

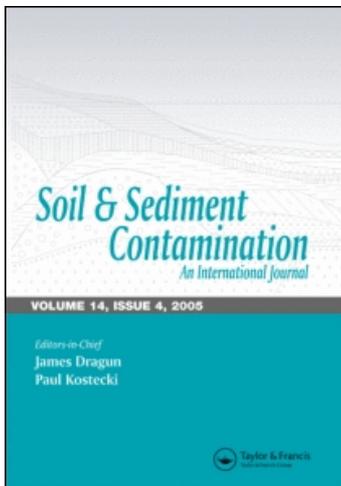
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Impact of Crude Oil Weathering on the Calculated Effective Solubility of Aromatic Compounds: Evaluation of Soils from Ecuadorian Oil Fields

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Effective solubility (Es) is the maximum dissolved concentration of a compound at equilibrium between an aqueous and organic phase. Published evaluations of crude oils suggest that the Es of only the most soluble aromatic compounds exceeds health-based drinking water goals. But because Es is a function of the concentration of a compound in the oil phase, it changes with weathering. The objective of this study was to evaluate weathering's impacts on the Es of aromatic hydrocarbon compounds. The Es of 20 aromatic hydrocarbons was calculated for Ecuadorian crude oil and 734 oiled soil samples collected in Ecuador. For the crude oil, the Es of mono-aromatic compounds exceeded health-based drinking water goals, while there were no exceedances for any polycyclic aromatic hydrocarbon (PAH). For the soil, the Es of benzene exceeded the health-based drinking water goal in nine (1.2 percent) of the 734 samples. There were no other exceedances. To further evaluate the impact of weathering, two concepts are introduced. The weathering index describes the extent of weathering of the bulk oil phase, while the concentrating factor is the relative change in concentration, and hence Es, of individual compounds. The weathering index and concentrating factor were calculated for 107 soil samples. The weathering index evaluation indicated that the oil associated with the soil was highly weathered. This reduced the Es of the mono-aromatic compounds because they were depleted to a greater extent than the bulk oil. Although the concentrating factor of some PAHs was as high as 256, their Es was still well below health-based drinking water goals. These results indicate that because of rapid weathering of the more soluble aromatics and the low effective solubility of larger PAHs, Ecuadorian crude oil impacted soil is unlikely to result in dissolved concentrations that exceed health-based drinking water goals.

Keywords aromatic hydrocarbons, effective solubility, oiled soil, weathering

Introduction

Assessment and remediation of crude oil-impacted sites should focus on risk identification and elimination. A common pathway of interest is the ingestion of dissolved organic compounds from groundwater. The maximum dissolved concentration of a contaminant resulting from oil/water partitioning is known as the compound's effective solubility (Es). The Es of a compound in groundwater resulting from crude oil contamination is limited by the compound's solubility and by its oil phase concentration (mg compound/kg oil [O'Reilly et al., 2001]). An evaluation of the concentration of 20 aromatic compounds

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of concern (benzene, toluene, ethylbenzene, xylene, [BTEX]) and the 16 EPA priority pollutant polycyclic aromatic hydrocarbons [PAHs]) in 60 crude oils from around the world indicates that the Es of three compounds (benzene, toluene, and naphthalene) can exceed conservative health-based drinking water goals (Kerr et al., 2001; O'Reilly et al., 2001). However, little work has focused on how weathering of oil may affect the Es of the more recalcitrant compounds.

The term "weathering" generically includes processes such as volatilization, dissolution, and biodegradation. In the environment, a compound's oil phase concentration will be influenced by the degree of weathering of the oil (Rutherford et al., 1997; Ortiz et al., 1999; Wang et al., 1998). If a specific compound is more subject to volatilization or degradation than bulk oil, its oil phase concentration and Es will decrease. The opposite is true if a compound weathers to a lesser extent than the oil (Jonker et al., 2006; Di Toro et al., 2007). Because of the volatility and biodegradability of BTEX, this differential weathering should result in a lower risk for oily soil than for fresh oil (Salanitro et al., 1997). It is unknown, however, if weathering can cause the Es of the more recalcitrant PAHs to exceed health-based goals.

To test the effect of weathering on the Es of the more recalcitrant aromatic compounds, the concentrations of the 20 aromatic compounds in 734 soil samples taken from an oil production area in Ecuador were evaluated. The Es of each of the compounds was calculated for fresh crude oil and for each soil sample. The risk to groundwater was assessed by comparing each calculated Es to health-based drinking water goals (WHO, 2004; U.S. EPA, 2003a; U.S. EPA, 1996a; DE 2144). Finally, the change in oil phase concentration and Es as a function of weathering was determined for the 107 soil samples with total petroleum hydrocarbon concentrations exceeding 1,000 mg/kg.

Theory

Effective Solubility

The effective solubility of a compound present in an oil phase is represented mathematically by a modified version of Raoult's Law (Shiu et al., 1988; Spence et al., 2001; Devlin and Barbaro, 2001; Burris et al., 2006):

$$E_s = x_a * S_a \quad (1)$$

where:

E_s = effective solubility of the compound (mg/L),

x_a = the mole fraction of the compound in the organic phase (mol compound/mol organic phase)

S_a = aqueous solubility of the pure compound in water (mg/L).

