

Sorption of organic compounds in soils: Do we sufficiently appreciate the importance of clays?

Rai S. Kookana¹ and William C. Koskinen²

¹CSIRO Land and Water, Waite Campus, Glen Osmond 5064, Australia.

¹School of Agriculture, Food and Wine, The University of Adelaide, Glen Osmond 5064, Australia.

²USDA-Agricultural Research Service, 1991 Upper Buford Circle, Rm. 439, St. Paul, MN 55108

Abstract

Sorption is one of the major processes that govern the ecological risks of organic compounds and pesticides in soils and sediments. It is generally assumed that the sorption behaviour of organic compounds is largely moderated by the content of organic matter in soil and sediments, and the role of clay minerals is generally ignored, especially during risk assessment. This is despite the fact that often soils are much richer in the mineral matter, i.e. its content in soils is often an order of magnitude higher than that of organic matter. Besides, numerous studies over the years have demonstrated that clay minerals, especially expandable smectites, do have a strong affinity for a variety of organic compounds such as pesticides and nitroaromatic compounds. For example, Laird et al. (1992) studied sorption of atrazine on soil smectite clays and showed that relatively pure smectites were quite effective sorbents of the herbicide, depending on their compositions. Similarly, clay minerals were found to be good sorbents for nitroaromatic compounds (e.g. Haderlien and Schwarzenbach, 1993). Despite the massive body of literature, the role of clays in determining the sorption behaviour of organic compounds and consequently their ecological risks in soils/sediments is still not fully appreciated and incorporated in the risk assessment models.

One of the major developments that led to a disproportionate dominance of the role of organic matter in sorption of organic compounds in soils is the introduction of the “partition theory” (Chiou et al. 1979). According to this theory soil organic matter essentially acts as a simple partitioning medium, akin of an immiscible solvent (such as octanol in water), and thus has the ability to linearly uptake an organic compound in proportion to its concentration in an aqueous solution. Generally a linear isotherm is taken as the evidence of partitioning mechanism. This theory allowed an easy extrapolation of sorption measured on one soil to other based on its carbon content alone, using the Koc parameter, which is simply a sorption coefficient (Kd) normalised with organic carbon (OC) content of soil/sediment ($Koc = Kd/fOC$, where fOC is the fraction of OC). The simplicity of the concept led to models which could account for sorption of organic compounds in soil/sediments by a universal Koc parameter, applicable to all soils/sediments. However, it is noteworthy that this concept is a simplification based on the sorption behaviour of non-ionic organic compounds, while a substantial proportion of organic compounds such as pesticides are ionic or ionisable (weakly basic, acidic) in nature. For example, the most used herbicides glyphosate is a zwitterions, the bypridilium herbicides (paraquat and diquat) are cationic in nature and the triazines (e.g. atrazine) are weakly basic compounds. Indeed the low ecological risk profiles of most commonly used herbicides glyphosate, paraquat and diquat are due to their strong adsorption on clay minerals. But for the ability of soil clays to “detoxify” them rapidly, their useability and environmental acceptance may not have been the same. Furthermore, the measured sorption isotherms of organic compounds in soils/sediments are more commonly non-linear in nature, contrary to the assumption of the partition theory. The non-linearity of sorption isotherms is indicative of complex organo-mineral interactions reflecting the role of chemistry of organic matter and/or clays in determining the sorption behaviour of organic compounds in soils. Our studies (e.g. Ahmad et al. 2001; Ahangar et al. 2008; Papiernik et al., 2006) clearly demonstrate that the organic matter content alone fails to adequately describe the sorption behaviour of organic compounds in soils. It has been suggested that when the ratio of clay to organic C (f_{cm}/f_{oc}) is <30, contribution of mineral surfaces is masked regardless of the clay content (Karickhoff, 1984). A more comprehensive approach incorporating soil organic as well as mineral matter (both contents as well as their chemistries) is therefore needed to fully incorporate the role of soil surfaces in sorption of organic compounds.

The recent developments in application of midinfrared spectroscopy (MIR) in characterisation of soils and sediments opens a window of opportunity to estimate the sorption of organic compounds based on the overall contributions of clays as well as organic matter in soils. Chemometric approaches, especially partial least squares (PLS) regression, with MIR have been found to be particularly effective in characterising soils in terms of a range of soil properties, such as organic carbon content, clay content, cation exchange capacity

etc (Janik and Skjemstad 1995). Our investigations have shown that MIR-PLS model can provide a faster, cost-effective, improved and locally relevant sorption estimates of pesticides in Australian soils (Forouzangohar et al. 2008; Kookana et al. 2008), which tend to be generally poorer in organic matter content.

This presentation would provide an overview on the role of clays and organic matter in soils in determining the sorption of organic compounds, especially pesticides and demonstrate how mid-infrared spectroscopy could pave the path of better appreciation of role of clays together with organic matter in sorption estimates that can allow improved risk assessment of organic compounds such as pesticides in soils.

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