

Indoor Vapor Intrusion with Oxygen-Limited Biodegradation for a Subsurface Gasoline Source

George DeVaul
Shell Global Solution US Inc.
Westhollow Technology Center
3333 Highway Six South
Houston, Texas 77082
e-mail: george.devaul@shell.com
telephone: 281-544-7430
facsimile: 281-544-8727

Supporting Information

Sections

A. Johnson and Ettinger model parameters - building characteristics	S.2
B. Chemical-specific properties.....	S.4
C. Gasoline source composition	S.6
D. Baseline soil respiration	S.7
E. Relationship between Y_f and Y_c	S.14
F. Nomenclature and parameter summary	S.17

Figures

Figure A.1. Range of Johnson and Ettinger model estimates.	S.3
Figure D.1. Baseline soil respiration.....	S.13

Tables

Table A.1. Parameter values for the Johnson and Ettinger model.....	S.2
Table A.2. Calculated foundation parameters.....	S.3
Table B.1. Chemical-specific physical properties	S.5
Table C.1. Gasoline composition and source concentrations	S.6
Table D.1. Soil respiration microcosm test results.	S.11
Table D.2. Soil column respiration test results.	S.12

A. Johnson and Ettinger Model Parameters - Building Characteristics

In the no-degradation case for indoor air vapor intrusion, the manuscript presents a representation of chemical mass transfer through a soil layer, a building foundation, and through a building enclosure in Eq. [7].

$$AF = \frac{c_e}{c_s} = \frac{\frac{1}{L_{mix} \cdot ER}}{\left(\frac{1}{L_{mix} \cdot ER} + \frac{1}{h} + \frac{L_T}{D_{eff}} \right)} \quad [A.1]$$

Eq. [8] gives the Johnson and Ettinger (3) model written in terms of the foundation mass transfer coefficient, h (cm/s). Ranges and suggested parameters for the Johnson and Ettinger model from several sources are included in Table A.1.

A plot of the Johnson and Ettinger (3) model results is included in Figure A.1. Nominal values of effective diffusivity applied in the plot were based on: vadose zone soil moisture fraction and soil porosity, $\theta_w = 0.1295 \text{ cm}^3\text{-water/cm}^3\text{-soil}$ and $\theta_r = 0.425 \text{ cm}^3\text{-void/cm}^3\text{-soil}$, respectively; soil-filled foundation crack moisture fraction and soil porosity, $\theta_w = 0 \text{ cm}^3\text{-water/cm}^3\text{-soil}$ and $\theta_w = 0.425 \text{ cm}^3\text{-void/cm}^3\text{-soil}$, respectively; molecular diffusivity in air, $D_{air} = 0.1 \text{ cm}^2\text{/sec}$, and Henry law coefficient, $H = \infty$ (insoluble). Intermediate parameters of mass transfer coefficient h (cm/s) and $L_{mix} \cdot ER$ (cm/s) are included in Table A.2.

reference:	scenario:	Q_s (L/min)	ER (1/day)	L_{crk} (cm)	η (cm ³ /cm ³)	L_{mix} (cm)	A_b (m ²)	A_f (m ²)
USEPA (1)	slab-on-grade	5	6	10	0.00038	244	106	100
	basement	5	6	10	0.0002	366	180	100
ASTM E1739-95 (2)	residential	0	12	15	0.01	200	70	70
	industrial	0	20	15	0.01	300	70	70
Hers et al. (4)	upper range	10	6	15	0.001	240	100	100
	lower range	1	24	10	0.00005	480	100	100

Notes: Q_s , volumetric flow of soil gas from basement to indoor air; ER , building air volume exchange rate; L_{crk} , foundation crack thickness; η , foundation crack fraction; L_{mix} , building volume/foundation area ratio; and A_b , slab area in contact with soil, including the foundation floor and sub-grade foundation walls. A_f is the derived building area footprint. Model parameter values that do not significantly affect calculated results are omitted from this table.

Table A.1. Ranges and suggested building parameter values for the Johnson and Ettinger (3) model.

reference:	scenario:	h (cm/s)	$ER \cdot L_{mix}$ (cm/s)	$AF = c_e / c_s$ (at $L_T = 0$)
USEPA (1)	slab-on-grade	7.90E-5	1.69E-2	4.64E-3
	basement	4.64E-5	2.54E-2	1.82E-3
ASTM E1739-95 (2)	residential	2.14E-5	2.78E-2	7.68E-4
	industrial	2.14E-5	6.94E-2	3.08E-4
Hers et al. (4)	upper range	1.68E-4	1.67E-2	1.00E-2
	lower range	1.67E-5	1.33E-1	1.25E-4

Notes: h , foundation mass transfer coefficient; $L_{mix} \cdot ER$, product of building air exchange rate and mixing height; AF , ratio of building enclosure concentration, c_e , to source concentration, c_s . L_T , foundation to source separation distance. Model parameters for estimating D_{eff} and D_{crk} are as presumed in the text.

Table A.2. Calculated foundation parameters for the Johnson and Ettinger (3) model. Scenarios are repeated from Table A.1.

