

Time series analysis of CO emissions from a coal fire, Eastern Kentucky

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Coal fires in natural outcrops, in abandoned and active coal mines, and in coal and coal-refuse piles are responsible for some uncontrolled emissions of gases, including CO, CO₂, H₂S, hydrocarbons, and volatile aromatics. Typically, measurements of gases at a mine vent are made over a short time interval, perhaps no more than 10 minutes, including the time for replicate measurements. Such timing provides little information on longer-term variations in emissions, although comparison of seasonal measurements suggest such changes do occur. To address this problem, we placed temperature and CO data loggers in vents at an *in situ* coal bed fire in Eastern Kentucky to collect time series measurements for periods of up to three weeks. For one experiment, 11 days of data collected at one-minute intervals indicated that the CO emissions were generally in the 400-550 ppmv range. However near daily depressions in CO concentrations occurred and in some cases fell below 50 ppmv. These depressions were followed by an increase to ~700-800-ppmv and, in turn, followed by a return to the ambient conditions. Data for a separate 21-day collection period in a different vent of the same fire exhibited similar trends, albeit at a higher CO concentration. The drop in CO concentration may be associated with a meteorologically-driven inhalation cycle of the fire, whereby air diluted the combustion generated CO. We propose this event was followed by a magnification in the intensity of the fire due to increased O₂ from the inhaled air, producing increased CO concentrations, before settling back to the ambient conditions.

Sorption of natural organic ligands to silver and zinc sulfide nanoparticles: Implications for aggregation and dissolution

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The environmental fate and mobility of metallic and mineral nanoparticles (NPs) can be strongly influenced by sorption of natural organic ligands, which modify particle surfaces and their reactivity during aggregation and dissolution processes. In this work we studied two types of nanomaterials: zero-valent Ag NPs, which are widely used in consumer products for antimicrobial applications, and ZnS NPs, which occur naturally in Zn-contaminated sediments and other environments and are also components of semi-conducting quantum dots. We studied the interactions between the nanoparticles and cysteine, a low molecular weight analogue for thiol ligands in anaerobic settings.

Aggregation experiments were performed with ZnS to demonstrate that thiol-containing ligands such as cysteine (rather than hydroxyl-containing ligands) enhanced the colloidal stability of the particles by reducing attachment efficiencies during aggregation. The reduction in attachment efficiencies was directly related to the amount of cysteine that adsorbed the ZnS particles. Cysteine also sorbed to Ag nanoparticles; however, sorption appeared to increase Ag aggregation rates rather than reduce it. The increase of aggregation rates depended on the type of surfactant that was utilized to manufacture the Ag NPs (e.g. citrate, polyvinylpyrrolidone (PVP)). Aggregation was enhanced, in particular, for PVP-coated Ag nanoparticles. The addition of cysteine to Ag NP suspensions also increased the dissolved Ag concentration. These results indicated that cysteine was simultaneously sorbing to the Ag NPs and promoting their dissolution, resulting in surface modifications that increased aggregation rates.

Overall, our study highlights the importance of metal-binding organic ligands for modifying the surface of metal and mineral nanomaterials in environmental settings. Sorption of natural organics alters the aggregation and solubility of the nanomaterials, and ultimately, will influence their persistence in the environment