



Fugacity Model for Predicting Phase Distribution and Biotreatment Feasibility of Mixed Organic Compounds and Non-Aqueous Phase Liquid

Pamela L Sheehan^{1*} and Jerome J Kukor²

¹Research Engineer, U.S. Futures Command, CCDC AC, USA

²School of Environmental and Biological Sciences, The state University of New Jersey, USA

*Corresponding author: Pamela L Sheehan, Research Engineer, U.S. Futures Command, CCDC AC, USA

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Abstract

Screening tools for predicting the feasibility of remediating complex mixtures of organic compounds are needed to reliably and cost effectively down-select remediation options. This study evaluates the use of a fugacity model as a tool for estimating phase distribution and bioavailability of mixed organic compounds in compost. The model is compared to field-scale composting data to validate model predictions. Fugacity calculations show that the initial mass distribution of 17 semi-volatile and volatile chemicals during a 30 day compost period is predominantly to the organic composting solids and NAPL phase compartments with a lesser distribution to the aqueous phase suggesting limited bioavailability of target compounds. A fugacity level 1 phase distribution model is therefore a useful screening tool for identifying composting limitations and engineering improvements needed for successful treatment of mixed organic compounds.

Introduction

Screening tools for predicting feasibility of hazardous waste treatment are needed to reliably and cost effectively down-select remediation options. Without these tools engineers must conduct complicated and expensive field tests at large enough scale to reflect operationally relevant conditions. This study evaluates the use of a fugacity model for phase distribution of mixed organic compounds as a screening tool to predict the efficacy of bio-treatment by composting. The model is compared to field-scale composting data to validate model predictions.

Composting is a demonstrated treatment technology for soils contaminated with gasoline, oil, coal tar, polychlorinated biphenyls and explosives [1-8]. Although this technology is based on the well-documented ability of naturally occurring soil microbes to degrade hydrocarbons [9-11], the process is characteristically unpredictable, site specific, and often incomplete [12,13]. Recalcitrance of hydrophobic compounds in biotreatment is not uncommon and is generally attributed to multiphase partitioning that separates organic compounds from the degrading microbial community. Weissenfels, et al. [14] for example, demonstrated

that recalcitrant polycyclic- aromatic hydrocarbons (PAHs) were degraded after extraction and reinjection into the same soil thereby showing that biodegradation was limited by compound availability and not biodegradability. The biodegradability of compounds such as PAHs that partition to the organic or non-aqueous phase liquid (NAPL) fractions is controlled by mass transfer [15] at the NAPL or organic carbon-water interface [12,16]. In this process the organic compound dissolves out of the NAPL and repartitions into the aqueous and soil phases where its bioavailability may be limited by sportive reactions [17-25]. Compound recalcitrance in bio-treatment is expected to be high when the dissolution and desorption rates are slow. Predicting the partitioning of hydrophobic compounds is needed to estimate compound bioavailability, especially for risk relevant compounds, in determining treatment feasibility.

Compound bioavailability has been measured using analytical methods based on chemical extraction limits [26,27] and by theoretical mass transfer calculations based on sorption and diffusion [22,28,29]. The mathematical approach has the advantage of predicting how much of a compound introduced into the environment partitions to the aqueous phase, where it is most

likely to biotransform [16], and how much remains in the sediment or volatilizes to the atmosphere. Fugacity based mathematical models are commonly applied to predict the fate and transport of pollutants in the environment [17,30,31] and recently have been used to predict the biotreatment potential of hydrophobic compounds in biopile remediation [15]. Four levels of the fugacity model are defined with model complexity increasing with each level [32]. Level I assumes system equilibrium and that chemical loss due to biotic or abiotic transformation or mineralization does not occur.

Fugacity is a thermodynamic principle related to chemical potential that uses pressure rather than energy to describe the likely movement of a compound out of a particular phase ("escaping tendency") [32]. In this approach compounds move along a fugacity gradient, from high to low, and equilibrium is achieved when the net escaping tendency between two phases is zero [33]. Fugacity (f) is related to concentration (C) by a fugacity capacity coefficient (Z) such that $C = Zf$ [32]. The fugacity capacity is a function of the partition coefficient (K) defined as the compound concentration ratio between two phases. If $C = Zf$ then the partition coefficient $K_{1,2}$ (between phase 1 and phase 2) is Z_{1f} / Z_{2f} or $K_{1,2} = Z_1 / Z_2$, since at equilibrium fugacity is constant [29]. The fugacity capacity for air (Z_a) is a fixed value based on the ideal gas law and at dilute compound concentrations $Z_a = 1/RT$. The fugacity capacity for water (Z_w) is an inverse of the Henry's Law coefficient (H) determined as the compound liquid state vapor pressure divided by the compound solubility [34]. The fugacity capacity for soil, sediment, or sludge (Z_s) is determined by the soil density (ρ_s), the soil-water partition