For compounds that are solid at 25°C, such as certain PAHs, the sub-cooled liquid solubility should be used to correct for enthalpy differences between dissolution of a compound from a solid and liquid (Peters et al., 1997).

Alternatively, E_s can be described as a function of the compound's oil:water partition coefficient (Spence et al., 2001; Jonker et al., 2003):

$$E_s = C_{a,oil}/K_{oil} \quad (2)$$

where:

$C_{a,oil}$ = concentration of compound 'a' in the oil (mg/kg oil)

K_{oil} = the oil:water partition coefficient for compound "a" ([mg/kg oil]/[mg/L water])

Predictions of water concentrations of individual aromatic compounds based on Raoult's Law and oil-water partitioning compare well with measured concentrations (e.g., Lane and Loehr, 1995; Ghoshal and Luthy, 1996; Devlin and Barbaro, 2001; Eberhardt and Grathwohl, 2002). Lane and Loehr (1995) reported that predicted E_s values for PAHs from both Raoult's and the K_{oil} partitioning method were generally within one order of magnitude of actual measured concentrations. Eberhardt and Grathwohl (2002) found good correlation between predicted aqueous concentrations of BTEX and PAHs (using Raoult's law) and measured values.

Weathering Index

One method used to assess the extent of weathering of the bulk oil phase is to evaluate the change in the oil phase concentration of a compound that is resistant to weathering (Douglas et al., 1996). By assuming the mass of the stable compound remains constant, an increase in its oil phase concentration is attributable to the loss of other oil constituents, so that

$$W_x = 1 - (SC_f/SC_w) \quad (3)$$

where:

W_x = weathering index

SC_f = oil phase concentration of the stable compound in fresh oil (mg SC/kg oil)

SC_w = oil phase concentration of the stable compound in weathered oil (mg SC/kg oil)

Using this method, fresh oil has a weathering index of 0, while the weathering index approaches 1.0 as the oil weathers.

Concentrating Factor

We used the concept of the concentrating factor as an indicator of how weathering changes the oil phase concentration of individual compounds. The concentrating factor is calculated by:

$$F_c = (C_w^a/C_f^a) \quad (4)$$

where:

F_c = concentrating factor

C_w^a = oil phase concentration of compound "a" in weathered oil (mg a/kg oil)

C_f^a = oil phase concentration of compound "a" in fresh oil (mg a/kg oil)

The concentrating factor is less than one if the concentration of the individual compound is less in weathered oil than in fresh oil, and greater than one if the concentration is greater in weathered oil than in fresh oil. Once calculated, the concentrating factor can be compared to the ratio between the fresh oil effective solubility of a compound and its health-based drinking water goal. Weathering is expected to result in an elevated risk only if it causes the E_s to exceed the health-based drinking water goal.

Methods

Sample Collection and Analysis

Crude oils were collected from eight areas within northeast Ecuador's oil production region. As part of site assessment activities, 734 soil samples were collected from 32 oil well sites and 10 production stations. Additionally, 171 groundwater samples were collected from shallow domestic water supply wells and from temporary sampling points located near the oil wells and production stations.

After collection, samples were shipped to a commercial laboratory facility in the United States for chemical analysis following standard quality assurance procedures as described by EPA Method 800B for sample preservation and holding times (U.S. EPA, 1994). BTEX was measured by gas chromatography/mass spectrometry (GC/MS) using EPA Method 8260, while PAHs were measured by GC/MS using EPA Method 8270 (U.S. EPA, 1994). The soil samples were also measured for total petroleum hydrocarbon (TPH) by EPA Method 8015 (U.S. EPA, 1994). The results were reported as gasoline range organics (GRO) (C6–C10) and diesel range organics (DRO) (>C10–C25). The total TPH was reported as the sum of the GRO and DRO results.

Effective Solubility

Equation 1 was used to determine the E_s of compounds in fresh crude oil ($E_{s_{oil}}$). For soil samples, the mole fraction, x_a , of each compound was calculated assuming the soil TPH was the oil phase such that:

$$x_a = (C_{soil}^a / C_{soil}^{TPH}) * (MW_{TPH} / MW_a) \quad (5)$$

where:

C_{soil}^a = concentration of compound "a" in soil (mg a/kg soil)

C_{soil}^{TPH} = concentration of TPH in soil (mg TPH/kg soil)

MW_{TPH} = average molecular weight of the TPH (g/mol)

MW_a = molecular weight of compound "a" (g/mol).

The average molecular weight of TPH depends on the source of the petroleum, and ranges from 200 to 250 g/mol (Spence et al., 2001). In this study, a molecular weight of 200 g/mol was assumed for both the fresh and weathered crude oil.

Weathering Index

The petroleum biomarker hopane was used as the stable compound for the weathering index determination (Douglas et al., 1996). Hopane data were available for 107 of soils samples with sufficient TPH for this analysis (>1000 mg TPH / kg). A weathering index was calculated for each oil sample using Equation 3, such that:

$$W_x = 1 - (HP_O / HP_S) \quad (6)$$

where:

W_x = weathering index

HP_O = concentration of hopane in fresh oil (mg HP/kg fresh oil).