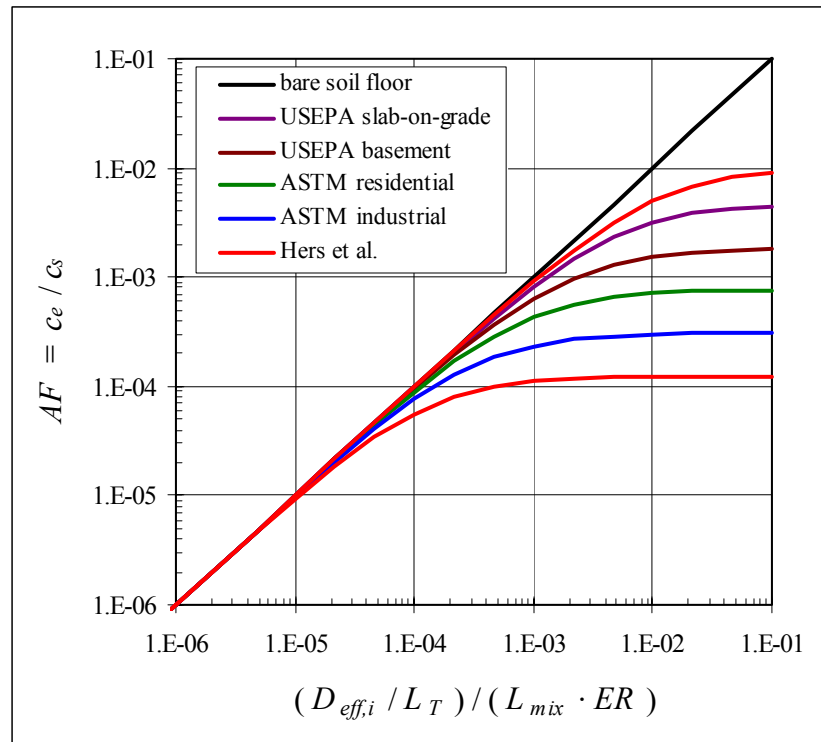


Figure A.1. Model estimates for the Johnson and Ettinger (3) model of Eqs. [7] and [8]. Plotted values use suggested values and ranges of building parameters from Table A.1. The ‘bare soil floor’ of Eq. [6] indicates an upper bound attenuation factor.

B. Chemical-specific properties

Hydrocarbon mixtures such as gasoline include many chemical species. The mixture is represented as a combination of identified pure chemical species and surrogates. The surrogates are a mixture of hydrocarbon chemicals within a normal boiling point range (or distillation 'cut') defined by the same boiling point range for the n-paraffin homolog series, and by the representative chemical class of either aromatics or aliphatics. Included chemicals and surrogates are listed in Table B.1 with representative property values (*A-I*). Surrogate hydrocarbon ranges are referenced in (*A*), principally as a set of empirical correlations. Molecular diffusivity is derived for selected chemicals from chemical property estimation methods (*H*). Aqueous solubility and vapor pressure are referenced at ambient environmental temperatures (20 to 25°C). Henry law coefficient unit conversion is presumed at ambient environmental temperatures (20 to 25°C), and atmospheric pressure (1 atm, 760 mmHg). Stoichiometric ratio is calculated from Eq. [31].

B. References:

- [A] Gustafson, J. B., J. G. Tell, and D. Orem, 1997: Total Petroleum Hydrocarbon Criteria Working Group Series, Volume 3, Selection of Representative TPH Fractions Based on fate and Transport Considerations, (Amherst Scientific Publishers, Amherst, Massachusetts, USA).
- [B] USEPA, 1996: Soil Screening Guidance: Technical Background Document, United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C., EPA/540/R-95/128, NTIS Accession No. PB96-963502, May.
- [C] USEPA, 1994: Air Emissions Models for Waste and Wastewater, United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, EPA-453/R-94-080A.
- [D] Mott, H. V., 1995: A Model for Determination of the Phase Distribution of Petroleum Hydrocarbons at Release Sites, Ground Water Monitoring and Remediation, 15,3,157-167, Summer.
- [E] Verschueren, Karel (1982): Handbook of Environmental Data on Organic Chemicals, 2nd edition, (Van Nostrand Reinhold, New York), ISBN 0-442-28802-6.
- [F] Mackay, D., W. Y. Shiu, and K. C. Ma, 1992: Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Volume 1, (Lewis Publishers, Boca Raton), ISBN 0-87371-513-6.
- [G] CRC, 1996: Properties of Organic Compounds, v. 5.0, (CRC Press, Inc., Boca Raton, FL), ISBN 0-8493-0447-4.
- [H] Lyman, W. J., W. F. Reehl, D. H. Rosenblatt, 1990: Handbook of Chemical Property Estimation Methods, McGraw-Hill Book Company, New York.
- [I] Perry, R. H., D. W. Green, J. O. Maloney, eds., 1984: Perry's Chemical Engineer's Handbook, Sixth Edition, McGraw-Hill Book Company.

normal boiling point (°C)	chemical name or class	formula	molecular weight (g/g-mol)	molecular diffusivity in air (cm ² /sec)	molecular diffusivity in water (cm ² /sec)	Henry's law coefficient (cm ³ /cm ³)	stoichiometric ratio (g-chem/g-O ₂)	(pure) chemical vapor pressure (mmHg)	(pure) chemical aqueous solubility (mg/L)
80.1	benzene	C ₆ H ₆	78.1	0.087	1.01E-5	0.23	0.33	95.2	1742.9
110.7	toluene	C ₇ H ₈	92.1	0.087	8.60E-6	0.28	0.32	30	526
136.2	ethylbenzene	C ₈ H ₁₀	106.2	0.075	7.80E-6	0.33	0.32	9.5	169
140.0	xylene (mixed isomers)	C ₈ H ₁₀	106.2	0.071	9.34E-6	0.22	0.32	8.5	180
147.9	EC >8 to 9 aromatic (-E -X)	C _{8.5} H _{8.5}	110.5	0.100	1.00E-5	0.56	0.33	8.53	82.2
172.4	EC >9 to 10 aromatic	C _{9.5} H _{9.5}	123.5	0.100	1.00E-5	0.33	0.33	2.70	50.7
195.2	EC >10 to 11 aromatic	C _{10.5} H _{10.5}	136.5	0.100	1.00E-5	0.19	0.33	0.85	31.3
217.9	naphthalene	C ₁₀ H ₈	128.2	0.059	7.50E-6	0.020	0.33	0.18	31
58.0	EC >5 to 6 aliphatic	C _{5.5} H ₁₃	79.0	0.100	1.00E-5	51	0.28	270	29.9
91.7	EC >6 to 7 aliphatic	C _{6.5} H ₁₅	93.0	0.100	1.00E-5	54	0.28	85.3	8.4
121.2	EC >7 to 8 aliphatic	C _{7.5} H ₁₇	107.0	0.100	1.00E-5	56	0.28	27.0	2.4
147.9	EC >8 to 9 aliphatic	C _{8.5} H ₁₉	121.0	0.100	1.00E-5	59	0.29	8.53	0.7
--	oxygen	O ₂	32.0	0.175	1.70E-5	45	--		