coefficient (K_d) and Z_w such that $Z_s = K_d \cdot \rho_s \cdot Z_w$ (35). The soil-water partition coefficient is used to predict soil adsorption and is determined as the fraction of organic carbon in the soil multiplied by the organic carbon partition coefficient (K_{oc}) of the compound ($K_d = f_{oc} \cdot K_{oc}$) [35]. The soil-water partition coefficient is replaced by the octanol-water coefficient when calculating the fugacity capacity of NAPLs since the NAPL is a miscible solvent and partitioning is by absorption, not adsorption. The equilibrium fugacity for all phases is derived by Mackay [33] as $f = M / \sum (V_i Z_i)$ where M is the total number of moles of a constituent and V_i is the phase volume. The compound concentration in each phase is obtained by calculating the number of moles in each phase ($M_i = f \cdot Z_i \cdot V_i$) and, since molarity is mass divided by volume each phase concentration (C_i) is obtained by the expression $C_i = f \cdot Z_i$ [35]. The objective of this study was to determine the relative phase distribution and concentration of a complex mixture of chemicals in compost using the Level 1 fugacity model. Results of the model screening analysis inform treatment selection prior to empirical testing.

Materials and Methods

Model Data

Compost data from a field -scale compost feasibility test was used for the fugacity model. Source material was collected from 2 areas at a former industrial facility. Samples were analyzed for volatile and semi-volatile organic compounds using EPA SW-846 Method 5035/8260B and EPA SW-846 Method 3550B/8270C respectively. The mass of 17 compounds at the initial (day 0) and final day (day 30) of composting are provided in Tables 1&2.

Table 1: Initial and final compounds after composting.

	Material 1 (g)		Material2 (g)	
	Initial	Final	Initial	Final
Benzene	38,880	108	23,920	792
Toluene	8424	252	31,320	2,868
Ethylbenzene	7524	540	1,500	612
Xylenes	41,940	3,546	18,960	5,388
Chlorobenzene	43,920	4,338	7,008	2,820
1,2-Dichlorobenzene	450	540	3,336	1,548
1,2,4-trichlorobenzene	7,308	4,968	36	72
Nitrobenzene	19,800	15,714	38,160	2,292
Aniline	13,338	3,726	28,680	1,680
N-Nitrosodiphenylamine	41,400	38,970	11,652	9,816
Carbazole	524	702	2,064	1,140
Dibenzofuran	524	522	36	432
Napthalene	60,480	3,924	42,840	4,308
2-Methylnapthalene	1,998	990	1,404	1,008
Acenapthalene	702	576	396	358
Fluorene	1,872	342	444	204
Benzo(a)anthracene	882	720	1,116	528

Table 2: Half -life values for compounds in two composting materials.

Compound	Material 1	Material 2
Benzene	5	9
Toluene	11	14
Ethylbenzene	8	41
Xylenes	18	29
Chlorobenzene	13	36
Nitrobenzene	ND	10
Naphthalene	10	13
Aniline	20	10

Data reported (dissertation) over a 49 day composting period.

ND indicates not degraded. Initial concentration was above 100.