HP_S = oil phase concentration of hopane in soil TPH (mg HP/kg soil)/(mg TPH/kg soil)

Concentrating Factor

Because trace background PAHs can interfere with the concentrating factor determination at low oil concentrations (Boehm et al., 2008), the 107 soil samples with TPH exceeding 1,000 mg TPH/kg soil were selected for this evaluation. The concentrating factor was calculated for the aromatic compounds of interest in the 107 samples based on the results of soil analysis using Equation 4. The concentration of compounds in the weathered oil (C_w^a) was calculated by

$$C_w^a = (C_{\text{soil}}^a / C_{\text{soil}}^{\text{TPH}}) * 10^6 \quad (7)$$

where:

C_w^a = concentration of “a” in weathered oil (mg a / kg TPH)

C_{soil}^a = concentration of compound “a” in soil (mg a/kg soil)

$C_{\text{soil}}^{\text{TPH}}$ = concentration of TPH in soil (mg TPH/kg soil)

If a compound was present in the fresh oil, but not detected in a soil sample, the concentrating factor was zero. Because calculating the concentrating factor requires knowledge of a compound’s concentration in fresh oil, it could not be determined for anthracene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene, because they were not detected in most of the eight fresh oil samples.

Health-Based Drinking Water Goals

Calculated Es values were compared to health-based goals for safe drinking water (Table 1). The health-based goals were determined from the World Health Organization’s (WHO’s) Guidelines for Drinking Water Quality (WHO, 2004), EPA’s maximum contaminant levels (MCLs) (U.S. EPA, 2003a), and the Ecuador 2144 drinking water standards for Ecuador (DE 2144). The lowest of the values from the three sources was used for each compound. If a value was not available from the three listed sources, the health-based goals were derived using the “water health-based limits” listed in EPA’s soil screening level (SSL) guidance (U.S. EPA, 1996a). For comparative purposes, a target risk factor of 10^{-5} was applied to the soil screening level guidance values for compounds with cancer endpoints (e.g., benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene).

Results

Analytical Results

Table 1 lists the aromatic compounds evaluated in this study, the maximum oil phase concentrations in fresh crude oil, and the calculated Es values for fresh oil and oiled soil samples. Fifteen of the 20 aromatic compounds analyzed were found in all eight of the fresh Ecuadorian crude oils (exceptions were acenaphthylene, anthracene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene, which were measured in two or fewer of the 8 oil samples). For compounds detected in each of the eight oils, the maximum concentration did not exceed the minimum concentration by four times or the mean by two times. The mean oil concentration of each compound was used as the C_{oil}^a to determine the weathering index and concentrating factors for the soil samples.

TPH concentrations in the 734 soil samples ranged from undetected to 96,000 mg/kg. Only 4 of the samples exceeded 28,000 mg/kg. For the 107 samples with sufficient TPH for

Table 1
Maximum oil phase concentrations and health-based goals for the aromatic hydrocarbons examined

Compound	Aqueous Solubility, ¹ S _a ¹ mg/L	Sub-cooled Liquid Solubility, S ₂ ² mg/L	Max Oil Phase Conc. (mg/kg)	HBG ³ (mg/L)	Es _{oil} (Max) mg/L	Es _{oil} > HBG	Es _{soil} (Max) (mg/L)	Es _{soil} > HBG	# Soil Samples > HBG
Benzene	1.75E + 03	1.75E + 03	1,100	0.005	5.07	Y	0.548	Y	9
Toluene	5.26E + 02	5.26E + 02	3,600	0.7	4.11	Y	0.0892	N	0
Ethylbenzene	1.69E + 02	1.69E + 02	1,400	0.3	0.45	Y	0.0511	N	0
Xylene	1.85E + 02	1.85E + 02	5,300	0.5	1.8	Y	0.288	N	0
Naphthalene	3.10E + 01	1.03E + 02	560	1.0	0.09	N	0.374	N	0
Acenaphthylene	3.93E + 00	1.79E + 01	5.8	2.0	0.00014	N	0.00187	N	0
Acenaphthene	4.24E + 00	2.12E + 01	20	2.0	0.00056	N	0.00416	N	0
Fluorene	1.98E + 00	1.24E + 01	53	1.0	0.00079	N	0.00647	N	0
Anthracene	4.34E - 02	4.34E + 01	1	10	5.00E-05	N	0.00621	N	0
Phenanthrene	9.94E - 01	3.68E + 00	150	1.0	0.00085	N	0.00712	N	0
Fluoranthene	2.60E - 01	1.63E + 00	4	1.0	4.16E-06	N	0.00102	N	0
Pyrene	1.35E - 01	1.04E + 00	12	1.0	1.96E-06	N	0.00153	N	0
Benz[a]anthracene	9.40E - 03	7.23E - 02	3.1	0.001	6.38E-07	N	5.79E - 06	N	0
Chrysene	1.60E - 03	1.60E + 00	22	0.1	3.18E-06	N	0.00096	N	0
Benzo[b]fluoranthene	1.50E - 03	3.85E - 02	3.1	0.001	7.00E-08	N	3.26E - 06	N	0
Benzo[k]fluoranthene	2.60E - 04	2.00E - 02	1.4	0.01	6.83E-07	N	8.42E - 07	N	0
Benzo[a]pyrene	1.62E - 03	5.40E - 02	1.8	0.0002	7.71E-08	N	1.80E - 05	N	0
Indeno[1,2,3-cd]pyrene	2.20E - 05	5.50E - 04	0.006	0.001	2.62E-07	N	2.32E - 08	N	0
Dibenz[a,h]anthracene	2.49E - 03	6.23E - 01	0.61	0.0001	2.73E-07	N	1.06E - 05	N	0
Benzo[ghi]perylene	5.50E - 04	1.38E - 01	2.5	1.0	7.71E-10	N	1.47E - 05	N	0

