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A simplified Nernst equation for predicting redox potentials in groundwater

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Oxidation-reduction potential, or redox potential (Eh), measures the tendency of a chemical species to accept or donate electrons. It serves as a primary indicator for the thermodynamic favorability and directionality of electron transfer processes, and hence a key parameter in characterizing groundwater redox conditions. However, current methodologies for evaluating redox potentials rely heavily on the Nernst equation, demanding high-quality data on the chemical composition of natural waters as well as intricate modeling of chemical speciation.

This study aimed to develop a simple algebraic equation to predict redox potentials from groundwater pH by leveraging recent advancements in geochemical modeling, big data analytics, and machine learning techniques. We assembled an extensive chemical dataset of groundwater from diverse hydrological and geochemical settings worldwide. We then simulated chemical speciation in groundwater, and computed redox potentials of common electron acceptors, including dissolved oxygen, nitrate, Mn(IV) oxides, Fe(III) oxyhydroxides, sulfate, and CO_2.

To identify potential physicochemical parameters as predictors of redox potentials, we analyzed correlations between redox potentials and those obtained in situ with redox probes or electrodes. Consistent with previous findings, the modeling-derived redox potentials did not correlate significantly with the probe measurements. However, we observed linear correlations between redox potential and pH, as well as between redox potentials and the product of pH and temperature.

We formulated a global Nernst equation to capture the primary influence of pH, and express reduction potentials in relation to pH and temperature. The equation's performance and effectiveness were evaluated with the train-test split method, and the results show that the equation provides a reasonable approximation to the redox potentials of common electron acceptors, with mean absolute error (MAE) ranging from 6 to 35 mV.

By expressing reduction potentials as a simple function of pH and temperature, this equation obviates the need for detailed groundwater chemical composition or geochemical modeling to assess redox state, thereby simplifying the simulation of abiotic and biological redox reactions. Overall, our findings highlight the potential of integrating geochemical modeling, big data analytics, and machine learning to enhance our understanding of fundamental chemical principles on a global scale.