Compost Model

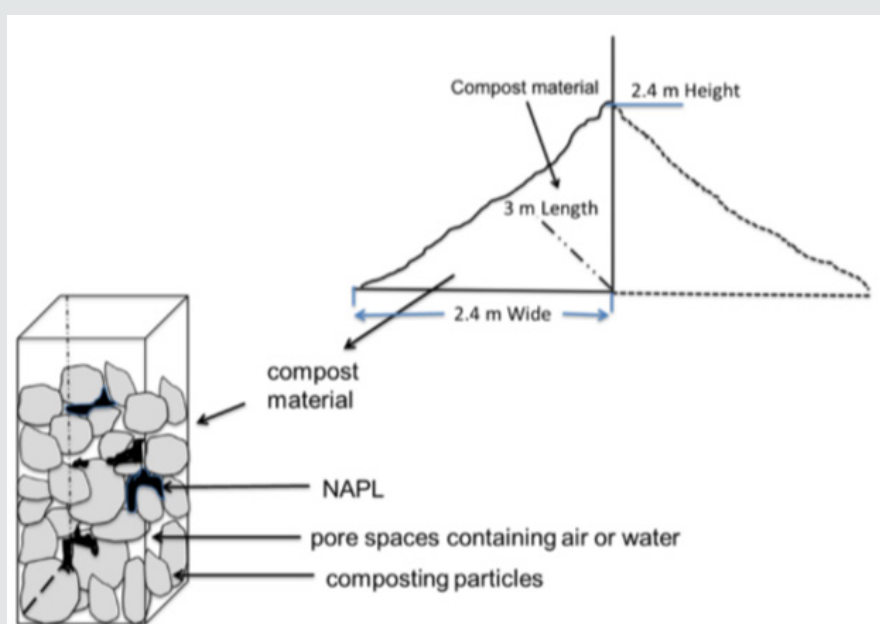


Figure 1: Phase compartment model for composting material.

A four-compartment model was used to describe separate but inter connected phases in the compost. Compartments are defined as pore space air, pore space water, compost solids, and NAPL as illustrated in Figure 1.

Phase compartment volume estimates were based on a total compost volume of 15 m³ with a 30% v/v porosity (4.5 m³ total

pore space). Water volume assumes that 30% of the total pore space is filled with water (1.35 m³) with the remaining 70% of the total pore space filled with air (3.15 m³). The NAPL compartment is defined as the total mass of all 17 organic compounds identified in the industrial waste. NAPL mass was converted to volume using a density of 970 kg/m³ consistent with work by Pollard, et al. [15]. Material characteristics used in the model are provided in Table 3.

Table 3: Compost characteristics defining the four compartment fugacity model.

Characteristic	Material 1	Material 2
Volume (m ³)	15	15
Bulk density (kg/m ³)	1200	800
Porosity	30	30
volume pore air (m ³)	31	3.1
volume pore water (m ³)	1.35	1.35
Organic carbon (%w/w)	30	30

Total initial mass of contaminants (kg)	290	218
Total final mass of contaminants (kg)	80	36
NAPL bulk density (kg/ m ³)	970	970
Initial NAPL volume (m ³)	0.3	0.22
Final NAPL volume (m ³)	0.08	0.04

The level 1 fugacity model assumes equilibrium among all phase compartments and is valid only when the composting pile is static, and biodegradation has either not begun or has ended.

Fugacity Calculations

Fugacity based concentrations of the 17 chemicals in the compost material were calculated for pore space air, pore space water, composting material and NAPL phase compartments using

the expression $f = M/\sum(V_iZ_i)$. Calculations were facilitated by an Excel spreadsheet made available by Nieman [35]. Physical properties for each compound are provided in Table 4. Phase compartments in equilibrium have equal fugacities as determined by the fugacity capacity and illustrated in Figure 2.A fugacity calculation for benzene is provided as an example using parameters in Table 5.

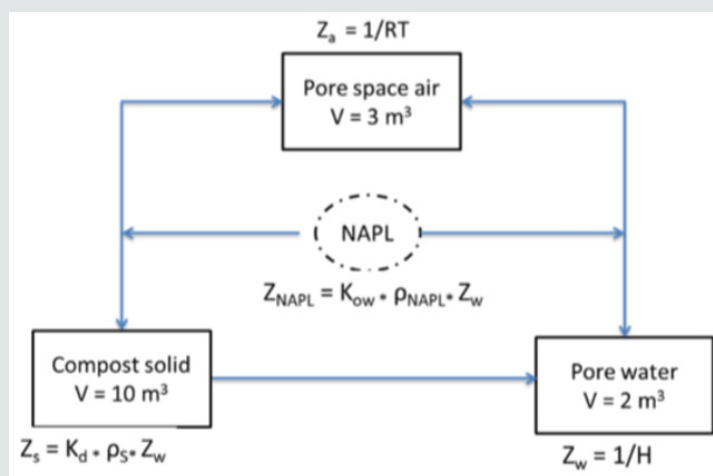


Figure 2: Volume and fugacity capacity of each model component.

Table 4: Physical-Chemical properties of compounds characterizing manufacturing waste sludge.