Table B.1. Chemical-specific physical properties for representative gasoline components and oxygen.

chemical name or class	T _{nbp} (°C)	molecular diffusivity in air (cm ² /sec)	molecular diffusivity in water (cm ² /sec)	Henry's law coefficient (cm ³ /cm ³)	(pure) chemical vapor pressure (mmHg)	(pure) chemical aqueous solubility (mg/L)
aromatic hydrocarbons						
benzene	C	B	B	B	C	B
toluene	C	B	B	B	C	B
ethylbenzene	F	B	B	B	D	B
xylene (mixed isomers)	C	C	C	C	C	E
EC >8 to 9 aromatic (-E -X)	A	A	A	A	A	A
EC >9 to 10 aromatic	A	A	A	A	A	A
EC >10 to 11 aromatic	A	A	A	A	A	A
naphthalene	G	B	B	B	D	B
aliphatic hydrocarbons						
EC >5 to 6 aliphatic	A	A	A	A	A	A
EC >6 to 7 aliphatic	A	A	A	A	A	A
EC >7 to 8 aliphatic	A	A	A	A	A	A
EC >8 to 9 aliphatic	A	A	A	A	A	A
others						
oxygen	--	H	H	I		

Table B.1. (continued) Indicated references.

C. Gasoline source composition

In defining saturated concentrations for a gasoline source, equilibrium Raoult law partitioning for the fractionally soluble constituents is applied. Water-phase source concentrations based on mixing into an initial volume of water and air is estimated as:

$$c_{w,i} = \frac{S_i \cdot y_i}{1 + \left(\frac{S_i \cdot y_i}{\chi_i \cdot \rho_o} \right) \cdot \left(\frac{V_w}{V_o} \right) + \left(\frac{H_i \cdot S_i \cdot y_i}{\chi_i \cdot \rho_o} \right) \cdot \left(\frac{V_a}{V_o} \right)} \quad [C.1]$$

Vapor concentrations are specified by:

$$c_{v,i} = H_i \cdot c_{w,i} \quad [C.2]$$

The value S_i is the pure chemical aqueous solubility limit, H_i is dimensionless Henry's law coefficient, y_i is the mole fraction of chemical in the gasoline, and χ_i as the mass fraction of chemical in gasoline. Gasoline density is ρ_o . The volume ratio of water to gasoline and air to gasoline, are, respectively, V_w/V_o and V_a/V_o .

Table C.1 includes a representative gasoline composition derived from data in Potter and Simmons (18). Estimates of source soil vapor and pore water concentrations are included in the table for a specified water-gasoline $V_w/V_o = 10$ and air-gasoline ratio $V_a/V_o = 0$. The resulting calculated concentrations are intended to be representative upper bound source-zone groundwater concentration measurements for the case of released residual gasoline in contact with groundwater. For a finite-volume release, soluble and volatile chemical source concentrations will decrease over time and the concentrations in Table C.1 will tend to be conservative overestimates.

normal boiling point (°C)	chemical name or surrogate class	petroleum gasoline (MoGas)		
		mass fraction (g/g)	aqueous solubility (mg/L)	vapor concentra- tion (mg/m ³)
aromatics:				
80.1	benzene	0.023	47.2	10800
110.7	toluene	0.1	53.4	14700
136.2	ethylbenzene	0.02	3.0	980
140.0	xylene (mixed isomers)	0.108	17.2	3760
147.9	EC >8 to 9 aromatic (-X -E)	0.003	0.21	117
172.4	EC >9 to 10 aromatic	0.09	3.5	1140
195.2	EC >10 to 11 aromatic	0.003	0.07	12.5
217.9	naphthalene	0.003	0.07	1.4
aliphatics:				
58.0	EC >5 to 6 aliphatic	0.303	10.8	553000
91.7	EC >6 to 7 aliphatic	0.171	1.5	78200
121.2	EC >7 to 8 aliphatic	0.099	0.20	11600
147.9	EC >8 to 9 aliphatic	0.077	0.04	2360
totals:		1.00	137.15	676390
average molecular weight:		94.1		

Table C.1. Gasoline composition and source concentration levels. The EC >8 to 9 aromatic fractions do not include ethylbenzene (-E) and xylenes (-X). The EC >11 to 12 aromatic fraction (which is zero) does not include naphthalene (-N). Average gasoline density is presumed $\rho_o = 0.91$ g/mL. Equivalent carbon, EC, represents a chemical fraction defined by the normal boiling points of a series of n-paraffin hydrocarbons.

D. Baseline Soil Respiration

Results and interpretation for baseline oxygen respiration for soils with no added substrate chemicals follow for a set of microcosm tests on five soil media types; for two soils in a set of diffusive column experiments; and from published literature. An empirical correlation of baseline soil oxygen respiration rate is derived, including confidence bounds.

