

EPA/600/R-06/035A
ERASC-012
April 2006

**APPLICATION OF EQUILIBRIUM PARTITIONING THEORY
TO SOIL PAH CONTAMINATION**

by

Anne Fairbrother
U.S. Environmental Protection Agency
Office of Research and Development
National Health and Environmental Effects Research Laboratory
Western Ecology Division
Corvallis, Oregon

Ecological Risk Assessment Support Center
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH

NOTICE

This report is an external draft for review purposes only and does not constitute Agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

TABLE OF CONTENTS

	<u>Page</u>
AUTHORS, CONTRIBUTORS AND REVIEWERS	iv
ACKNOWLEDGMENTS	iv
BACKGROUND	1
EQUILIBRIUM PARTITIONING THEORY	2
APPLICATION OF EqP THEORY TO SOILS	3
EQUILIBRIUM ASSUMPTION	3
ORGANIC CARBON	4
WEATHERING	5
AGING	5
MICROBIAL DEGRADATION	6
PARTICLE SIZE INFLUENCES K_{OC}	6
POREWATER - ORGANISM RELATIONSHIP	7
CONCLUSIONS	8
REFERENCES	9

AUTHORS, CONTRIBUTORS AND REVIEWERS

AUTHOR

Anne Fairbrother
U.S. Environmental Protection Agency
Office of Research and Development
National Health and Environmental Effects Research Laboratory
Western Ecology Division
Corvallis, OR 97330

CONTRIBUTOR

Michael Kravitz
U.S. Environmental Protection Agency
Office of Research and Development
National Center for Environmental Assessment
Cincinnati, OH 45268

REVIEWERS

Mace Barron
U.S. Environmental Protection Agency
Office of Research and Development
National Health and Environmental Effects Research Laboratory
Gulf Breeze, FL 32561

Robert Ozretich
U.S. Environmental Protection Agency
Office of Research and Development
National Health and Environmental Effects Research Laboratory
Western Ecology Division
Corvallis, OR 97330

ACKNOWLEDGMENTS

Programmatic review of the document was conducted by the Trichairs of EPA's Ecological Risk Assessment Forum: Gina Ferreira, EPA Region 2; Dale Haroski, Office of Solid Waste and Emergency Response, Office of Superfund Remediation and Technology Innovation (OSWER/OSRTI); and Dale Hoff, EPA Region 8.

1 **BACKGROUND**

2 In March 2004, ORD’s Ecological Risk Assessment Support Center (ERASC) received a
3 request from the Ecological Risk Assessment Forum (ERAF) to provide insight into the issue of
4 whether equilibrium partitioning (EqP) techniques can be used to predict the toxicity of
5 polycyclic aromatic hydrocarbon (PAH) mixtures in field-collected soil. Specifically, the
6 following set of questions was asked:

7 Can equilibrium partitioning techniques be used to predict toxicity of polycyclic
8 aromatic hydrocarbon (PAH) mixtures in field-collected soil, in support of more
9 realistic ecological screening assessment for PAHs in soil? Can this approach include
10 alkylated PAHs? Can a unified theory for estimating the bioavailable fraction be
11 developed for a broad range of PAH compounds for ecological assessments in soil?
12

13 PAHs are found in soil at many Superfund and RCRA sites (e.g., manufactured gas
14 plants, wood treating facilities [creosote], rail facilities, refineries). Regions are using a
15 variety of ecological soil screening values, some of which are very conservative (e.g., United
16 States Fish and Wildlife Service [Beyer, 1990] and Ministry of Housing, Spatial Planning and
17 Environment [MHSPE, 1994]). PAHs are identified as chemicals of potential concern at sites
18 with low levels of contamination and where toxicity in terrestrial organisms is not observed.
19 The primary mode of toxic action for PAHs in soil dwelling terrestrial receptors (e.g.,
20 invertebrates) is non-specific, nonpolar narcosis (Sverdrup et al., 2002a), similar as for aquatic
21 organisms. Ma et al. (1998) showed that the biota-soil accumulation factor for low molecular
22 weight PAHs ($\log K_{ow} < 5.2$) in earthworms is independent of K_{ow} , and toxicity increases with
23 increasing lipophilicity. These and other similar data support the hypothesis that the uptake of
24 PAHs by earthworms occurs primarily by direct contact with the soluble phase of the soil
25 solution (interstitial porewater). This is similar to what occurs with sediment invertebrates,
26 where EqP theory for PAHs has been used successfully to derive ecological screening