Property	Benzene	Ethyl benzene	Toluene	o-Xylene	Chlorobenzene	Dichloro benzene	Trichloro benzene	Nitrobenzene	Aniline
Molecular weight (g/ mole)	78.11	106.2	92.1	106.17	112.6	141	181.44	123	93.1
Molecular weight (g/ mole)	1.78E +03	1.52E+02	5.15E+02	1.70E+02	4.90E+02	1.00E+02	3.00E+02	1.90E+03	3.50E+03
vapour pressure (mm Hg)	7.60E+03	7	2.20E+01	7	8.80E+00	9.60E-01	6.60E-01	1.50E-01	6.70E-01
Henry's Law Coefficient (atm-m ³ / mol)	5.43E-03	7.90E-03	6.61E-03	4.91E-03	1.88E-03	1.88E-03	1.42E-03	2.40E-03	1.90E-06
Log k_{ow}	2.13	3.15	2.73	3.12	3.38E+00	3.38E+00	4.02E+00	1.87E+00	9.00E-01
Log k_{a}	1.81	2.83E+02	2.41	2.84E+02	2.20E+00	3.06E+00	3.22E+00	1.56E+00	3.59E+00
Property	N-Nitroso-Di phylamane	Carbazole	Dibenzofuran	Napthal-ene	2-Methyl-Napthalene	Fluorene	Acenapthal-ene	Benzo(a)-anthracene	
Molecular weight (g/ mole)	74.08	167.2	168.19	128.2	142.2	166.22	154.21	228.3	

Molecular weight (g/mole)	3.51E+01	7.48	1.7	3.10E+01	2.54E+01	1.90E+00	3.88E+00	1.40E+00	
vapour pressure (mm Hg)	1.00E-01	2.66E-04	8.30E-04	3.10E+01	2.54E+01	1.90E+00	3.88E+00	1.16E-07	
Henry's Law Coefficient (atm-m ³ /mol)	5.00E-06	1.50E-08	1.01E-04	1.27E-03	5.06E-02	7.65E-05	1.20E-03	4.50E-06	
Log k _{ow}	3.16	3.59	4.05	3.3	3.86	4.18	3.92	5.61	
Log k _a	3.11	3.5	4.05	3.11	3.93	3.9	3.7	6.14	

Table 5: Values used to parameterize fugacity equation.

Property	Benzene
Molecular weight (MW)	78.18g/mol
Total mass in compost	38,880g
Total moles of compound in compost	(38,880g)/(78.18g/mole)=497mol benzene
Henry's Law coefficient (H)	550m ³ Pa/mol
Organic carbon normalized coefficient (koc)	64.5
Organic carbon in compost (foc)	30%
Soil water partition coefficient (Kd)	Kd=foc * koc+(0.3)*(64.5)=19.35
Octanol-water partition coefficient (Kow)	134
Composting density (ρ)Material 1	1.2kg/L
Total pore volume (30% of composting material v/v)	4.5 m ³
Volume air (v _a) = 30% of total pore volume	3.1m ³
Volume water (V _w) = 30% of total pore volume	1.6m ³
Volume composting solids (V _c) (15.3 m ³ -4.5m ³)	10m ³
Volume NAPL in material 1 (V _n)	0.3 m ³
Volume total (V _t)10m ³ +3.1 m ³ +1.6m ³	15 m ³

$$Z_a = 1/RT = 1/(8.3145)(293 \text{ oK}) = 0.00041 \text{ mol/m}^3\text{-Pa}$$

$$Z_w = 1/H = 1/550 = 0.00182 \text{ mol/m}^3\text{-Pa}$$

$$Z_s = K_d * \rho_s * Z_w = (19.35) * (1.2) * (0.00182) = 0.042 \text{ mol/m}^3\text{-Pa}$$

$$Z_n = Z_w * K_{ow} = (0.00182) * (134) = 0.24 \text{ mol/m}^3\text{-Pa}$$

The fugacity equation $f = M / \sum Z_i V_i$ for benzene between compartments was calculated using fugacity capacity and compartment volumes.

$$f = M / (Z_a * V_a) + (Z_w * V_w) + (Z_s * V_s) + (Z_n * V_n)$$

$$f = 497 / (0.00041 * 3.1) + (0.00182 * 1.6) + (0.042 * 10) + (0.24 * 0.3)$$

$$f = 497 / 0.0013 + 0.0029 + 0.42 + 0.072$$

$$f = 497 / 0.4962$$

$$f = 1,001.6 \text{ Pa}$$

Benzene concentration in each compartment is calculated as:

$$f = M / Z_i * V_i \text{ rearranged to:}$$

$$M = f * Z_i * V_i \text{ since } M = \text{concentration} * \text{volume:}$$

$$C_i = f * Z_i$$

The fugacity of air, water, composting solids and NAPL is assumed to be equal for Level 1 fugacity calculations. Thus the concentration of benzene in each phase is given by:

