



Small pores in soils: Is the physico-chemical environment accurately reflected in biogeochemical models ?

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Free water is a prerequisite to chemical reactions and biological activity in earth's upper crust essential to life. The void volume between the solid compounds provides space for water, air, and organisms that thrive on the consumption of minerals and organic matter thereby regulating soil carbon turnover. However, not all water in the pore space in soils and sediments is in its liquid state. This is a result of the adhesive forces which reduce the water activity in small pores and charged mineral surfaces. This water has a lower tendency to react chemically in solution as this additional binding energy lowers its activity. In this work, we estimated the amount of soil pore water that is thermodynamically different from a simple aqueous solution.

The quantity of soil pore water with properties different to liquid water was found to systematically increase with increasing clay content. The significance of this is that the grain size and surface area apparently affects the thermodynamic state of water. This implies that current methods to determine the amount of water content, traditionally determined from bulk density or gravimetric water content after drying at 105°C overestimates the amount of free water in a soil especially at higher clay content. Our findings have consequences for biogeochemical processes in soils, e.g. nutrients may be contained in water which is not free which could enhance preservation.

From water activity measurements on a set of various soils with 0 to 100 wt-% clay, we can show that 5 to 130 mg H₂O per g of soil can generally be considered as unsuitable for microbial respiration. These results may therefore provide a unifying explanation for the grain size dependency of organic matter preservation in sedimentary environments and call for a revised view on the biogeochemical environment in soils and sediments. This could allow a different type of process oriented modelling.