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Identification and quantification of anomalous diffusion in rock, soil, and sediment layers

BRIAN BERKOWITZ[1], RALF METZLER[2,3], ISHAI DROR[1] AND ASHISH RAJYAGURU[4]

[1]Weizmann Institute of Science
[2]University of Potsdam
[3]Asia Pacific Centre for Theoretical Physics
[4]Paul Scherrer Institut

Molecular diffusion of chemical species in rock formations, and soil, marine, river and lake sediments, plays a critical role in a variety of dynamic processes that affect water chemistry. We investigate and quantify the occurrence of anomalous (non-Fickian) diffusion behavior, which is distinct from classically-assumed Fickian diffusion. We recently reported measurements of molecular diffusion in several chalk and dolomite rock samples, over a period of about two months, and demonstrated diffusion behavior that is significantly different than Fickian. Anomalous diffusion strongly impacts data interpretation and modelling predictions of chemical transport and reactions in the subsurface. In this presentation, we describe the anomalous diffusion using a continuous time random walk (CTRW) framework, tailored to quantify diffusion in heterogeneous porous materials such as rock. Solutions of the governing diffusion equation show long-time tailing of tracer advance as compared to conventional Fickian diffusion processes. From the clear mechanistic underpinning of the CTRW framework, which is based on power laws to describe chemical migration, solutions of an associated fractional diffusion equation are derived over a broad range of power law exponents that describe diffusion behaviors from nearly Fickian to highly anomalous. We present temporal breakthrough curves and spatial concentration profiles of diffusing solutes that align with experimental data in scenarios where solute diffusion displays anomalous behavior. In particular, the solutions enable clear differentiation between early-time Fickian and anomalous diffusion, which becomes more pronounced over longer durations. The finding that diffusion in natural rocks can display distinct and possibly ubiquitous anomalous behavior implies that diffusion-driven processes in subsurface zones should be analyzed using tools that account for non-Fickian diffusion.