$$\text{Air: } M \text{ benzene} = f * Z_a * V_a = 1001.6 * 0.00041 * 3.1 = 1.27 \text{ moles}$$

$$C_a = f * Z_a = (1001.6 * 0.0004) = 0.4812 \text{ moles/m}^3 * 78.18 \text{ g/mole} = 32 \text{ mg/L in air}$$

$$\text{Water: } M \text{ benzene} = f * Z_w * V_w = 1001.6 * 0.00182 * 1.6 = 3.5 \text{ moles}$$

$$C_w = f * Z_w = (1001.6 * 0.00182) = 1.8 \text{ moles/m}^3 * 78.1 \text{ g/mole} = 142 \text{ mg/L in water}$$

$$\text{Solid: } M \text{ benzene} = f * Z_s * V_s = 1001.6 * 0.042 * 10 = 420.7 \text{ moles}$$

$$C_c = f * Z_c = (1001.6 * 0.042) = 42 \text{ moles/m}^3 * 78.18 \text{ g/mole} = 3,285 \text{ mg/L in solids}$$

$$M \text{ benzene} = f * Z_n * V_n = 1001.6 * 0.24 * 0.3 = 72 \text{ moles}$$

$C_n = f * Z_n = (1001.6 * 0.24) = 240 \text{ moles/m}^3 * 78.18 \text{ g/mole} = 18,774 \text{ mg/L in NAPL}$

Thus the relative phase distribution of benzene to each compartment at equilibrium is:

Mass distribution to air = $(1.27 \text{ moles} / 497 \text{ moles}) * 100 = 0.26\%$

Mass distribution to water = $(3.47 \text{ moles} / 497 \text{ moles}) * 100 = 0.70\%$

Mass distribution to composting solids = $(421 \text{ moles} / 497 \text{ moles}) * 100 = 84.7\%$

Mass distribution to NAPL = $(72 \text{ moles} / 497 \text{ moles}) * 100 = 14.5\%$

The relative importance of including a NAPL phase separate from the organic carbon content of composting solids was determined by calculating fugacity concentration for pore water in the absence and presence of a NAPL phase and comparing changes in distribution results.

Table 6: Fugacity distribution by percent of initial and final compound mass in material 1.

Compound	Material 1 Phase Distribution (%)							
	Air		Water		Compost		NAPL	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Benzene	0.25	0.42	0.58	0.95	85	92	15	6
Toluene	0.08	0.09	0.15	0.16	85	95	15	4
Ethylbenzene	0.04	0.09	0.06	0.06	85	96	15	4
Xylenes	0.02	0.02	0.06	0.06	86	96	14	4
Chlorobenzene	0.06	0.07	0.21	0.21	73	91	27	9
1,2-Dichlorobenzene	<0.01	0.01	0.03	0.03	85	96	15	4
1,2,4-trichlorobenzene	<0.01	<0.01	0.02	0.02	66	88	35	12
Nitrobenzene	<0.01	<0.01	1.04	1.16	85	95	14	4
Aniline	<0.01	<0.01	0.01	0.01	99.7	99.9	0.02	0
N-Nitrosodiphenylamine	<0.01	<0.01	0.03	0.03	91	98	9	2
Carbazole	<0.01	<0.01	0.01	0.01	91	97	9	3
Dibenzofuran	<0.01	<0.01	<0.01	<0.01	92	98	8	2
Naphthalene	<0.01	<0.01	0.03	0.03	89	97	11	3
2-Methylnaphthalene	0.02	0.02	<0.01	0.01	93	98	7	2
Acenaphthalene	<0.01	<0.01	0.01	0.01	88	96	12	4
Fluorene	<0.01	<0.01	<0.01	0.01	86	96	14	4
Benzo(a)anthracene	<0.01	<0.01	<0.01	<0.01	98	99.3	2	10

Table 7: Fugacity distribution by percent of initial and final compound mass in material 2.