Note: Es—maximum effective solubility.

Y—yes.

N—no.

Max—maximum.

Conc.—concentration.

¹Pure compound solubility (S_a) from U.S. EPA (1996a)

²Sub-cooled Liquid Solubility, calculated by multiplying the pure compound solubility by the activity factor from Peters et al. (1997). This value is used as S when calculating the effective solubility.

³Health-based drinking water goals (HBG) are defined by the World Health Organization's Guidelines for Drinking Water Quality (WHO, 2004), EPA's maximum contaminant levels (U.S. EPA, 2003a), Ecuador 2144 drinking water standards (DE, 2144), or as derived from EPA's soil screening guidance water health based limits, using a 10⁻⁵ target risk for compounds with cancer endpoints (U.S. EPA, 1996b).

concentrating factor determination, BTEX concentrations ranged from undetected to 90.2 mg/kg and individual PAH concentrations ranged from undetected to 44 mg/kg.

Two of the 171 groundwater samples contained aromatic concentrations exceeding health-based drinking water goals. One sample had a concentration of 0.014 mg/L benzene, which is about three times the goal of 0.005 mg/L. Another sample had an estimated (below the method reporting limit) dibenz[a,h]anthracene concentration of 0.0002 mg/L.

Effective Solubility

In fresh crude oil, the predicted effective solubility of BTEX exceeded the health-based drinking water goals (Table 1). The health-based drinking water goals were compared to the calculated E_s for fresh oil ($E_{s_{oil}}$) and to the calculated E_s for oiled-soil samples ($E_{s_{soil}}$); a “yes” (Y) or “no” (N) is indicated depending on whether the E_s values were greater than or less than the health-based drinking water goal. The E_s of the remaining aromatic compounds were below these goals. Only 12 of the 734 soil samples analyzed had detectable benzene concentrations. The E_s of benzene exceeded the health-based drinking water goal for 9 of the 12 soil samples. Those 9 soil samples were collected from 5 of the 10 production stations, but not from any of the 32 individual wells. There were no calculated exceedances for any of the other compounds in oiled soil samples. Naphthalene was the only PAH with an effective solubility within one order of magnitude of the health-based drinking water goal.

Weathering Index and Concentrating Factor

To summarize the range and distribution of weathering indexes, quartile values for the data set were determined. While the weathering index ranged between 0.34 and 0.97, it exceeded 0.80 in 75 percent of the samples, 0.87 in half the samples, and 0.92 in 25 percent of the samples, indicating extensive weathering in most of the samples. Only one sample had a weathering index below 0.50. There was no relationship between the weathering index and either the TPH ($R^2 < 0.01$) or log TPH ($R^2 = 0.01$) concentration.

The range and distribution of concentrating factors for each compound are summarized in Figure 1 and Table 2. Both the median and maximum concentrating factor values trend for the most part, with molecular size. That is, as the number of rings increases from 1 (i.e., BTEX compounds) to 6 (i.e., benzo[ghi]perylene) the concentrating factor increases, indicating greater increases in concentrations of higher molecular weight PAHs in weathered samples compared to the changes in the concentrations of lower molecular weight compounds. There appears to be a plateau effect for compounds with four or more aromatic rings. The single-ringed BTEX compounds were not detected in most of the soil samples. The maximum concentrating factor for the BTEX compounds was less than 1 (e.g., maximum concentrating factor value for benzene was 0.2) indicating that BTEX, as expected, weathered at a significantly higher rate than the bulk TPH in soil. For naphthalene (two rings), the concentrating factor values ranged from less than 1 to less than 6. A third quartile value of 0.7 indicated that naphthalene typically weathered faster than the bulk oil. For the three-ringed PAHs (acenaphthene, fluorene, phenanthrene), the maximum concentrating factor ranged from about 9 to 13, and the median ranged between 2 and 3, indicating that the compounds weathered more slowly than the oil. While the maximum concentrating factor for two of the 4, four-ringed PAHs (i.e., fluoranthene and pyrene) was about 250, the median for all four analytes was between 5.5 and 8. For the

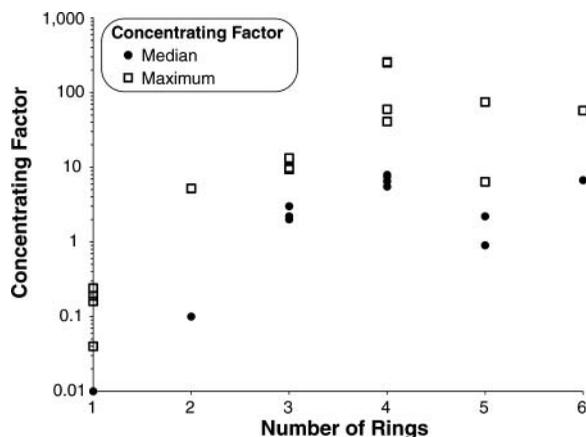


Figure 1. Median and maximum concentrating factor values for individual analytes (BTEX and PAHs) versus number of aromatic rings.

five-ringed PAHs the maximum concentrating factor ranged from 6 to 75, with a range of the median from about 1 to 2.