D.1 Conservation Equations

Microcosms

Sealed vials containing soil, air, and water are used in laboratory tests of soil respiration. Aliquots of air or water taken from the microcosms over a period of time are analyzed for the disappearance or appearance of chemical constituents. For oxygen a baseline soil respiration term is determined as

$$\left(V_w + V_a \cdot H_{O_2}\right) \cdot \frac{dc_{w,O_2}}{dt} = m_s \cdot \Lambda_{base,O_2} \quad [D.1]$$

with t (day) as time; c_{w,O_2} (mg/L) as water-phase oxygen concentration; m_s (kg) is total soil mass; Λ_{T,O_2} [mg/(day · kg-soil)] as the mass-specific respiration rate in the soil; V_w (L-water) is the water volume within the microcosm; V_a (L-air) is the air volume within the microcosm; and H_{O_2} (L-water/L-air) is the Henry's law coefficient for oxygen.

Diffusive Soil Columns

For oxygen and carbon dioxide in a aerobic soil column of length, L , with homogeneous soil conditions; a concentration boundary condition at the open column end ($z = L$); and a zero flux condition at the closed column end ($z = 0$):

$$\Lambda_{base,j} = \frac{2 \cdot (1 - \beta) \cdot D_{eff,j} \cdot H_i \cdot c_{w,j}(z = 0)}{\rho_s \cdot L^2} \quad [D.2]$$

with

$$\left(\frac{c_{w,j}(z = L)}{c_{w,j}(z = 0)}\right) = \beta \quad [D.3]$$

where j refers either to CO_2 or O_2 . These are related:

$$\Lambda_{T,O_2} = \frac{\Lambda_{T,CO_2}}{\phi_{[CO_2/O_2]}} \quad [D.4]$$

and $\phi_{[CO_2/O_2]}$ is approximately equal to the ratio of carbon dioxide to oxygen molecular weight.

D.2 Experimental Apparatus and Results

Microcosms

The decreasing partial pressure of oxygen over time was measured for soils in sealed aerobic microcosms. No chemical substrates were amended. The test apparatus included 1000 mL sealed microcosms, with 50 g of soil and 800 mL of water each. Prior to sealing, the microcosms were sparged with zero grade air for 15 minutes, and then

capped and sealed with an air headspace. A potassium hydroxide (KOH) trap was included within the headspace of the microcosm to capture generated CO₂. Internal microcosm pressure was monitored and recorded at 30-minute time intervals. A magnetic stir bar was used to agitate the soil continuously for one minute in every 15 minutes. Intermittent stirring was intended to reduce the development of concentration gradients within a stagnant layer of soil, while minimizing breakdown of the particulate soil structure. Duplicate microcosm samples were run for five media and soil types. The measured organic carbon fraction ranged from 0.00032 g-oc/g-soil (glass beads) to 0.19 g-oc/g-soil (Houston black clay). The organic carbon fraction was determined as the fractional mass loss of oven-dried soils (at 100°C), when further heated to 600°C in air.

Oxygen decrease in the microcosm incubation is due to baseline soil respiration. Decrease in the internal microcosm pressure is directly proportional to the disappearance of oxygen. Tests were terminated either when the calculated oxygen level had either decreased from the initial 21% v/v to less than 4% v/v, or after up to five days of incubation. In data analysis, the initial slope of the pressure versus time measurements was determined using a least-squares data analysis. This was related to oxygen uptake rates using Eq. [D.1]. Error bounds were estimated at a 95% confidence level for each test.

The minimum resolution of the test apparatus is within the range of approximately ~ 0.04 mg-O₂/g-soil day. This is primarily limited by variation in atmospheric pressure over the test duration and the response of the differential pressure transducer instrumentation. Replicate tests on baseline soils gave a measure of test-to-test variability. Results of the microcosm test series are summarized in Table D.1.

Soil columns

Homogeneous soil columns of 1 m length and 10 cm diameter were configured with a sealed reservoir at the lower chamber and clean humidified sweep air at the upper chamber. Two soil types were used. Multiple sampling ports along the column were provided for syringe collection and analysis of vapor samples. Profile measurements were made for oxygen and carbon dioxide concentrations in air. Eq. [D.2] is used in estimating baseline oxygen respiration under these conditions. Results of the estimate are shown in Table D.2.

D.3 Literature

Neale, et al. (35) reports on oxygen utilization rates for nine soils at three moisture levels each. Rates were measured in a 250 mL closed-chamber respirometer packed with 100 g of soil in incubations of 40 hours duration. Results were reported as oxygen consumption rate per unit mass of soil. Higher respiration rates in selected soils were reported at increased soil moisture levels. Reported organic carbon fractions ranged from 0.38 g-oc/g-soil (peat) to 0.0004 g-oc/g-soil (sand).

Hendry et al. (36) reported on microbial respiration rates through a 3.2 m thick layer of a sandy unsaturated soil zone in a 4.6m high by 2.4m diameter mesocosm. Soil-gas CO₂ profile concentrations were monitored, with an estimate of CO₂ respiration from a

diffusion model fit. Consistent microbial respiration rates of $0.2 \mu\text{g-C}/(\text{g-soil} \cdot \text{day})$ were reported through most of the zone, with a decrease to 10^{-4} to $10^{-3} \mu\text{g-C}/(\text{g-soil} \cdot \text{day})$ in the capillary fringe [author note: diffusion-limited oxygen transport in the capillary fringe may be an explanation]. Microcosms of 500 g of soil were also used in estimating respiration rates, with results approximately an order of magnitude greater than the mesocosm test. Microcosms were incubated over a range of temperatures from 4° to 30°C and a range of volumetric moisture levels from 0.044 to 0.37. Higher respiration rates for the microcosms were attributed to greater soil disturbance (in preparation) than the mesocosm test. For comparison with oxygen respiration data, the published C - normalized CO_2 generation rate was multiplied by the molecular weight ratio of oxygen to carbon [$32.00 \text{ g-O}_2/\text{g-mole} / 12.01 \text{ g-C/g-mole}$].

D.4 Baseline Oxygen Soil Respiration Correlation

Measured microcosm soil respiration rates, soil column respiration rates, and the reported oxygen respiration measurements of Neale, et al. (35), and Hendry et al. (36) are plotted in Figure D.1 as respiration rate versus soil organic carbon level. These results have been used in developing a correlation between measured oxygen uptake rates and soil organic carbon fraction.