Compound	Material 1 Phase Distribution (%)							
	Air		Water		Compost		NAPL	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Benzene	0.37	0.43	0.86	0.98	83	95	16	3
Toluene	0.12	0.13	0.22	0.25	84	96	16	3
Ethylbenzene	0.05	0.06	0.08	0.1	84	97	16	3
Xylenes	0.03	0.04	0.08	0.08	85	97	15	3
Chlorobenzene	0.08	0.11	0.3	0.39	71	93	29	7
1,2-Dichlorobenzene	0.01	0.01	0.05	0.06	84	97	16	4

1,2,4-trichlorobenzene	<0.01	<0.01	0.03	0.04	63	91	37	10
Nitrobenzene	<0.01	<0.01	1.52	1.74	83	95	16	3
Aniline	<0.01	<0.01	0.02	0.02	99.9	99.9	0.02	0
N-Nitrosodiphenylamine	<0.01	<0.01	0.05	0.05	91	98	9	9
Carbozole	<0.01	<0.01	0.02	0.02	90	98	10	10
Dibenzofuran	<0.01	<0.01	0.01	0.01	92	98	8	8
Napthalene	<0.01	<0.01	0.05	0.05	88	97	12	12
2-Methylnapthalene	0.03	0.03	0.01	0.01	93	98	7	7
Acenapthalene	<0.01	<0.01	0.01	0.01	87	97	13	13
Fluorene	<0.01	<0.01	0.01	0.01	85	97	15	15
Benzo(a)anthracene	<0.01	<0.01	<0.01	<0.01	97	99.5	3	0.49

Fugacity calculations show that at the completion of composting the measured residual concentration and the predicted compost organic carbon concentration are directly correlated ($R_2 = 0.99$) in both test materials (Tables 8&9). Due to the relatively small NAPL volume remaining at the end of composting, compounds shown to partition to the NAPL phase are highly concentrated.

Table 8: Comparison of measured residual compound concentration with predicted concentration in other phase compartments in Material 1.

Compound	Measured concentration		Predicted concentration	
	Residual (mg/kg)	Water(mg/L)	solids (mg/kg)	NAPL (mg/kg)
Benzene	6	0.64	10	87
sToluene	14	0.26	24	139
Ethylbenzene	30	0.21	52	299
Xylenes	197	1.4	340	1,800
Chlorobenzene	241	6.9	394	4,780
1,2,Dichlorobenzene	30	0.01	52	299
1,2,4-trichlorobenzene	276	0.73	436	7630
Nitrobenzene	873	114	1490	8430
Aniline	207	0.26	373	2
N-Nitrosodiphenylamine	2,165	0.82	3800	11800
Carbozole	39	0.06	68	233
Dibenzofuran	29	0.01	51	142
Napthalene	218	0.8	379	1,630
2-Methylnapthalene	55	0.03	97	230
Acenapthalene	32	0.03	56	256
Fluorene	19	0.01	174	30700
Benzo(a)anthracene	40	0.0001	71	59

Table 9: Comparison of measured residual compound concentration with predicted concentration in other phase compartments in Material 2.

Compound	Measured concentration		Predicted concentration	
	Residual (mg/kg)	Water(mg/L)	solids (mg/kg)	NAPL (mg/kg)
Benzene	66	4.87	73	657
Toluene	239	4.45	275	2400
Ethylbenzene	51	0.36	59	514
Xylenes	449	3.14	522	4,140
Chlorobenzene	235	6.88	262	4,760
1,2,Dichlorobenzene	129	0.05	149	1,300
1,2,4-trichlorobenzene	6	0.02	7	171
Nitrobenzene	191	25	22	1850

Aniline	140	0.18	168	1
N-Nitrosodiphenylamine	818	3.11	963	4500
Carbozole	95	0.15	112	473
Dibenzofuran	36	0.02	43	177
Napthalene	359	1.39	420	2,710
2-Methylnapthalene	84	0.05	99	352
Acenapthalene	29	0.03	34	234
Fluorene	17	0.01	20	157
Benzo(a)anthracene	44	0.0001	53	65

Bioavailability

The initial and residual mass of each compound in the compost were used in fugacity calculations to predict compound concentrations in pore space water (Table 10). Solubility is a key

Table 10: Fugacity predicted concentration in pore space water.

Compound	Solubility	Co	Cf	Co	Cf
Benzene	1780	141	0.64	155	4.9
Toluene	515	8	0.26	42	4.4
Ethylbenzene	152	3	0.21	0.78	0.36
Xylenes	170	15	1.4	10	3.1
Chlorobenzene	490	56	6.9	13	6.9
1,2-Dichlorobenzene	100	0.09	0.01	1	0.05
1,2,4-trichlorobenzene	300	0.8	0.73	<0.01	0.02
Nitrobenzene	1700	128	114	360	25
Aniline	35000	0.95	0.26	3	0.18
N-Nitrosodiphenylamine	35	8	0.82	3	3.1
Carbozole	7.48	0.04	0.06	0.24	0.15
Dibenzofuran	1.7	0.012	0.01	<0.01	0.02
Napthalene	31	12	0.8	12	1.4
2-Methylnapthalene	25	0.06	0.03	0.06	0.5
Acenapthalene	3.8	0.03	0.03	0.029	0.3
Fluorene	1.9	0.057	0.01	0.02	0.01
Benzo(a)anthracene	0.015	<0.01	<0.01	<0.01	<0.01

C_o = initial concentration

C_f = final concentration

¹Final compost concentration is above regulatory threshold for non-residential soils.

factor in determining partition distribution to the water phase and although it was not used directly in calculating fugacity it was used (with vapor pressure) to calculate Henry's Law coefficient and the fugacity capacity of the water phase.

