, the salinity of the equilibrium aqueous phase also increases and, therefore, the oil solubility decreases (Schwarzenbach *et al.*, 1995). On the other hand, this effect is more important than the age. This same conclusion arises from the observation of a decrease in K_d when the initial aqueous phase salinity increases (simulation 5). Under these conditions the equilibrium aqueous phase salinity decrease (due to the adsorption of ions by soil) and this would imply an increase of the oil solubility in relation to the simulation 1.

An increase in K_d when increasing age of the residual, has been observed in all the simulations. However, the equilibrium aqueous phase salinity minimizes this effect, while the clays content makes the differences more evident (simulation 3 and 4). This is in agreement with our recent observations (Nudelman *et al.*, 2000), that the increase of K_d with the clays content could, in principle, be attributed to an increase in the sorption area. Since a differential uptake is observed for the different fractions, this is interpreted as an indication of a strong specific interaction among polar components of the sorbate and the clays.

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Received: November 15, 2002.

Accepted for publication: September 1, 2003.

Recommended by Editor A. Bandoni.