An empirical correlation of the data in Figure D.1 is given by:

$$\Lambda_{base, O_2} = - \left(1.69 \frac{mg - O_2}{g - oc \cdot day} \right) \cdot f_{oc} \quad [D.5]$$

with, in this case, baseline respiration rate Λ_{base, O_2} [$\text{mg-O}_2/(\text{g-soil} \cdot \text{day})$] and organic carbon fraction in soil f_{oc} (g-oc/g-soil). A 95% confidence interval on this correlation is included in Figure D.1. For the included range of data $0.0004 < f_{oc} < 0.4$, at this 95% confidence, errors in the respiration estimate are within a factor (\times/\div) of approximately 10 of the correlation.

Variability in the measured data is noted. Stirred versus quiescent soil incubation, variations in the bioavailability and types of soil organic carbon, diffusion limitations within soil layers and with the soil matrix, and soil heterogeneity between tests all contribute to this variability. Dependence of soil respiration on temperature or moisture levels is not included in the correlation as the variability between data sets is greater than the indicated dependence in specific tests.

To relate the oxygen respiration rate to a disappearance rate of soil organic carbon, we represent organic carbon decay as a first-order rate, k_{oc}

$$k_{oc} = \frac{\varphi_i}{f_{oc}} \cdot \Lambda_{base, O_2} \quad [D.6]$$

With $\varphi_i = 1$ (for sugars and starches) approximately, this yields $k_{oc} = 0.00169/\text{day} \times/\div 10$, or a half-life of 410 days (ranging from 41 to 4100 days at a 95% confidence interval) for soil organic carbon.

Soil organic carbon includes plant matter (tops and roots), animal bodies, and microorganisms. In composition, it includes sugars, starches, proteins, fats, oils, waxes, cellulose, and lignins. Highly altered organic matter is characterized as humus; this is a class of organic substances of variable composition and high molecular weight, including fluvic acids, humic acids, and humin. All soils have varying fractions of these constituents and it is expected that the components biodegrade at varying rates. Characterizing soils with a single measure of soil organic carbon fraction and a single respiration rate is useful in the present application, if the inherent assumptions and limitations of this approach are recognized.

soil or media type:	Glass Beads	Filter Sand	Lakeland	Norwood	Houston Black
measured organic carbon in soil (g/g):	0.00032	0.0009	0.012	0.055	0.19
test indicator:	A#P001	A#P002	A#P003	A#P004	A#P005
mass of soil (g):	50	50	50	50	50
water volume (mL):	800	800	800	800	800
air volume (mL):	281	281	270	283	270
bottle size (mL):	1000	1000	1000	1000	1000
points, N, in linear data range:	92	86	54	86	121
assigned confidence limit (CI=95%)	0.95	0.95	0.95	0.95	0.95
net oxygen decrease in headspace (% atm)	0.4%	2.2%	2.5%	3.8%	12.3%
slope (inH ₂ O/day)	0.86	4.98	9.15	8.67	20.09
+/- error in slope estimate (inH ₂ O/day)	0.96	1.07	0.53	1.11	2.38
slope (mg-O ₂ /g-soil day)	0.02	0.10	0.17	0.17	0.38
+/- error in slope estimate (mg-O ₂ /g-soil day)	0.02	0.02	0.01	0.02	0.05
test indicator:	B#P001	B#P002	B#P003	B#P004	B#P005
mass of soil (g):	50	50	50	50	50
water volume (mL):	800	800	800	800	800
air volume (mL):	277	262	276	272	292
bottle size (mL):	1000	1000	1000	1000	1000
points, N, in linear data range:	140	166	140	92	91
assigned confidence limit (CI=95%)	0.95	0.95	0.95	0.95	0.95
net oxygen decrease in headspace (% atm)	0.7%	0.0%	3.2%	2.2%	11.5%
slope (inH ₂ O/day)	1.05	-0.02	4.38	4.51	24.96
+/- error in slope estimate (inH ₂ O/day)	4.50	2.07	1.96	1.24	3.65
slope (mg-O ₂ /g-soil day)	0.02	0.00	0.09	0.09	0.51
+/- error in slope estimate (mg-O ₂ /g-soil day)	0.09	0.04	0.04	0.02	0.07

Table D.1. Soil Respiration Microcosm test results.

soil type:	Kalkaska	Norwood / Baccto
test column indicator	C. 1	C. 2
soil column length (cm):	95	95
total organic carbon (g/g):	0.0008	0.0365
water fraction (cm ³ -water/cm ³ -soil):	0.031	0.175
void fraction (cm ³ -void/cm ³ -soil)	0.469	0.563
bulk dry soil density (g/cm ³)	1.34	1.14
O₂ oxygen		
Henry's law coefficient (20°C, 1 atm) (cm ³ -water/cm ³ -air)	44.6	44.6
effective diffusion coefficient (cm ² /sec)	5.09E-02	2.36E-02
O ₂ - concentration column top (mol/mol)	0.209	0.21
O ₂ concentration - column bottom (mol/mol)	0.2	0.205
ratio concentration - top to bottom	1.05	1.02
oxygen concentration at column bottom (mg/L-water)	5.97	6.11
zero-order rate of oxygen generation (sink) mg-O ₂ /g-soil - day	-8.71E-03	-2.64E-03
95% confidence bounds (+/-)	8.13E-04	3.67E-04
CO₂ carbon dioxide		
Henry's law coefficient (20°C, 1 atm) (cm ³ -water/cm ³ -air)	1.08	1.08
effective diffusion coefficient (cm ² /sec)	4.40E-02	2.04E-02
CO ₂ concentration - column top (ppmv)	31.7	0
CO ₂ concentration - column bottom (ppmv)	4000	6700
ratio concentration - top to bottom	0.00793	0
carbon dioxide concentration at column bottom (mg-CO ₂ /L-water)	6.8	11.3
zero-order rate of carbon dioxide generation (mg-CO ₂ /g-soil - day)	4.57E-03	4.20E-03
95% confidence bounds (+/-)	2.13E-03	2.99E-03

Table D.2. Soil Column baseline respiration oxygen and carbon dioxide results.