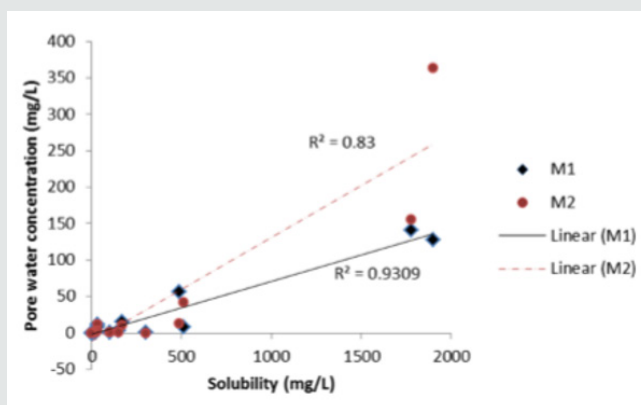


Figure 3: Correlation between compound solubility and predicted initial concentration in composting material pore water (aniline excluded).

Compound solubility and pore water concentration correlate ($R^2 = 0.83 - 0.93$) only if aniline is removed from the analysis (Figure 3). Including aniline in the analysis resulted in poor overall correlation between pore water concentration and compound solubility in both materials ($R^2 < 0.01$). Aniline is anomalous due its relatively high solubility but low predicted concentration in the pore water. Unlike other compounds virtually all of the aniline (99.8%) partitions to

the compost organic carbon due to its relatively high K_{oc} .

Compounds are most available to microbes in soluble form and biodegradation is expected to occur mainly in the water phase of the compost. Compound concentration in pore water, however, did not correlate well ($p < 0.05$) with half-life data (Table 2) for Material 1 ($R^2 = 0.31$) or Material 2 ($R^2 = 0.22$) (Figure 4).

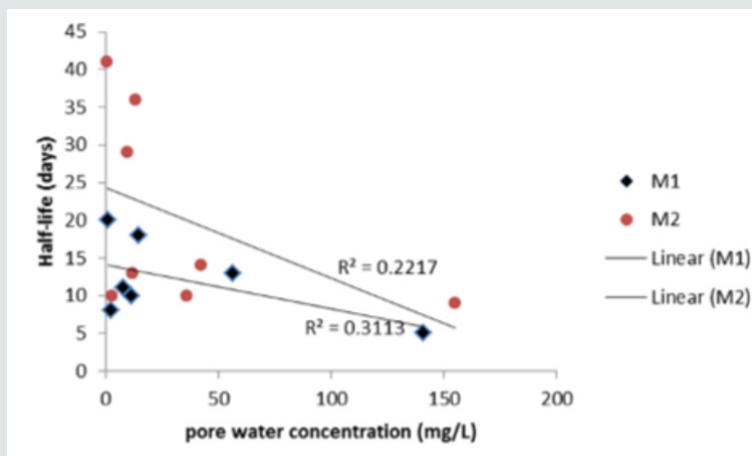


Figure 4: Correlation between pore water concentration and degradation half-life in Materials 1 and 2 (excluding aniline).

Table 11: Comparison of measured residual compound concentration with predicted concentration in other phase compartments in Material 2.

Compound	Concentration(mg/L)	
	w/o NAPL	w/o NAPL
Benzene	166	141
Toluene	9	8
Ethylbenzene	3	3
Xylenes	17	15
Chlorobenzene	77	56
1,2-Dichlorobenzene	0.1	0.09
1,2,4-trichlorobenzene	1.2	0.8
Nitrobenzene	150	128
Aniline	0.95	0.95
N-Nitrosodiphenylamine	9	8
Carbozole	0.047	0.04
Dibenzofuran	0.0134	0.012
Napthalene	13	12
2-Methylnapthalene	0.065	0.06
Acenapthalene	0.0389	0.03
Fluorene	0.066	0.057
Benzo(a)anthracene	0.0002	0.0002

Fugacity calculations that excluded NAPL as a separate phase predicted an increase in pore water concentration (Table 11). An independent samples t-test was used to determine if including a NAPL phase in the fugacity model significantly ($p < 0.05$) influenced

the pore water compound concentration. No significant difference is indicated between predicted concentrations when the model included or excluded NAPL ($df = 35, p < 0.05$).

