

# Comment on “Sorption of organic chemicals to soil organic matter: Influence of soil variability and pH dependence”

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## Keywords:

Sorption, Organic chemicals, pH dependence, Hydrolysis

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In their article, Bronner and Goss [1] investigate the pH dependence of organic chemical sorption to soil organic matter. Supporting Information Table SI-7 from ref. [1] lists the “Experimental NOM/air partition coefficients for 10 natural organic matters measured at 15°C and 98% rh converted to log  $K_{oc}$ . Included in Table SI-7 is log  $K_{oc}$  data for benzoyl chloride (CAS RN 98-88-4). It is not clear how the authors could report a log  $K_{oc}$  for this compound in aqueous solution. Benzoyl chloride has a hydrolysis half-life of only 16 seconds in water [2, 3]. This timeframe is far too short to allow the measurement of any equilibrium based partitioning coefficients. Consequently, one suspects that the log  $K_{oc}$  value reported for benzoyl chloride in ref. [1] is likely that of its hydrolysis product: benzoic acid.

Furthermore, Bronner and Goss [1] state that “the pH has no significant effect (average deviation of  $K_{oc}$  between pH 4.5 and pH 7.2 less than 0.06 log units) on the  $K_{oc}$  of nonionic compounds regardless of their polarity. This counterintuitive finding indicates that acidic groups do not represent favorable sorption sites even for polar organic molecules” and that “[t]his result indicates that protonation/deprotonation of carboxylic groups in humic matter has no significant influence on sorption.” Experimental  $pK_a$  values for bulk humic acids from soil are known to range as low as 2.4-2.5 [4]. Thus, the choice of pH values by Bronner and Goss [1] is confusing. It appears that the authors may have chosen two experimental conditions (pH 4.5 and 7.2) between which the ionization state of the carboxylic acids in the organic matter may have changed very little, and could instead have remained in effectively the same net ionization state (i.e., effectively entirely dissociated) between the two experimental pH endpoints.

As a result, there does not appear to be sufficient evidence in ref. [1] to support the general claim therein that “protonation/deprotonation of carboxylic groups in humic matter has no significant influence on sorption ... even for polar organic molecules.” A conclusive study would involve sorption experiments at a pH value of  $\sim 2$  (providing humic acid solubility is not a limiting issue, and where all

carboxylic acid groups would assuredly be protonated) for comparison with the current study at pH 7.2.

## References

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