UvA-DARE (Digital Academic Repository)

Response to comment "Adsorption of CO₂ and N₂ on soil organic matter: nature of porosity, surface area, and diffusion mechanisms.

de Jonge, H.; Mittelmeijer-Hazeleger, M.C.

DOI

[10.1021/es962011r](https://doi.org/10.1021/es962011r)

Publication date

1996

Published in

Environmental Science and Technology

[Link to publication](#)

Citation for published version (APA):

de Jonge, H., & Mittelmeijer-Hazeleger, M. C. (1996). Response to comment "Adsorption of CO₂ and N₂ on soil organic matter: nature of porosity, surface area, and diffusion mechanisms. *Environmental Science and Technology*, 30(12), 3636-3637. <https://doi.org/10.1021/es962011r>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Response to Comment on "Adsorption of CO₂ and N₂ on Soil Organic Matter: Nature of Porosity, Surface Area, and Diffusion Mechanisms"

SIR: We thank Kopinke and Stottmeister (1) for their interest in our work (2), from which they concluded that large organic molecules would not be able to enter the "interior" of soil organic matter (SOM). This would disagree with results in the sorption literature. However, such a conclusion cannot be drawn on the basis of our surface area measurements for three reasons. First, it must be emphasized that 0.5 nm quantifies an approximate *restriction* of the micropores, which is not the same as a pore *diameter*. Second, the 25–195-fold difference between the CO₂ and the N₂ surface areas quantifies only part of the total pore space, namely, the pore space formed by pores with restrictions of approximately 0.5 nm. Larger external pores are also present, as was indicated by N₂ surface areas that were 20–100 times larger as compared to the particle surface area that was estimated from microscopic analysis (2). Third, Kopinke and Stottmeister correctly argue that SOM most likely has a flexible structure, implying that the micropore restrictions of approximately 0.5 nm, as measured on dried samples, are not directly applicable to hydrated SOM samples.

These three points require further elaboration. Considering the first point, the maximum pore width can far exceed the restriction width of the micropore and, hence, can exceed the critical diameter of larger organic molecules. Flat molecules in particular, such as PAHs and PCBs, would be able to diffuse into or at least be immobilized in slit-shaped micropores. Hence, Kopinke and Stottmeister's statement that PCBs, with a critical diameter of 0.68 nm (3), "are clearly above the proposed micropore dimensions" of 0.5 nm does not necessarily imply that PCBs cannot enter SOM micropores.

The second point concerns the presence of larger pores. Our conclusion, that the majority of the *surface area* is formed by subnanometer-scale pores, does not imply that the *volume* of larger pores is negligible. Macroporosity can for example be demonstrated by flotation experiments in organic solvents (4). We observed that the majority of air-dried organic matter particles, e.g., the peat soil used in our study (2), do not sediment in 1,1,1-trichloroethane, having a density of 1.32 g/cm³. It follows that the lower limit of the total pore space is 0.071 cm³/g_{SOM}. This is more than two times higher than the estimated SOM microporosity for the material (0.034 cm³/g). This relatively large pore volume with a relatively low surface area indicates the presence of larger pores. It follows that the pore space of macroparticulate SOM is strongly disordered. A continuously disordered, fractal-like pore structure is confirmed at the micropore scale by new measurements of sorption isotherms of gaseous hydrocarbons for SOM (all at 273 K), yielding increasing surface areas with decreasing critical diameter of the adsorbate in the range of 0.24–0.44 nm (4). Other arguments for a continuous pore structure include mercury intrusion measurements, indicating abundant porosity in the region > 100 nm (4), and the disordered

structure of humic materials, measured using small angle X-ray scattering (5). It follows that linear DR relations are not necessarily indicating a narrow pore size distribution, as was previously concluded (2). In such a disordered pore structure, the distinction between adsorption and absorption becomes irrelevant for nonpolar compounds with nonspecific adsorbent–adsorbate interactions, since the sorption mechanism is some combination of the two concepts (6).

The third point concerns the elasticity of the polymer structure. In our paper (2), we did not use the term "fixed-pore network", as suggested by Kopinke and Stottmeister. On the contrary, we agree that the SOM structure should be envisaged as a flexible polymer mesh rather than a fixed-pore network. This does not contradict our conclusion that the structural changes of SOM due to drying "are dependent on the composition of SOM" and that "the microporous structure is *not strongly* affected by hydration". The measured limiting partition capacities for water in SOM are 0.25–0.37 cm³/g (7, 8), which corresponds to a pore space that is 3.5–5 times larger as compared to our dried peat sample (0.071 cm³/g). Note that a change in pore volume and pore diameter is not linearly related for closed, interconnected pore systems: a 5-fold increase in pore volume only leads to a 1.7-fold increase in the pore diameter of a sphere or a cubic pore. Thus, an increase of the pore dimensions by orders of magnitude after hydration is not expected for particulate SOM.

The above assumes isotropic swelling of the matrix; however, anisotropic swelling is much likelier to occur. The effects of hydration will generally depend on the local structural properties, namely, the cross-linking density and the strength of the bonds between the building blocks of the SOM structure. The long equilibration time, i.e., days to weeks, for sorption of water and other vapors (8, 9) and hydration of SOM (2) indicate the presence of hydrophobic regions that are only very slowly hydrated. Kopinke and Stottmeister propose, without proof, a structure of hydrated SOM in which any definite pore structure disappears, but this is only likely to occur in the case of a low cross-linking density and in the absence of complexing multivalent cations such as Ca²⁺, Fe³⁺, and Al³⁺.