The last two columns in Table 2 provide critical data. The Fc-maximum column presents the maximum concentrating factor value calculated for each analyte, while the

Table 2

Range and quartile distribution of concentrating factors (Fc) calculated for each aromatic hydrocarbon

Compound (# of rings)	Fc— Minimum	Fc— 25th%	Fc— Median	Fc— 75th%	Fc— Maximum	HBG/ (Es _{oil})
Benzene (1)	0.0	0.0	0.0	0.0	0.2	0.0
Toluene (1)	0.0	0.0	0.0	0.0	0.04	0.2
Ethylbenzene (1)	0.0	0.0	0.0	0.0	0.0	0.7
Xylene (total) (1)	0.0	0.0	0.0	0.0	0.2	0.3
Naphthalene (2)	0.0	0.0	0.1	0.7	5.2	11
Acenaphthene (3)	0.0	0.9	2.0	3.1	9.4	1.43E + 04
Fluorene (3)	0.0	1.1	2.2	4.0	9.8	1.27E + 03
Phenanthrene (3)	0.0	1.2	3.0	4.7	13.3	1.18E + 03
Fluoranthene (4)	0.0	3.2	5.5	11.4	256	2.40E + 05
Pyrene (4)	0.0	3.7	7.5	12.5	250	5.10E + 05
Benz[a]anthracene (4)	0.0	4.1	7.9	13.6	60	1.57E + 03
Chrysene (4)	0.0	4.1	6.5	11.5	41	3.14E + 04
Benzo[b]fluoranthene (5)	0.0	0.4	0.9	1.8	6.4	1.43E + 04
Benzo[k]fluoranthene (5)	0.0	0.0	2.2	7.0	75	1.46E + 04
Benzo[ghi]perylene (6)	0.0	2.7	6.7	13.0	58	1.30E + 09

Note: Fc—concentrating factor.

HBG—health-based drinking water goals.

HBG/ Es_{oil}—ratio of the health-based goal to the maximum Es of fresh Ecuadorian crude.

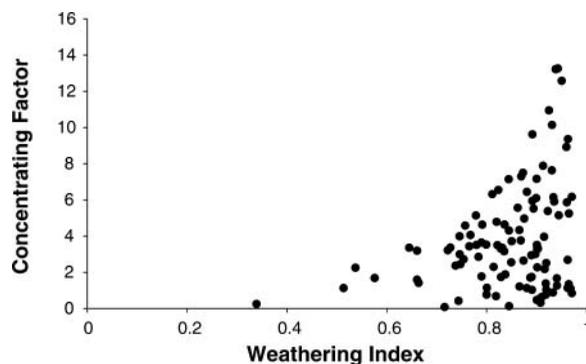


Figure 2. Concentrating factor versus weathering index for phenanthrene.

final column is the ratio between the health-based drinking water goal and the E_s calculated for fresh oil and the compound's ($HBG/E_{s_{oil}}$). As long as the maximum concentrating factor is less than this ratio, weathering should not result in a dissolved concentration exceeding the drinking water goals. The concentrating factor did not exceed the fresh oil $HBG/E_{s_{oil}}$ ratio for any of these compounds. This is confirmed in the last column of Table 1, which presents the number of soil samples for which the E_s exceeded the health-based goal. Except for benzene in nine samples, none of the other aromatic compounds exhibited E_s values that exceeded the health-based drinking water goal.

Figures 2 and 3 demonstrate the relationship between the weathering index of the oil and the concentrating factor for a three-ringed (i.e., phenanthrene), and four-ringed (i.e., chrysene) compound. The general trend demonstrated that samples with a low weathering index have a low concentrating factor. There was more variability in the concentrating factor with greater sample weathering. While the highest concentrating factor typically indicated that the individual compound was highly weathered, there were samples showing highly weathered bulk oil that had a lower individual compound concentrating factor as well. For example, concentrating factor values for phenanthrene varied by approximately one order of magnitude (i.e., from ~ 1 to 13) for soil samples with a similar degree of bulk oil weathering (~ 95 percent) (Figure 2).

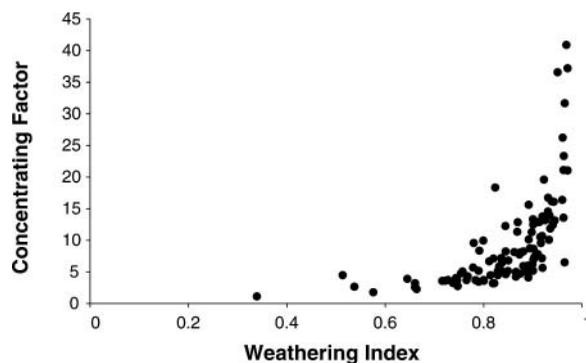


Figure 3. Concentrating factor versus weathering index for chrysene.

