

Industrial trace element contamination in wetlands: the effect of the precipitation of biogenic sulfides

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Abstract

Wetlands are conducive to precipitating and maintaining biogenic metal sulfide mineralization. The transformation of oxidized industrial contaminants into authigenic sulfides is widespread in contaminated wetlands, occurring even close (a few cm) to the surface and at only occasionally waterlogged sites. The characteristic feature of the authigenic sulfides is their strong spacial association with organic tissues. They commonly form micro-sized globular aggregates, more massive botryoidal or bulbous crusts on plant fragments, infillings in plant voids and cells, and pseudomorphs after microbial cells. Hidden in plant tissues or encapsulated in microbial biofilms, sulfides have increased resistance to oxidation and mechanical displacement. Most authigenic sulfides are nanocrystalline. Impurities, substitutions, solid solutions, and multi-sulfide submicrometre aggregates are common in addition to single-metal sulfide minerals. The trace elements sequestration into stable hardly-soluble secondary phases limits their mobility and toxicity, giving a chance for a safer environment if the wetlands are adequately managed. Additionally, contaminated wetlands can be used to understand the geochemical and biological evolution of the Earth and to reconstruct ancient ore deposits' genesis and mechanisms of formation.

Resumen

Los humedales son ambientes propicios para la precipitación y el mantenimiento de las mineralizaciones de sulfuros metálicos biogénicos. La transformación de contaminantes industriales oxidados en sulfuros autigénicos es muy común en los humedales contaminados, produciéndose, incluso, cerca (unos pocos centímetros) de la superficie y solo ocasionalmente en lugares inundados. El rasgo característico de los sulfuros autigénicos es su fuerte asociación espacial con tejidos orgánicos. Por lo general, forman agregados globulares de tamaño micrométrico, costras botrioidales o bulbosas más masivas en fragmentos de plantas, rellenos en huecos y células de plantas, y pseudomorfos de células microbianas. Ocultos en tejidos vegetales o encapsulados en biopelículas microbianas, los sulfuros tienen una mayor resistencia a la oxidación y al desplazamiento mecánico. La mayoría de los sulfuros autigénicos son nanocristalinos. Además de los sulfuros de un solo metal, son comunes las impurezas, las sustituciones, las soluciones sólidas y los agregados submicrómetros de sulfuros múltiples. El secuestro de elementos traza en fases secundarias estables y poco solubles limita su movilidad y toxicidad, lo que brinda la posibilidad de conseguir un medio ambiente más seguro si los humedales se manejan adecuadamente. Además, los humedales contaminados se pueden utilizar para comprender la evolución geoquímica y biológica de la Tierra y para reconstruir la génesis y los mecanismos de formación de los antiguos depósitos de minerales..

Key-words: *metal sulfides; wetland; Recent Earth's surface processes, trace elements immobilization, sulfate reduction*

1. Introduction

Sulfides are a large group of minerals from which several can precipitate under low pressure and temperature conditions of the Earth's surface (e.g., Baas Becking and Moore, 1961). Iron sulfides (pyrite, mackinawite, greigite) dominate due to the overwhelming abundance of Fe relative to other chalcophile metals in both marine and terrestrial sediments (Rickard et al., 2017). Larger accumulations of the less common sulfides in modern natural environments are rare (e.g., Lett and Fletcher, 1980; Yoon et al., 2012; Awid-Pascual et al., 2015). Conversely, they seem quite common in industry-affected regions. Biogenic sulfides were found in freshwater canal and river sediments, wetlands, soils, and flooded mines (Sobolewski, 1996; Gammons and Frandsen, 2001; Large et al., 2001;

Sonke et al., 2002; Moreau et al., 2004; Smicja-Król et al., 2015; Ciszewski et al., 2017; Mantha et al., 2019; Myagkaya et al., 2020; Quevedo et al., 2020). Human activities create unique geochemical conditions favorable for metal sulfide precipitation by modifying trace elements cycling on local and global scales. Mine drainage, for example, is often responsible for high sulfate concentrations in wetlands, i.e., a condition otherwise not encountered in freshwater wetlands.