1 benchmarks (ESBs) for sediments (Pavlou, 1987; US EPA, 2003; Swartz et al., 1990; Di Toro
2 et al., 1991; MacDonald, 1994). The question arises as to the general applicability of EqP
3 theory to soils, for derivation of Ecological Soil Screening Levels (EcoSSLs) for PAHs.
4 Additional questions are whether (and to what extent) bioavailability of PAHs in soils is
5 affected by organic carbon quality and quantity, aging and weathering, microbial action,
6 methylation/hydroxylation, adsorption/desorption hysteresis and ultra-violet light interaction.

7 **EQUILIBRIUM PARTITIONING THEORY**

8 EqP theory was developed in the late 1980s/early 1990s as a means of predicting
9 toxicity of PAHs to sediment-dwelling organisms (Di Toro et al., 1991). Simply stated,
10 toxicity to sediment organisms is directly proportional to the amount of unbound PAH
11 dissolved in sediment porewater. Therefore, if one can predict how much of the bulk sediment
12 PAH is bound to the organic carbon on sediment particles (and, therefore, by difference
13 calculate how much is in the porewater), then toxicity prediction can be done solely on the
14 basis of LC₅₀s (or, alternatively, Water Quality Criteria) derived from water-only studies.
15 Binding of PAHs to sediment particles is a function of their solubility and amount of organic
16 matter present in the sediment. Under equilibrium conditions, the relative distribution of
17 PAHs between porewater and sediment organic carbon can be predicted on the basis of
18 organic carbon-water partition coefficients (K_{oc}). Additionally, biota-sediment accumulation
19 factors are a function of the sediment type and the PAH mixture. Therefore, values derived by
20 the EqP method also must account for differences in relative bioavailability. Note that the
21 assumption of benthic organism exposure via sediment porewater has recently been refuted as
22 being applicable only to a subset of species (Kraaij et al., 2002). Others, most notably
23 bivalves and other deposit feeders, acquire much of their exposure through ingestion of

1 sediment particles so toxicity cannot be predicted based on bioassays conducted only in water.
2 This may also hold true for earthworms that ingest PAH contaminated soil particles or detritus,
3 depending upon the relative bioavailability of the chemicals in porewater and solid material.

4 **APPLICATION OF EqP THEORY TO SOILS**

5 Soils are similar to sediments in that they consist of particles of sand, silt, and/or clay
6 with porewater within the interstitial matrix of these particles. Therefore, it intuitively seems
7 feasible to apply the same type of EqP theory to soils as has been derived for sediments and
8 therefore develop a more accurate estimate of toxicity for soil dwelling organisms (plants,
9 invertebrates, microbes). Several recent studies have demonstrated a fairly predictable
10 relationship between bioaccumulation or toxic effects of PAHs to soil invertebrates and soil
11 porewater concentrations (e.g., Ma et al., 1998; Lanno et al., 2004). Such relationships are
12 most predictable for low molecular weight compounds, with significant variability occurring
13 for high molecular weight PAHs, such as benzo(a)pyrene (Ma et al., 1998). However, the
14 application of EqP to soils also requires the prediction of porewater concentrations based on
15 bulk soil concentrations and soil properties (especially soil organic matter). There are,
16 however, several underlying flaws in the logic underlying the EqP theories that result in this
17 approach being able to provide only a very general estimate of relative bioavailability of PAHs
18 at a particular site within carefully specified soil characteristics.