Discussion

The Level 1 fugacity model used in this analysis is a simple screening method for quantifying chemical partitioning in a heterogeneous matrix. Others have used fugacity to estimate the fate and transport of chemical pollutants, particularly hydrophobic organic compounds, in the environment [36,37]. This is the first study to apply fugacity analysis to predict the phase distribution of a complex mixture of hydrophobic compounds in compost. This study modifies the basic environmental model defined by Mackay, et al. [38] to include a NAPL phase in addition to air, water and solids leaving out biota, sediment and aerosols.

An identified NAPL phase representing the total mass of contaminants and considered separately from the organic compound concentration is not common in ex situ treatment. Pollard, et al. [15] used this approach in a fugacity analysis of biopile treatment of benzene and PAHs. The results of the present study are consistent with the observations of Pollard et al. that NAPL and soil organic carbon are the main distribution phases with minor distribution to pore space air or water. Zemanek, et al. [19] demonstrated that 71% of PAHs (by weight) distributed to oil present at 2% of the soil mass. Results presented here predict that when the contaminant mass is approximately 2% of the total compost mass (Material 2), 85 to 98% of the PAHs distribute to

the organic compost and only 3 to 13% to NAPL. Pollard, et al. [15] showed that as the percent carbon increased in bio piles from 9% to 15%, PAH distribution to NAPL decreased from 58% to 32% for benzene, 62% to 36% for anthracene and 13% to 5% for benzo(a) pyrene. The present study is consistent with these results showing by extension that a further increase in organic carbon to 30% results in only 16% distribution to NAPL for benzene, 13% for acenaphthene and 3% for benzo(a)anthracene. Thus, identifying a NAPL phase separate from the organic carbon content becomes increasingly important as the percent carbon in the treatment material decreases. Residual concentrations partitioned to the NAPL phase are typically a long-term source of contamination and mass transfer from NAPL to the water phase is the rate limiting reaction for compound bioavailability. Thus, not including NAPL as a separate phase from organic carbon in highly contaminated materials may result in an overestimation of treatment potential.

Since the bulk of the compounds distribute to the NAPL and compost organic carbon, limited biodegradation might be expected. Guerin and Boyd [39], however, observed degradation rates and extents for naphthalene that exceeded predictions based on bioavailability assays and cautioned that bioavailability can be influenced by microorganisms not accounted for in phase distribution models. The opposite is also true and not all compounds with predicted bioavailability are biodegraded, since this also depends on the metabolic capacity of indigenous microorganisms. Results of the present study predict that nitrobenzene is available for biodegradation based on fugacity concentrations in the pore water of 128 mg/L in Material 1 and 360 mg/L in Material 2 at the start of composting. A final concentration of 114 mg/L in Material 1 pore water suggests compound availability but not biodegradability whereas a final concentration of 25 mg/L in Material 2 pore water suggests both bioavailability and biodegradability. This observation is consistent with biodegradation half-life data (Table 2). The significance of this finding is that treatment improvement may require two different compost management strategies: one to improve growth and specific metabolic activity of indigenous microbes and the other to improve compound bioavailability.

Conclusion

The fugacity Level 1 model is a useful screening tool to identify potential treatment limitations due to phase distribution of complex mixtures of organic compounds. NAPL and organic carbon are the predominant partition phases for hydrophobic compounds. The importance of including a NAPL phase in the fugacity model is increasingly important in materials with a low natural organic carbon content. Excluding a NAPL phase from the fugacity model may result in an underestimate of risk relevant compounds in residual materials. The presence or absence of a NAPL phase in the fugacity distribution model did not significantly ($p < 0.05$) influence the predicted pore water concentrations of target compounds. Water phase concentrations appear to correlate with

compound solubility but not to biotransformation rates quantified by degradation half-life. Thus, compound bioavailability, indicated by the pore water concentration, does not necessarily indicate compound biodegradability. A comparison of soluble compound concentrations of recalcitrant compounds before and after composting provides additional information for distinguishing between bioavailability and biodegradability limitations. A fugacity Level 1 phase distribution model is therefore a useful screening tool for identifying composting limitations and improvements needed for a more complete treatment of hydrophobic chemicals.

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