Wetlands, which cover about 5 to 8% of the land surface, are especially well suited for contaminants immobilization and are often called "the kidneys of the landscape" because they function as the downstream receivers of water and wastes from both natural and human sources. They can be loosely defined as constantly or periodically waterlogged ecosystems that accumulate organic plant material that decomposes slowly and support various plants and animals adapted to saturated conditions (Mitsch and Gosselink, 2007). Several metal sequestration processes are envisaged in both natural and artificially constructed wetlands, occurring simultaneously or separated spatially and temporally (Figure 1). In addition to sulfide precipitation, these include particle sedimentation, plant uptake, sorption onto organic matter (mainly Cu, Ni, U, Pb), oxidation and hydrolysis (Fe, Al, Mn), carbonate precipitation (Fe, Cu, Ni), reduction to non-mobile forms (Cu, U, Cr, Se), and sorption onto metal hydroxides (As, Pb, Co, Ni, Zn, Cu, U), making wetlands extremely complex geochemical systems (Sobolewski, 1996; Sheoran and Sheoran, 2006).

The article summarizes the current state of knowledge on the biogenic sulfide formation in wetlands and its role in metal sequestration. Methods of sulfide identification, the textural and structural organization of the mineral phases, and precipitation conditions are presented. Finally, the implications of sulfide formation in the water-saturated contaminated sites are indicated.

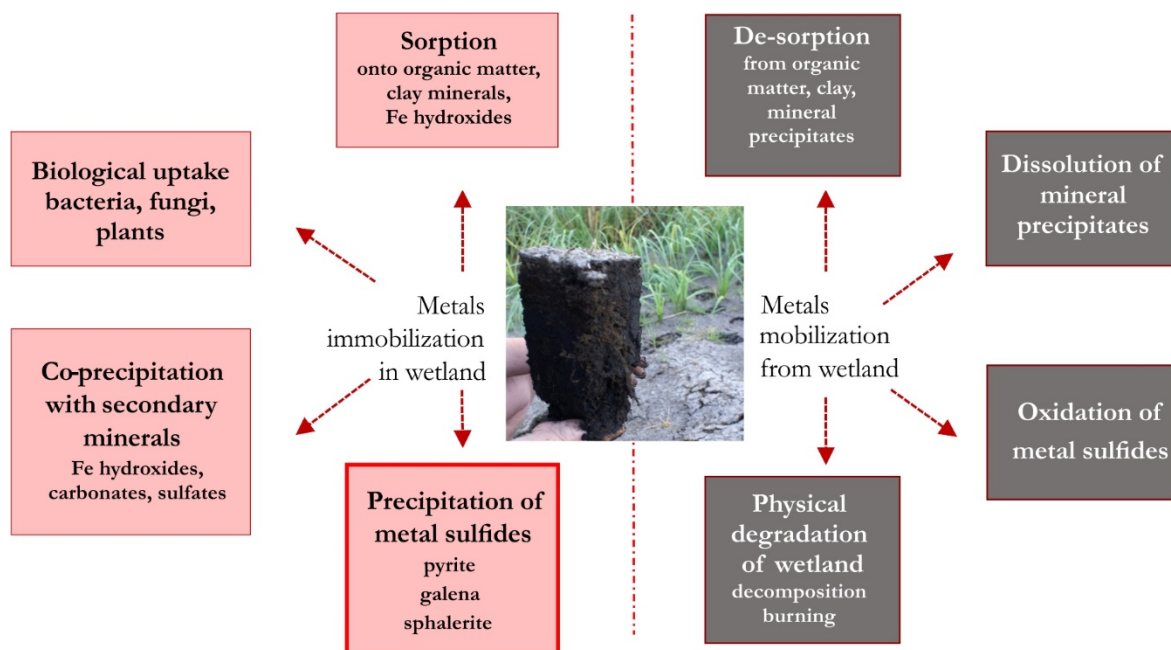


Fig. 1. Processes controlling metals behavior in contaminated wetlands.

2. Methods used for sulfide identification

Metal sulfide investigation in wetlands is challenging. The wetland sediment is a crumbling inhomogeneous mixture of organic and inorganic matter. Furthermore, it is water-saturated, redox-sensitive, and prone to alteration due to sample excavation and handling. Consequently, studies directly confirming the *in situ* precipitation of sulfide minerals are rare.