19 **EQUILIBRIUM ASSUMPTION**

20 It is clearly stated that ESBs for sediments “only apply to sediments permanently
21 inundated with water... or inudated periodically for durations sufficient to permit development
22 of benthic assemblages” and that they “should not be applied to occasionally inundated soils
23 containing terrestrial organisms” (U.S. EPA, 2003). Furthermore, EqP theory, even in

1 sediments, is applicable only for chronically exposed sediments, not for acute spills, as
2 equilibrium conditions need to be established for reasonable predictions to be made.
3 Equilibrium assumptions are violated in nearly all soils. Soils generally are not saturated (i.e.,
4 are below 100% water holding capacity), so chemicals in the interstitial waters are not at
5 equilibrium with those on the soil particles. This is particularly true in noncompact soils,
6 where water moves quickly through surface layers into subsurface groundwaters, or in xeric
7 soils in the arid west, where the vadose zone may contain no water for extended time periods.
8 Furthermore, soils are a tremendously heterogeneous environmental matrix with spatial and
9 temporal gradients of organic carbon, pH, and particle size distribution occurring over
10 relatively small areas. Intermittent and variable precipitation contributes to temporal
11 variability in saturation levels. This can make it difficult to generalize exposure values
12 (especially bioavailability differences) even across relatively small contaminated sites.

13 **ORGANIC CARBON**

14 In sediments, EqP theories are applicable only for those with >0.2% organic carbon
15 (OC). Nearly all sediments meet this criterion. However, soils are more variable in their
16 composition, and highly xeric soils frequently have very low amounts of organic carbon (as
17 well as soil moisture). Therefore, there are likely to be more terrestrial areas that violate this
18 basic assumption of EqP than there are sediments with extremely low OC. Furthermore, while
19 the majority of chemical will partition and bind to OC on soil or sediment particles, there can
20 be substantial amounts that bind to dissolved organic carbon (DOC) within the porewater.
21 Because of limitations in methodological procedures for measuring chemicals in porewater, it
22 is difficult to apportion the amount of chemical bound to DOC. In fact, it is difficult to
23 estimate the amount of DOC itself. Under equilibrium conditions, it is irrelevant if the organic

1 matter is particulate or dissolved, as PAH will partition proportionately to porewater and to the
2 total organic carbon regardless of type (Di Toro et al., 1991). For these reasons, computations
3 of interstitial concentrations will likely **over** predict the amount of freely dissolved chemical
4 (and, by extension, the toxicity of the soil).

5 **WEATHERING**

6 PAHs in soils undergo a weathering process such that the lighter fractions (i.e., shorter
7 chain molecules) are removed. This occurs mainly by volatilization, but some proportion of
8 the material moves through the soil vadose zone and into the groundwater. Heavier fractions
9 tend to bind more readily to the soil organic matter and remain behind in the top soil horizons.
10 Weathering occurs in sediments as well, but much more slowly. In some areas, heat and
11 compression turn soil PAH contamination into a form of asphalt, and given sufficient time
12 (e.g., >50 years), only inert carbons will remain. As the chemical mixture ages, its biota-soil
13 accumulation factor will change, as the fractions remaining tend to be those that bind the most
14 tightly.