Discussion

Only the most soluble aromatic compounds are present in crude oil at sufficient concentration to be a potential risk to groundwater (Kerr et al., 2001; O'Reilly et al., 2001). In a screening of 60 crude oils from around the world, benzene, toluene, and naphthalene were the aromatic compounds of concern where the effective solubility exceeded health-based drinking water goals. Similarly, in this study using fresh Ecuadorian crude, only the Es of BTEX exceeded the health-based goals. The Es of the remaining aromatic compounds did not exceed the health-based goals.

The objective of this study was to determine how weathering impacts the Es of aromatic hydrocarbon compounds in the environment. As expected, weathering reduced the risk of benzene and toluene, as evidenced by the fact that these compounds were significantly or completely depleted in all the soil samples (i.e., only nine of 734 soil samples had concentrations that resulted in an Es exceeding the health-based drinking water goal for benzene). This observation is in agreement with other reports in the literature that demonstrate the loss of the volatile and highly degradable compounds with weathering (Jonker et al., 2006; Di Toro et al., 2007). This is also demonstrated by the maximum concentrating factor values calculated in this study, which were less than 0.20 for benzene, and 0.04 for toluene. The Es of the remaining aromatic hydrocarbons never exceeded the health-based drinking water goals for any of the soil samples.

While fresh Ecuadorian crude oil should not result in aqueous PAH concentrations of concern, it is important to understand whether weathering of the oil in the environment could result in an elevated risk as a result of the increase in oil phase concentration of recalcitrant compounds. Weathered oil should not result in an Es that exceeds a health-based goal unless the concentrating factor exceeds the HBG/Es ratio for the fresh oil. But as shown in the last two columns of Table 2, the HBG/Es ratio of the more recalcitrant PAHs exceeds the concentrating factor by orders of magnitude. As non-aromatic fractions of crude oils have been shown to be more resistant to weathering than PAHs (Boehm et al., 2008), this large difference indicates that even with additional weathering, the Es will not exceed the health-based drinking water goal. After reaching a degradation endpoint that is based on compositional chemistry, only minor changes in bulk oil concentrations are expected (Huesemann, 1995). Although only one type of oil was investigated in this study, the findings support the hypothesis that the risk of crude oil contaminating groundwater should first decrease with time because of the loss of the more labile components, and furthermore will not later exceed health-based drinking water goals despite a relative increase in the oil phase concentration of the more recalcitrant compounds.

It should be noted that while an Es below the health-based goal indicates that the measured dissolved contaminant concentration is unlikely to exceed this target, an Es value that is greater than the health goal does not necessarily indicate that the contaminated soil poses a risk to groundwater. Rather, Equation 1 predicts only the maximum dissolved concentration in soil pore water; it likely overestimates the potential maximum groundwater concentration. For example, the Es calculation does not take into account additional variables that may reduce dissolved phase concentrations, including dilution between leachate and groundwater, additional partitioning of compounds with natural organic matter in soil, and/or additional degradation between the soil and any potential receptor. A number of environmental risk models include a consideration of soil / water partitioning in estimating leachate concentration (U.S. EPA, 1996a), but fail to consider partitioning with an oil phase. As compounds will partition into both oil and soil organic matter, the organic matter will further reduce the maximum dissolved concentration (O'Reilly et al., 2001). Thus, the Es

likely serves as a conservative estimate of the true measured dissolved concentration of contaminant.

The methods used in this study are based on modeling the behavior of chemicals in the environment. As there are a range of published values for such factors such as solubility or partitioning coefficient (Verschueren, 2008), the results of such models should be considered to be an estimate. Laboratory results with fresh oils suggest that calculated E_s should be within an order of magnitude of the measured results (Lane and Loehr, 1995). As such, these estimates are more accurate than many regulatory-approved risk assessment approaches. For example, EPA promotes the use of sediment/water partitioning estimates to predict the toxicity of PAHs to benthic organisms (U.S. EPA, 2003b) even though such an approach may overestimate toxicity by two or more orders of magnitude (Hawthorn et al., 2006).

Calculated E_s values can be used to locate areas where further assessment may be warranted by identifying soil that may pose a risk to groundwater. The nine soil samples for which the E_s for benzene exceeded the health-based drinking water goals were collected from five of the 10 production stations; the E_s of none of the soil samples from the 32 individual well sites exceeded the health-based goals. Within these production stations, areas of potential impacts were quite localized. Some of the soil samples that produced potential exceedances were collected at the same sample location, but from different depths, or from adjacent locations. Furthermore, at each production station, a total of 16 to 38 soil samples were collected, yet no more than three samples had an E_s of concern. While such areas may be considered for a more detailed site assessment or risk analysis, it is important to note that no benzene was found in any of the domestic drinking water wells located near these five stations.