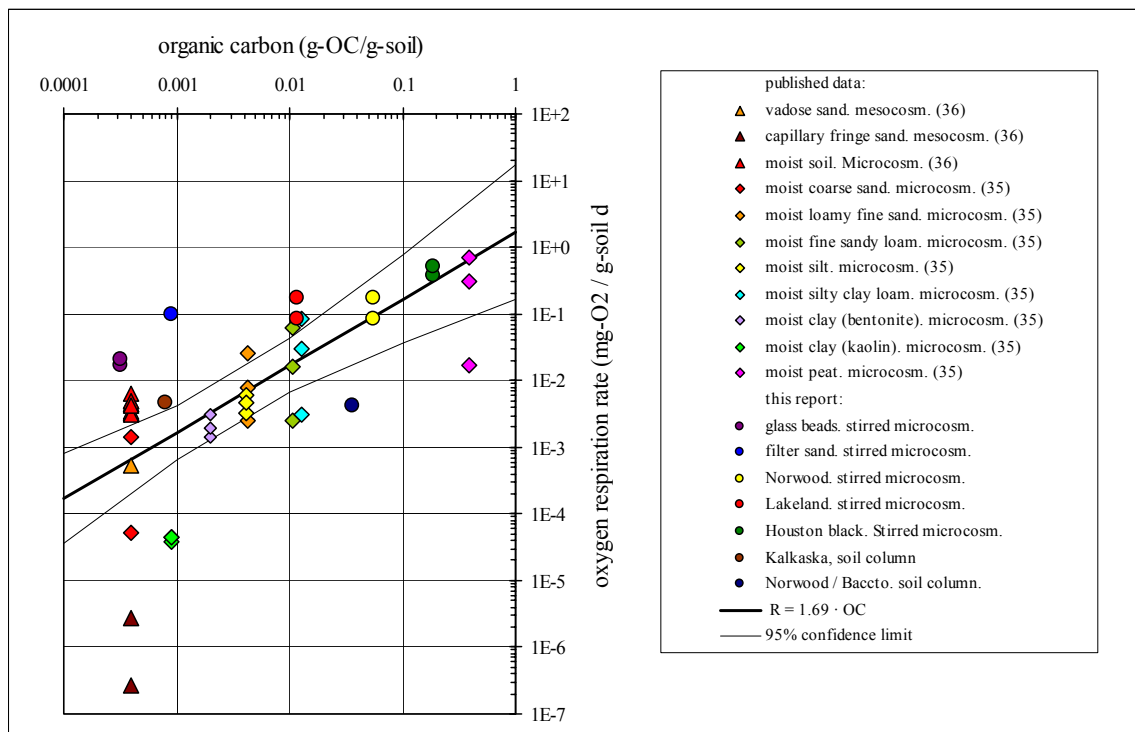


Figure D.1. Baseline soil respiration. Oxygen respiration rate is plotted as a function of soil organic carbon.

E. Relationship between Y_f and Y_c .

This analysis illustrates the relationship between the defined Y_f and Y_c terms.

E.1 Aerobic Soil Layer

Eqs. [15] and [32] in the manuscript define a chemical-specific diffusion-reaction length

$$L_{R,i} = \frac{L_a}{\alpha_{a,i}} = \sqrt{\frac{D_{eff,i} \cdot H_i}{k_{w,i} \cdot \theta_w}} \quad [E.1]$$

The relationship between oxygen flux and oxygen concentration is given in the manuscript for the aerobic soil layer by Eq. [29]. With Eq. [E.2] this is:

$$\frac{J_{e,O_2} \cdot L_a}{D_{eff,O_2} \cdot c_{e,O_2}} = \frac{\sum_{i=1}^N \frac{1}{\varphi_i} \cdot \frac{D_{eff,i} \cdot c_{t,i}}{L_{R,i}} \cdot \frac{2 - \exp(-\alpha_{a,i}) - \exp(\alpha_{a,i})}{\exp(\alpha_{a,i}) - \exp(-\alpha_{a,i})} + \rho_s \cdot L_a \cdot \Lambda_{base,O_2}}{\sum_{i=1}^N \left(\frac{D_{eff,i}}{L_a} \right) \cdot \frac{c_{t,i}}{\varphi_i} - \left(\frac{\rho_s \cdot \Lambda_{base,O_2} \cdot L_a}{2} \right)} \quad [E.2]$$

no chemical biodegradation

For the case of no chemical biodegradation, we substitute $c_{t,i} = 0$ for all chemicals in Eq. [E.1]:

$$\frac{J_{e,O_2} \cdot L_a}{D_{eff,O_2} \cdot c_{e,O_2}} = -2 \quad [E.3]$$

This indicates that the dimensionless oxygen flux is a constant value when soil respiration dominates the oxygen demand.

no soil respiration oxygen demand

For the case of no soil respiration, we substitute $\Lambda_{base,O_2} = 0$ into Eq. [E.2]

$$\frac{J_{e,O_2} \cdot L_a}{D_{eff,O_2} \cdot c_{e,O_2}} = \frac{\sum_{i=1}^N \frac{1}{\varphi_i} \cdot \frac{D_{eff,i} \cdot c_{t,i}}{L_{R,i}} \cdot \frac{2 - \exp(-\alpha_{a,i}) - \exp(\alpha_{a,i})}{\exp(\alpha_{a,i}) - \exp(-\alpha_{a,i})}}{\sum_{i=1}^N \left(\frac{D_{eff,i}}{L_a} \right) \cdot \frac{c_{t,i}}{\varphi_i}} \quad [E.4]$$