15 **AGING**

16 In addition to weathering (i.e., loss of volatile short-chain fractions), physical processes
17 of aging also occur. Chemicals in soils “age” by becoming incorporated inside the crystal
18 lattice structure of the soil particle, or partitioning onto organic matter or soil nanopores (Nam
19 et al., 1998), so they are no longer available for uptake by organisms. This is, for all practical
20 purposes, an irreversible reaction. Although bulk soil chemistry methods can extract and
21 measure the PAH that has been sequestered in this manner, organisms cannot retrieve it.
22 Thus, aging significantly reduces bioavailability (Johnson et al., 2002). However, aging is
23 confounded by biodegradation (microbial processes) and soil characteristics, and so is not a

1 linearly predictive relationship (Sverdrup et al., 2002b; Reichenberg, 2004). Furthermore,
2 PAHs that are the result of combustion processes (e.g., soot) are inserted into particulate
3 lattices during their formation, thereby appearing to be “aged” even when recently deposited
4 into soils. Using EqP principles that only assume sorption onto OC on particle surfaces,
5 bioavailability of soil PAHs (i.e., the freely dissolved porewater concentrations) will be over
6 estimated, and this overestimation will increase with time as the PAH mixture ages.

7 **MICROBIAL DEGRADATION**

8 Microbial degradation of PAHs is a key process in the environmental dissipation of
9 these pollutants. The relative rate of biodegradation is dependent upon nutrient content of soil
10 and the bacterial community present. Various external processes (e.g., nutrient addition,
11 increasing soil temperature) have been used to enhance microbial biodegradation rates as a
12 means of soil remediation particularly after a recent spill. Microbial biodegradation disrupts
13 the physico-chemical processes that otherwise would lead to equilibrium of the PAH between
14 aqueous and solid phases in the soil. This increases the uncertainty in predictions of soil
15 porewater concentrations based on EqP theory (which depends on equilibrium conditions).

16 **PARTICLE SIZE INFLUENCES K_{OC}**

17 PAHs have different soil organic carbon-water partition coefficients (K_{OCs}) depending
18 upon size of the associated soil particles (Krauss and Wilcke, 2002). Mean K_{OC} values of
19 individual PAHs are highest in silt (fine particles), followed by clay and then sand. The K_{OC}
20 values of PAHs can vary up to a factor of 100 among soils with different particle sizes,
21 significantly influencing their binding and subsequent partitioning to porewater. Thus, any
22 models that may be aimed at predicting porewater concentrations must include an adjustment
23 for particle size (e.g., % clay).

1 **POREWATER – ORGANISM RELATIONSHIPS**

2 Soil porewater concentrations of PAHs are more predictive of biological responses
3 (toxicity and/or bioaccumulation) in soil organisms than are bulk soil concentrations. Highly
4 predictive relationships have been developed between soil porewater concentrations and lipid-
5 adjusted body residues (i.e., bioaccumulation) or toxicity endpoints (e.g., lethality). Lanno et
6 al. (2004) demonstrated that non-depletive solid-phase microextraction (SPME) methods can
7 be used to quantify porewater PAH with relative ease, and showed that such concentrations are
8 highly correlated with biological responses of soil invertebrates (earthworms, enchytraeids,
9 and collembolan) exposed to phenanthrene and pyrene. These predictive relationships were
10 applicable to five soils differing in physical/chemical characteristics. However, Ter Laak et al.
11 (2004) pointed out that the accuracy of this method is dependent upon matrix kinetics, with its
12 predictive value significantly increasing at equilibrium.

13 Hawthorne et al. (2004) suggest that a supercritical fluid extraction (SFE) from bulk
14 soils will also yield information that can predict bioaccumulation values in soil invertebrates,
15 especially if they are normalized to lipid concentrations. They developed a simple non-linear
16 model for individual PAHs to predict lipid PAH concentrations in earthworms based on
17 extracted PAHs, soil carbon matrix type (C/H ratio), and PAH octanol/water partitioning
18 coefficients for individual PAHs. This model successfully predicted lipid concentrations of
19 two- to six-ring PAHs within a factor of 10, for bulk soil PAH concentrations ranging over
20 three orders of magnitude and soil carbon contents ranging from 2 to 87%.