The calculated E_s for the oil-impacted soil samples cannot be compared directly to the measured concentrations in groundwater from this study, because the groundwater samples were not obtained immediately adjacent to the oil-impacted soil samples. Instead, groundwater samples were collected from nearby existing drinking water wells or temporary monitoring wells. Nevertheless, the results indicate that groundwater in the vicinity of the oily soils is not impacted, which is consistent with the calculated E_s values. Only two of the 171 groundwater samples contained detectable concentrations of aromatic compounds above the health-based goals (i.e., benzene and dibenz[a,h]anthracene). Additional investigation suggested that oily soil was not the cause of these exceedances, because one of the samples was from a well near a leaking produced water injection point, while the other was obtained from an abandoned water well that had been used for dumping trash.

In addition to indicating the effect of weathering on the E_s of aromatic compounds, the results can be used to evaluate differences in the weathering behavior of the compounds. The trend shown in Figure 1 between calculated concentrating factors and molecular size is to be expected based on the physical-chemical properties of the aromatic compounds. For example, compounds such as benzene that are known to degrade faster than bulk oil would be expected to exhibit low concentrating factor values. In contrast, the four- and five-ringed PAHs, which have low volatility and are known to resist biodegradation, would be expected to have elevated values. It is interesting to note the narrow range in concentrating factor values for the 3 three-ringed compounds, suggesting similar degradability among them, whereas the four- and five-ringed PAHs exhibited wider ranges in concentrating factor values. This may reflect the wider range of structural variations among the four- and five-ringed compounds versus the three-ringed compounds, which may influence the degradation of the individual compound.

The variability in concentrating factor for similarly weathered oily soil samples (i.e., similar weathering index values) for a given compound suggests that the weathering rate of a chemical relative to the bulk oil is not constant. For example, the concentrating factor values for chrysene in oily soils with ~90 percent degradation ranged from about 4 to 40, exhibiting about an order of magnitude difference. Site-specific differences in the rates of abiotic and biotic degradation of different oil components may contribute to this variability. Differences in degradation rates will influence the concentration of an individual analyte in weathered versus fresh oil, which in turn influences the concentrating factor. Multiple variables influence weathering, thereby causing a range of concentrating factor values among different soil samples with the same degree of weathering. Despite similar degrees of weathering, the processes taking place will differ depending on numerous environmental parameters (e.g., oxygen availability, presence of microorganisms, chemical molecular size) (Ghoshal and Luthy, 1996; Jonker et al., 2006).

Conclusions

The calculated effective solubilities of aromatic hydrocarbons in fresh oil and weathered soils predict that only the most water soluble compounds (i.e., BTEX) may result in dissolved concentrations that exceed health-based drinking water goals. Weathering reduces the risk of these compounds because of a decrease in their oil phase concentration and hence effective solubility. While the oil phase concentration and Es of more recalcitrant compounds can increase, these increases are not sufficient to result in dissolved concentrations that exceed health-based drinking water goals. These results can be applied to streamlining site assessments by directing excavation and remediation to areas with greater risk for potential groundwater impact.

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References

- Boehm, P. D., Page, D. S., Brown, J. S., Neff, J. M., Bragg, J. R., and Atlas, R. M. 2008. Distribution and weathering of crude oil residues on shorelines 18 years after the Exxon Valdez spill. *Environ. Sci. Technol.* **42**, 9210–9216.
- Burris, D. R., Reisinger, H. J., and Lundegard, P. D. 2006. Fingerprinting approach for relating nonaqueous-phase liquid, soil, and groundwater data. *Environ. Forens.* **7**, 247–257.
- DE 2144. 1989. *Reglamento para la Prevencion y Control de la Contaminacion Ambiental en lo Relativo al Recurso Agua, Acuerdo Ministerial No. 2144* [translated as Regulations for the Prevention and Control of Environmental Pollution with regard to Water Resources, Ministerial Agreement No. 2144], Republic of Ecuador, Quito, Ecuador.
- Devlin, J. F., and Barbaro, J. R. 2001. A method of estimating multicomponent nonaqueous-phase liquid mass in porous media using aqueous concentration ratios. *Environ. Toxicol. Chem.* **20**, 2443–2449.
- Di Toro, D. M., McGrath, J. A., and Stubblefield, W. A. 2007. Predicting toxicity of neat and weathered crude oil: toxic potential and the toxicity of saturated mixtures. *Environ. Toxicol. Chem.* **26**, 24–36.
- Douglas, G. S., Bence, A. E., Prince, R. C., McMillen, S. J., and Butler, E. L. 1996. Environmental stability of selected petroleum hydrocarbon source and weathering ratios. *Environ. Sci. Technol.* **30**, 2332–2339.