In the majority, the removal of metals by precipitation with sulfide is elaborated by monitoring changes in the aqueous chemistry of wetlands, e.g., the metal removal rates during sulfate reduction/sulfide generation (Machemer and Wildeman, 1992; Christensen et al., 1996; Webb et al., 1998; Batty et al., 2006). Also, seasonal changes in water sulfur isotopic composition ($\delta^{34}\text{S}$) are indicative of active sulfide formation (Wu et al., 2011). Bacterial reactions

favor the lighter isotope (^{32}S) so that fractionation is produced in going from a sulfate reactant to sulfide products (Konhauser, 2007).

Indirect methods used to estimate the fraction of metals incorporated into sulfide phases include acid-volatile sulfide (AVS) and chromium-reducible sulfides (CRS) extraction/distillation methods of Canfield et al. (1986) for monosulfide and disulfide minerals, respectively (Debusk et al., 1996; Moreau et al., 2013). Sequential extraction techniques involve using specific reagents to selectively dissolve phases in sediment with which metals may be associated. The technique is used to provide a quantitative measure of sulfides in wetlands (e.g., Sobolewski, 1999). All the methods are "operationally defined" and not always 100% selective. Most sequential extraction procedures (e.g., the Tessier scheme) significantly underestimate the content of metals associated with sulfide phases or do not distinguish organically bound metals from sulfides in organic-rich wetland sediments (Peltier et al., 2005).

Both optical and electron-beam microscopy provide direct evidence of sulfide occurrence in organic sediments. The size, shape, aggregation, relation to organic tissues, and semi-quantitative determination of chemical composition are best accomplished by analyzing whole mineralized plant remains using scanning electron microscopy (SEM). Several chemical fixation and dehydration techniques are used to preserve the organic part of the sample (plant cells, fungal hyphae, microbial cells, and exudates) and learn more about organic-mineral interactions (e.g., Fratesi et al., 2004). Quantitative chemical composition and trace substitutions are determined using mounts or thin sections and electron microprobe (EMPA). However, the small size and intermixture with organic components commonly result in low analytical totals (Moreau et al., 2013). Specific characterization at the nanometric level can be done using transmission electron microscopy (TEM). Selected area electron diffraction (SAED) is a crystallographic technique performed using TEM, which allows for identifying crystal structures, polycrystalline materials, and the measurement of crystal parameters, i.e., d-spacing even in very small crystallites. High-angle annular dark-field (HAADF) is a powerful method in the scanning transmission electron microscope (STEM) system providing Z-contrast images. HAADF allows recognizing subtle changes in chemical composition at nanometric distances, nanometer-sized inclusions, and detecting nanoporosity. A combination of focused ion beam (FIB) technology with TEM enables the extraction of desired mineral aggregate from the organic matter substance and conducting in-depth nanoscale observation (Wirth, 2009; Mantha et al., 2019; Smieja-Król et al., 2022a).

Synchrotron-based spectroscopy and diffraction analyses are perspective tools to quantify and determine the elemental speciation of metals and metalloids in wetlands (Yoon et al., 2012). They extend the range of structural and chemical investigation possible, allowing studies at low concentrations and with a redox-sensitive material.

3. Inventory of nonferrous sulfides identified in wetlands

Only a few sulfide minerals have been uniquely identified. Zinc sulfide is the best-elaborated and probably most common nonferrous sulfide formed in wetlands. It was found in peatlands contaminated through atmospheric deposition (Sonke et al., 2002; Smieja-Król et al., 2010; Smieja-Król et al., 2015), even at low bulk Zn contents in the organic sediment (~ 200 ppm). Zn sulfides were documented in natural wetlands receiving acid mine drainage (Moreau et al., 2013; Myagkaya et al., 2020) and anaerobic treatment wetland purifying storm waters in an industrially affected region (Butte, Montana; Gammons and Frandsen, 2001). Sphalerite (cubic ZnS) was confirmed using TEM in Pb-Zn smelter-contaminated peatland in Upper Silesia (Smieja-Król et al., 2022b). Wurtzite (hexagonal ZnS) was identified using synchrotron-based XRD to dominate over sphalerite in naturally metal-enriched peatland in western New York (Yoon et al., 2012).