21 Van Beelen et al. (2003) investigated the application of the EqP method by comparing
22 aquatic and terrestrial toxicity data. They multiplied the aquatic toxicity critical value (e.g.,
23 the LC₅₀) by the appropriate partition coefficient (to express it as mg/kg solid concentration)

1 and then looked to see if this value would predict the toxicity threshold of soil organisms.
2 They concluded that this method was inaccurate, and sometimes over predicted terrestrial
3 toxicity and at other times under predicted. However, the terrestrial toxicity thresholds that
4 were used were derived from bulk soil chemistry values. It may be that a predictable
5 correlation between aquatic and terrestrial toxicity values will emerge once the terrestrial
6 database is corrected for bioavailability factors (discussed above).

7 **CONCLUSIONS**

8 This overview was prepared in response to a set of questions posed by regional risk
9 assessors to EPA/ORD's Ecological Risk Assessment Support Center:

10 Can equilibrium partitioning techniques be used to predict toxicity of polycyclic
11 aromatic hydrocarbon (PAH) mixtures in field-collected soil, in support of more
12 realistic ecological screening assessment for PAHs in soil? Can this approach include
13 alkylated PAHs? Can a unified theory for estimating the bioavailable fraction be
14 developed for a broad range of PAH compounds for ecological assessments in soil?
15

16 Soils are not in equilibrium between their solid and liquid phases, they are highly variable in
17 physico-chemical characteristics even over small areas, experience significant weathering, aging
18 and microbial degradation processes that alter even further the equilibrium assumptions, and
19 have highly variable levels of hydration due to unpredictable precipitation events (particularly in
20 xeric soils). Further confounding variables include differential ratios of OC on particles vs.
21 DOC, and influence of particle size (clay vs. sand) on OC binding characteristics. Therefore, it
22 is unlikely that further efforts will develop a predictive EqP model for PAHs (including
23 alkylated PAHs) in soils. That said, EqP theory might still be useful to identify conservative
24 screening levels of PAHs in soil, below which there would likely not be appreciable ecological
25 risk from PAHs. Any such model must include a *conservative* adjustment for particle size, due

1 to the influence of particle size on K_{oc} (discussed earlier), as well as measurements of soil
2 organic carbon.

3 With the advent of techniques to measure soil porewater concentrations of individual
4 PAHs, one may question the practical advantage of using a modified EqP approach for
5 performing a screening level assessment for PAHs. The prediction of bioaccumulation or toxic
6 responses in soil invertebrates is best accomplished through measurement of soil porewater
7 concentrations of individual PAHs. By refining methods (e.g., SPME) for measuring porewater
8 concentrations directly, or using concentrations in fluids extracted from bulk soils (SFE) along
9 with soil characteristics, it may be possible to develop a standardized approach for assessing
10 ecological risk of a broad range of PAH compounds in soil.