- Eberhardt, C., and Grathwohl, P. 2002. Time scales of organic contaminant dissolution from complex source zones: coal tar pools vs. blobs. *J. Contam. Hydrol.* **59**, 45–66.
- Ghoshal, S., and Luthy, R. G. 1996. Bioavailability of hydrophobic organic compounds from nonaqueous-phase liquids: the biodegradation of naphthalene from coal tar. *Environ. Toxicol. Chem.* **15**, 1894–1900.
- Hawthorn, S. B., Grabanski, C. B., and Miller, D. J. 2006. Measured partitioning coefficients for parent and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments: Part 1. Koc values. *Environ. Toxicol. Chem.* **25**, 2901–2911.
- Huesemann, M.H. 1995. Predictive model for estimating the extent of petroleum hydrocarbon biodegradation in contaminated soil. *Environ. Sci. Technol.* **29**, 7–18.
- Jonker, M. T. O., Brils, J. M., Sinke, A. J. C., Murk, A. J., and Koelmans, A. A. 2006. Weathering and toxicity of marine sediments contaminated with oils and polycyclic aromatic hydrocarbons. *Environ. Toxicol. Chem.* **25**, 1345–1353.
- Jonker, M. T. O., Sinke, A. J. C., Brils, J. M., and Koelmans, A. A. 2003. Sorption of polycyclic aromatic hydrocarbons to oil contaminated sediment: unresolved complex? *Environ. Sci. Technol.* **37**, 5197–5203.
- Kerr, J. M., McMillen, S. J., Magaw, R. I., Melton, H. R., and Naughton, G. 2001. Risk-based screening levels for crude oil: the role of polyaromatic hydrocarbons. In: *Risk Based Decision Making for Assessing Petroleum Impacts at Exploration and Production Sites*, pp 142–155 (McMillen, S. J., Magaw, R. I., and Carovillano, R. L., eds.), U.S. Department of Energy, Washington, DC.
- Lane, W. F., and Loehr, R. C. 1995. Predicting aqueous concentrations of polynuclear aromatic hydrocarbons in complex mixtures. *Water Environ. Res.* **67**, 169–173.
- O'Reilly, K. T., Magaw, R. I., and Rixey, W. G. 2001. Predicting the effect of hydrocarbon and hydrocarbon-impacted soil on groundwater. *American Petroleum Institute Soil & Groundwater Technical Task Force Report 14*.
- Ortiz, E., Kraatz, M., and Luthy, R. G. 1999. Organic phase resistance to dissolution of polycyclic aromatic hydrocarbon compounds. *Environ. Sci. Technol.* **23**, 235–242.
- Peters, C. A., Mukherji, S., Knightes, C. D., and Weber, W. J. 1997. Phase stability of multicomponent NAPLs containing PAHs. *Environ. Sci. Technol.* **31**, 2540–2546.
- Rutherford, P. M., Gray, M. R., and Dudas, M. J. 1997. Desorption of [¹⁴C]naphthalene from bioremediated and nonbioremediated soils contaminated with creosote compounds. *Environ. Sci. Technol.* **37**, 2515–2519.
- Salanitro, J. P., Dorn, P. B., Huesemann, M. H., Moore, K. O., Rhodes, I. A., Rice-Jackson, L. M., Vipond, T. E., and Wisniewski, H. L. 1997. Crude oil hydrocarbon bioremediation and soil ecotoxicity. *Environ. Sci. Technol.* **31**, 1769–1776.
- Shiu, W. Y., Maijanen, A., Ng, A. L. Y., and Mackay, D. M. 1988. Preparation of aqueous solutions of sparingly soluble organic substances. II. Multicomponent systems—Hydrocarbon mixtures and petroleum products. *Environ. Toxicol. Chem.* **7**, 125–137.
- Spence, L. R., O'Reilly, K. T., Magaw, R. I., and Rixey, W. G. 2001. Predicting the fate and transport of hydrocarbons in soil and groundwater. In: *Risk Based Decision Making for Assessing Petroleum Impacts at Exploration and Production Sites*, pp 89–110 (McMillen, S. J., Magaw, R. I. and Carovillano, R. L., eds.) U.S. Department of Energy, Washington, DC.
- U.S. EPA (U.S. Environmental Protection Agency). 1994. *Test Methods for Evaluating Solid Waste—Physical/Chemical Methods, SW-846*. Revised methods., 3rd edition. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
- U.S. EPA (U.S. Environmental Protection Agency). 1996a. Development of pathway specific soil screening levels. In: *Soil Screening Guidance: Technical Background Document*, 10–13 EPA/540/R-95/128.
- U.S. EPA (U.S. Environmental Protection Agency). 1996b. Chemical specific parameters. In: *Soil Screening Guidance: Technical Background Document*, 134–136, EPA/540/R-95/128.
- U.S. EPA (U. S. Environmental Protection Agency). 2003a. *National Primary Drinking Water Standards*, EPA 816-F-03–016.

- U.S. EPA (U.S. Environmental Protection Agency). 2003b. *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures*. EPA/600/R-02/013
- Verschueren, K. 2008. *Handbook of Environmental Data on Organic Chemicals*, 5th edition, John Wiley & Sons, Inc., Hoboken, NJ.
- Wang, Z., Fingas, M., Blenkinsopp, S., Sergy, G., Landriault, M., Sigouin, L., Foght, J., Semple, K., and Westlake, D. W. S. 1998. Comparison of oil composition changes due to biodegradation and physical weathering in different oils. *J. Chromatogr. A*. **809**, 89–107.
- WHO (World Health Organization). 2004. Chemical summary tables. In: *Guidelines for Drinking Water Quality*, 3rd edition, Annex 4, 488–493, World Health Organization, Geneva, Switzerland.