The above viewpoints do not conflict with the experimental evidence put forward by Kopinke and Stottmeister regarding sorption of organic contaminants, but two issues need attention. First, the increased desorption of organic contaminants after hydration of a humic acid (1) could indeed be explained by increased diffusivity due to swelling. However, it is well-known that dried humic acids are hygroscopic, indicating a high interaction energy for water adsorption. Therefore, increased desorption could also be explained by competition between organic compounds and water for sorption sites. Such effects have been found for trichloroethene adsorption in dry soils (10).

The second issue concerns the log *K*_{ow}–log *K*_{om} correlations. Kopinke and Stottmeister failed to mention that Karickhoff (11, 12) did indeed observe steric hindrance for sorption of larger molecules, particularly high molecular weight chlorinated compounds. Further, due to the highly nonlinear relation between molecular volume and aqueous solubility, the adsorbed volumes of large molecules per

FIGURE 1. Maximum partition capacities in SOM (left y-axis) and in octanol (right y-axis), calculated from the product of the aqueous solubility, S (mol/L), molar volume, V (L/mol), and K_{om} (L/kg) for SOM, and for octanol calculated from SVK_{ow}/ρ , where ρ is the liquid density of octanol (kg/L). The data are for benzene, benzene derivatives, and PCBs, from ref 15.

mass of SOM, such as PAHs, are very low: 2–4 orders of magnitude lower than the estimated total porosity of SOM (13, 14) (note that the isotherm data for pyrene in ref 14 were misprinted, see ref 13). Hence, uptake in larger pores can explain the observed relations, and steric hindrance is not necessarily a critical factor in the uptake of these compounds through the aqueous phase.

Considering the study by Chiou et al. (15), the aqueous solubilities of the compounds differed by 4 orders of magnitude, while the molar volumes of the compounds differed only by a factor 2. Hence, it is not surprising that the aqueous solubility is the major factor determining the values of K_{ow} and K_{oc} . The conclusion in ref 15 that a 8–25 times higher partition capacity of octanol compared to SOM (see Figure 1) only being caused by a difference in polarity is questionable. Entropic effects cannot be excluded as the Flory–Huggins interaction parameter, χ , is affected both by entropic (χ_s) and enthalpic (χ_H) contributions. The value of the empirical parameter χ_s depends on the accessibility and flexibility of the polymer (16), and this parameter was not determined independently. A final consideration is that short-term uptake experiments, from which K_{om} values are usually derived (13, 15), are not useful in identifying hindered diffusion in micropores because only “rapid”

uptake is quantified (17). Desorption experiments with historically contaminated soils show steric hindrance even for relatively small compounds, such as halogenated ethanes (18, 19).

Acknowledgments

The authors are grateful to L. W. Petersen and P. Moldrup for their comments and suggestions.

Literature Cited

- (1) Kopinke, F.-D.; Stottmeister, U. *Environ. Sci. Technol.* **1996**, *30*, 3634–3635.
- (2) de Jonge, H.; Mittelmeijer-Hazeleger, M. C. *Environ. Sci. Technol.* **1996**, *30*, 408.
- (3) Carrol, K. M.; Harkness, M. R.; Bracco, A. A.; Balcarel, R. R. *Environ. Sci. Technol.* **1994**, *28*, 253.
- (4) de Jonge, H.; Mittelmeijer-Hazeleger, M. C. ASA-CSSA-SSSA 1996 Annual meeting, Nov 3–8 Indianapolis, IN, 1996.
- (5) Rice, J. A.; Lin, J.-S. *Environ. Sci. Technol.* **1993**, *27*, 413.
- (6) Brusseau, M. L. *Environ. Toxicol. Chem.* **1993**, *12*, 1835.
- (7) Rutherford, D. W.; Chiou, C. T. *Environ. Sci. Technol.* **1992**, *26*, 956.
- (8) Chiou, C. T.; Kile, D. E.; Malcolm, R. L. *Environ. Sci. Technol.* **1988**, *22*, 298.
- (9) Chiou, C. T.; Kile, D. E. *Environ. Sci. Technol.* **1994**, *28*, 1139.
- (10) Petersen, L. W.; El-Farhan, Y. H.; Moldrup, P.; Rolston, D. E.; Yamaguchi, T. *J. Environ. Qual.* In press.
- (11) Karickhoff, S. W. *Chemosphere* **1981**, *8*, 833.
- (12) Karickhoff, S. W. *J. Hydraul. Eng.* **1984**, *110*, 707.
- (13) Hasset, J. J.; Means, J. C.; Banwart, W. L.; Wood, S. G. *Sorption Properties of Sediments and Energy-Related Pollutants*, EPA-600/3-80-041; U.S. EPA: Athens, GA, 1980.
- (14) Means, J. C.; Wood, S. G.; Hasset, J. J.; Banwart, W. L. *Environ. Sci. Technol.* **1980**, *14*, 1524.
- (15) Chiou, C. T.; Porter, P. E.; Schmedding, D. W. *Environ. Sci. Technol.* **1983**, *17*, 227.
- (16) Chiou, C. T. In *Reactions and Movement of Organic Chemicals in Soils*; Linn, D. E., Ed.; SSSA ASA: Madison, WI, 1989; pp 1–30.
- (17) Pignatello, J. J.; Xing, B. *Environ. Sci. Technol.* **1996**, *30*, 1.
- (18) Pignatello, J. J. *Environ. Toxicol. Chem.* **1990**, *9*, 1107.
- (19) Steinberg, S. M.; Pignatello, J. J.; Sawhney, B. L. *Environ. Sci. Technol.* **1987**, *21*, 1201.

Hubert de Jonge*

Danish Institute of Plant and Soil Science
Research Centre Foulum
P.O. Box 23
8830 Tjele, Denmark

Marjo C. Mittelmeijer-Hazeleger

Department of Chemical Engineering
University of Amsterdam
Amsterdam, The Netherlands

ES962011R