In the limit for large $\alpha_{a,i}$, Eq. [E.4] yields

$$\frac{J_{e,O_2} \cdot L_a}{D_{eff,O_2} \cdot c_{e,O_2}} = L_a \cdot \frac{-\sum_{i=1}^N \frac{D_{eff,i} \cdot c_{t,i}}{\varphi_i} \cdot \frac{1}{L_{R,i}}}{\sum_{i=1}^N \frac{D_{eff,i} \cdot c_{t,i}}{\varphi_i}} \quad [E.5]$$

Eq. [E.5] includes a weighted harmonic mean of diffusion-reaction lengths:

$$\bar{L}_{R,t} = \frac{\sum_{i=1}^N \frac{D_{eff,i} \cdot c_{t,i}}{\varphi_i}}{\sum_{i=1}^N \frac{D_{eff,i} \cdot c_{t,i}}{\varphi_i} \cdot \frac{1}{L_{R,i}}} \quad [E.6]$$

With Eq. [E.6] in [E.5]:

$$\frac{J_{e,O_2} \cdot L_a}{D_{eff,O_2} \cdot c_{e,O_2}} = -\frac{L_a}{L_{R,t}} \quad [E.7]$$

E.2 Total Soil Layer

The intent is to develop a relationship similar to Eq. [E.2], but which applies for the total soil depth, L_T , not just the aerobic depth, L_a .

From Eq. [34] in the manuscript and [E.1] we get:

$$Y_f \cdot J_{e,O_2} = \sum_{i=1}^N \left(\frac{D_{eff,i} \cdot c_{s,i}}{\phi_i} \cdot \frac{1}{L_{R,i}} \cdot \frac{2 - \exp(-\alpha_{T,i}) - \exp(\alpha_{T,i})}{\exp(\alpha_{T,i}) - \exp(-\alpha_{T,i})} \right) + L_T \cdot \rho_s \cdot \Lambda_{base,O_2} \quad [E.8]$$

with $\alpha_{T,i} = L_T / L_{R,i}$. From Eq. [35] in the main paper,

$$Y_c^2 \cdot \frac{D_{eff,O_2} \cdot c_{e,O_2}}{L_T} = \left(\frac{\sum_{i=1}^N D_{eff,i} \cdot [c_{s,i} / \phi_i]}{L_T} \right) - \left(\frac{L_T \cdot \rho_s \cdot \Lambda_{base,O_2}}{2} \right) \quad [E.9]$$

The ratio of Eq.[E.8] and [E.9] is

$$\frac{J_{e,O_2} \cdot L_T}{D_{eff,O_2} \cdot c_{e,O_2}} \cdot \left(\frac{Y_f}{Y_c^2} \right) = \frac{\sum_{i=1}^N \left(\frac{D_{eff,i} \cdot c_{s,i}}{\phi_i} \cdot \frac{1}{L_R} \cdot \frac{2 - \exp(-\alpha_{T,i}) - \exp(\alpha_{T,i})}{\exp(\alpha_{T,i}) - \exp(-\alpha_{T,i})} \right) + L_T \cdot \rho_s \cdot \Lambda_{base,O_2}}{\sum_{i=1}^N \left(\frac{D_{eff,i}}{L_T} \right) \cdot \frac{c_{s,i}}{\phi_i} - \left(\frac{L_T \cdot \rho_s \cdot \Lambda_{base,O_2}}{2} \right)} \quad [E.10]$$

Similarity of Eq. [E.2] and [E.10] is noted.

no soil respiration oxygen demand

For the case of no chemical biodegradation, we substitute $c_{t,i} = 0$ for all chemicals into Eq. [E.10] to get:

$$\frac{J_{e,O_2} \cdot L_T}{D_{eff,O_2} \cdot c_{e,O_2}} \cdot \left(\frac{Y_f}{Y_c^2} \right) = -2 \quad [E.11]$$

With Eqs. [E.3] and [E.11]

$$\left(\frac{Y_f}{Y_c^2} \right) = \frac{L_a}{L_T} \quad [E.12]$$

no soil respiration oxygen demand

For the case of no soil respiration, we substitute $\Lambda_{base,O_2} = 0$ into Eq. [E.10]

$$\frac{J_{e,O_2} \cdot L_T}{D_{eff,O_2} \cdot c_{e,O_2}} \cdot \left(\frac{Y_f}{Y_c^2} \right) = \frac{\sum_{i=1}^N \left(\frac{D_{eff,i} \cdot c_{s,i}}{\phi_i} \cdot \frac{1}{L_R} \cdot \frac{2 - \exp(-\alpha_{T,i}) - \exp(\alpha_{T,i})}{\exp(\alpha_{T,i}) - \exp(-\alpha_{T,i})} \right)}{\sum_{i=1}^N \left(\frac{D_{eff,i}}{L_T} \right) \cdot \frac{c_{s,i}}{\phi_i}} \quad [E.13]$$

In the limit for large $\alpha_{T,i}$, Eq. [E.13] is:

$$\frac{J_{e,O_2} \cdot L_T}{D_{eff,O_2} \cdot c_{e,O_2}} \cdot \left(\frac{Y_f}{Y_c^2} \right) = L_T \cdot \frac{-\sum_{i=1}^N \frac{D_{eff,i} \cdot c_{s,i}}{\phi_i} \cdot \frac{1}{L_{R,i}}}{\sum_{i=1}^N \frac{D_{eff,i} \cdot c_{s,i}}{\phi_i}} \quad [E.14]$$