1 REFERENCES

- 2 Beyer, W.N. 1990. Evaluating soil contamination. United States Fish and Wildlife Service,
3 Biological Report 90 (2). Washington, DC.
4
- 5 Di Toro, D.M., C.S. Zarba, D.J. Hansen et al. 1991. Technical basis for establishing sediment
6 quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol.*
7 *Chem.* 10:1541-1583.
8
- 9 Hawthorne, S.B., J. Kreitinger, C.B. Grabanski and D.J. Miller. 2004. Predicting PAH uptake in
10 terrestrial worms using selective supercritical fluid extraction and carbon matrix characteristics.
11 Presented at the 14th Annual SETAC Europe meeting, Prague.
12
- 13 Johnson, D.L., K.C. Jones, C.J. Langdon, T.G. Pearce and K.T. Semple. 2002. Temporal
14 changes in earthworm availability and extractability of polycyclic aromatic hydrocarbons in soil.
15 *Soil Biol. Biochem.* 34:1363-1370.
16
- 17 Kraaij, R., W. Seinen, J. Tolls, G. Cornelissen and A.C. Belfroid. 2002. Direct evidence of
18 sequestration in sediments affecting the bioavailability of hydrophobic organic chemicals to
19 benthic deposit-feeders. *Environ. Sci. Technol.* 36:3525-3529.
20
- 21 Krauss, M. and W. Wilcke. 2002. Sorption strength of persistent organic pollutants in particle-
22 size fractions of urban soils. *Soil Sci. Soc. Am. J.* 66:430-437.
23
- 24 Lanno, R.P., A. Voigt, B. Tost, A. Nagy and L. Booth. 2004. Bioavailability of PAHs in soil:
25 Different methods for assessing bioavailability to soil invertebrates and their application in
26 environmental guideline development. Presented at the 14th Annual SETAC Europe meeting,
27 Prague.
28
- 29 Ma, W-C., A. Van Kleumen, J. Immerzeel, P. De Maagd and J. Gert. 1998. Bioaccumulation of
30 polycyclic aromatic hydrocarbons by earthworms; Assessment of equilibrium partitioning theory
31 in *in situ* studies and water experiments. *Environ. Toxicol. Chem.* 17:1730-1737.
32
- 33 MacDonald, D.D. 1994. Approach to the Assessment of Sediment Quality in Florida Coastal
34 Waters. Prepared by MacDonald Environmental Sciences Ltd. for Office of Water Policy, Florida
35 Department of Environmental Protection. Tallahassee, Florida. 199 p.
36
- 37 MHSPE (Ministry of Housing, Spatial Planning and Environment). 1994. Intervention Values
38 and Target Values - Soil Quality Standards. Directorate-General for Environmental Protection,
39 Department of Soil Protection, The Hague, The Netherlands.
40
- 41 Nam, K., N. Chung and M. Alexander. 1998. Relationship between organic matter content of soil
42 and the sequestration of phenanthrene. *Environ. Sci. Technol.* 32:3785-3788.
43

1 Pavlou, S.P. 1987. The use of the equilibrium partitioning approach in determining safe levels of
2 contaminants in marine sediments. In: Fate and Effects of Sediment-bound Chemicals in Aquatic
3 Systems, K.L. Dickson, A.W. Maki and W.A. Brungs, Ed. Proc. of the Sixth Pellston Workshop.
4 Pergamon Press, Toronto, Ontario.
5

6 Reichenberg, A. 2004. Estimation of available PAHs in aged field contaminated soil using a long
7 term leaching setup. Presented at the 14th Annual SETAC Europe meeting, Prague.
8

9 Sverdrup, L.E., N. Torben and P.H. Krogh. 2002a. Soil ecotoxicity of polycyclic aromatic
10 hydrocarbons in relation to soil sorption, lipophilicity, and water solubility. Environ. Sci.
11 Technol. 36:2429-2435.
12

13 Sverdrup, L. E., J. Jensen, P.H. Krogh and J. Stenersen. 2002b. Studies on the effect of soil aging
14 on the toxicity of pyrene and phenanthrene to a soil-dwelling springtail. Environ. Toxicol. Chem.
15 21:489-492.
16

17 Swartz, R.C., D.W. Schults, T.H. DeWitt, R. Ditsworth and J.O. Lamberson. 1990. Toxicity of
18 fluoranthene in sediment to marine amphipods: A test of the equilibrium partitioning approach to
19 sediment quality criteria. Environ. Toxicol. Chem. 9:1071-1080.
20

21 Ter Laak, T.L., A. Barendregt, L. Joop and M. Hermens. 2004. Partitioning behavior of PAHs to
22 a 30µm PDMS fiber in a soil slurry: does the matrix influence kinetics? Presented at the 14th
23 Annual SETAC Europe meeting, Prague.
24

25 U.S. EPA. 2003. Procedures for the Derivation of Equilibrium Partitioning Sediment
26 Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures. Office of Research
27 and Development, Washington, D.C. EPA/600/R-02/013. Available in pdf format at:
28 <http://www.epa.gov/nheerl/publications/files/PAHESB.pdf>.