Eq. [E.14] includes a weighted harmonic mean of diffusion-reaction lengths:

$$\bar{L}_{R,s} = \frac{\sum_{i=1}^N \frac{D_{eff,i} \cdot c_{s,i}}{\phi_i}}{\sum_{i=1}^N \frac{D_{eff,i} \cdot c_{s,i}}{\phi_i} \cdot \frac{1}{L_{R,i}}} \quad [E.15]$$

Substituting Eq. [E.15] in [E.14]

$$\frac{J_{e,O_2} \cdot L_T}{D_{eff,O_2} \cdot c_{e,O_2}} \cdot \left(\frac{Y_f}{Y_c^2} \right) = -\frac{L_T}{\bar{L}_{R,s}} \quad [E.16]$$

With Eq. [E.16] and [E.7]

$$\left(\frac{Y_f}{Y_c^2} \right) = \frac{\bar{L}_{R,t}}{\bar{L}_{R,s}} \quad [E.17]$$

E.3 Summary

Results of this analysis illustrate that under several asymptotic conditions, either: (1) with dominant soil respiration, or (2) with dominant and significant chemical reaction, a consistent relationship between the defined Y_f and Y_c values is seen.

For oxygen demand equal to oxygen availability, $Y_f = 1$ and $Y_c = 1$. Under defined conditions, this occurs when the soil layer L_T is entirely aerobic, that is, with $L_a = L_T$ and $c_{t,i} = c_{s,i}$.

For conditions with oxygen demand greater than oxygen availability, $Y_f > 1$ and $Y_c > 1$, Eqs. [E.12] and [E.17] give a justification for including the square-root in the definition of Y_c in Eq. [35] of the manuscript.

F. Nomenclature and Parameter Summary

All equations in the manuscript are dimensionally consistent.

AF	(-- Attenuation factor, or ratio of indoor air to subsurface soil vapor concentration, ($= c_e / c_s$).
A_b	(cm ²) Building foundation area in contact with soil.
A	(-- Grouped term defined by Eq. [37], used in Figure 4.
a, b	(-- Subscripts designating aerobic (a) or anaerobic (b) soil layers
c_w	(mg/cm ³ -water) Water-phase chemical concentration. Chemical-specific.
c	(mg/cm ³ -air) Chemical vapor concentration subscripted as vapor (v) indicated at the source (s), within the indoor building enclosure (e), or at the anaerobic - aerobic interface, (t). Also as a reference chemical vapor concentration (at $z = 0$) of c_0 . Chemical-specific.
c_{amb,O_2}	(mg/cm ³) Ambient oxygen concentration in air ($= 0.279$ mg/cm ³).
D	(cm ² /sec) Effective diffusivity in foundation cracks (<i>crk</i>) or in the porous soil media (<i>eff</i>). Molecular diffusion coefficients for chemical vapor (v) in air, and water (w). Chemical-specific.
ER	(1/day) Building air exchange rate, as volume exchanges per unit time.
H	(cm ³ -water/cm ³ -air) Henry Law coefficient. Chemical-specific.
h	(cm/sec) foundation mass transfer coefficient. Chemical-specific.
i	(-- subscript for chemical index, for $i = 1$ to N chemicals and for oxygen (O_2)
J	(mg/cm ² -sec) Chemical flux subscript indicated at the source (s), within the indoor building enclosure (e), or at the anaerobic - aerobic interface, (t). Chemical-specific.
f_{oc}	(g-oc/g-soil) Soil organic carbon level.
k_w	(h ⁻¹) First-order chemical degradation rate. Chemical specific.
L_{crk}	(cm) Foundation thickness.
L_T	(cm) Chemical source to building foundation separation distance ($= L_a + L_b$)
L_a	(cm) Aerobic soil layer depth.
L_b	(cm) Anaerobic soil layer depth.
L_{mix}	(cm) Indoor air mixing height (or ratio of building interior volume to foundation area in contact with soil, A_b)
L_R	(cm) diffusive reaction length. Chemical specific. $L_R = (D_{eff} \cdot H / k_w \cdot \theta_w)^{0.5} = L / L_R$.
z	(cm) Vertical coordinate direction.
Q_s	(cm ³ -air/s) or (L-air/min) Convective volumetric airflow, entering the building through foundation cracks.
MW	(g/g-mol) molecular weight. Chemical specific.
Y	(-- Maximum oxygen demand relative to oxygen availability. Based on specified oxygen concentration (c) or flux (f) below the building foundation.
α	(-- square root of diffusive Damkohler number, $\alpha = L \cdot (k_w \cdot \theta_w / D_{eff} \cdot H)^{0.5} = L / L_R$. Defined for aerobic soil layer (a) or total soil layer (T). Chemical specific.
β	(-- Concentration ratio for either the aerobic (a) soil layer, $\beta_a = c_e / c_t$; or anaerobic (b) soil layer, $\beta_b = c_t / c_s$.

θ_T	(cm ³ -void/cm ³ -soil) Soil porosity = ($\theta_T = \theta_a + \theta_w$)
θ_w	(cm ³ -water/cm ³ -soil) Soil moisture
θ_v	(cm ³ -air/cm ³ -soil) Vapor-filled soil porosity
η	(cm ² /cm ²) Area fraction of cracks in a foundation of total area A_b .
ξ	(--) Dimensionless ratio of convection to diffusion flow through the building foundation $\xi = (Q_s \cdot L_{crk} / A_b \cdot D_{crk} \cdot \eta) \cdot \text{Chemical specific.}$
Λ	(mg-chemical/g-soil·day) Biodegradation rate per unit mass of soil. Chemical-specific. Sign convention as a source (+) or sink (–). Subscripted for chemical (i), oxygen (O_2), or for baseline soil oxygen respiration ($base, O_2$).
ρ_s	(g-soil/cm ³ -soil) soil bulk density
ϕ_i	(mg-chemical/mg-O ₂) is a chemical-specific mass ratio of oxygen to chemical consumption