Galena (PbS) forms in wetlands affected by Zn-Pb industry, although the phase is much less common than sphalerite despite comparable bulk Zn and Pb concentrations in the sediment (Smieja-Król et al., 2022a). Galena is easily identified by chemical composition and characteristic cuboidal shape using SEM. Its atomic structure was confirmed by STEM and TEM-SAED techniques (Smieja-Król et al., 2022b).

HgS was described by Myagkaya et al. (2020) to co-occur with ZnS. Polhemusite (Zn,Hg)S was suggested but not identified unambiguously.

The knowledge about Cu sulfide mineralogy in redox-sensitive ecosystems is derived mainly from laboratory experiments (Weber et al., 2009; Hofacker et al., 2013; Hoffmann et al., 2020). Chalcopyrite (CuFeS_2) rims on pyrite framboids and idiomorphic covellite (CuS) grains, identified by reflected light microscopy and SEM, are known from an early work of Lett and Fletcher (1980) to precipitate in naturally copper-rich peatland in British Columbia. Sonke et al. (2002) identified chalcopyrite contours on plant cells by EMPA in the subsurface (0-8 cm) of contaminated peatland in Maatheide Natural Reserve.

4. Sulfide characteristics

The characteristic feature of the authigenic sulfides is their strong spatial association with organic tissues (Figure 2a and 2b): plant remains, bacterial cells, microbial biofilms, and fungal hyphae. They commonly form micro-sized globular aggregates, more massive botryoidal or bulbous crusts on plant fragments, infillings in plant voids and cells, and pseudomorphs after microbial cells or biogenic Ca oxalate crystals (e.g., Smieja-Król et al., 2014; Awid-Pascual et al., 2015; Myagkaya et al., 2020). Most authigenic sulfides are nanocrystalline. ZnS nanoparticles are within the range <3 to 80 nm (Yoon et al., 2012; Myagkaya et al., 2020; Smieja-Król et al., 2022a; Smieja-Król et al., 2022b). With time (counted in tens of years), the crystallinity of ZnS tends to increase. An aging mechanism was described as leading to the formation of submicrometre highly-defected platy crystals through an oriented attachment mechanism for sphalerite (Smieja-Król et al., 2022b). Galena forms slightly larger, defect-free crystals, between 10 nm to hundreds of nm, often with well-developed faces (Figure 2c). Large (up to 2.5 μm) spheroidal aggregates of nanometer-sized PbS particles were found inside fungal hypha and encrusting fungal spores (Smieja-Król et al., 2015). Individual PbS nanocrystals also reside inside ZnS aggregates (Smieja-Król et al., 2022a; Smieja-Król et al., 2022b).

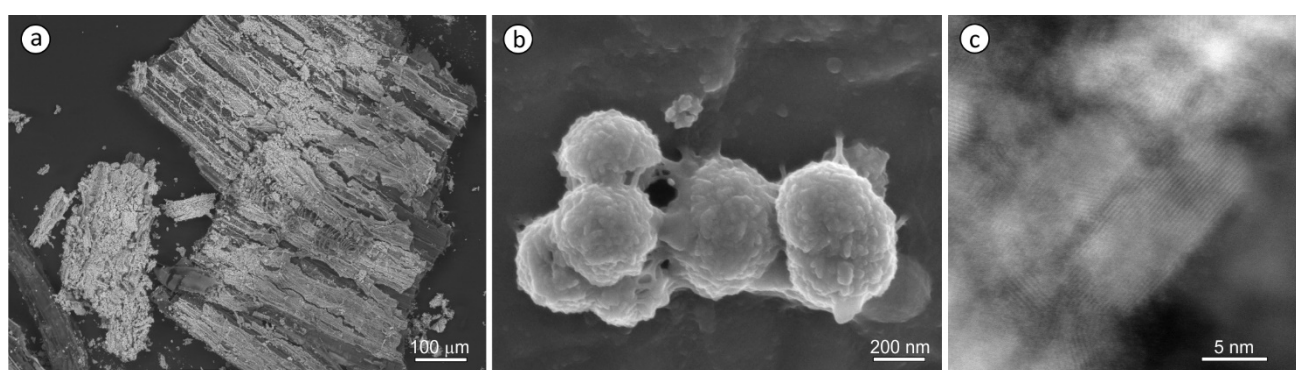


Fig. 2. Biogenic metal sulfides. (a) SEM BSE image of ZnS mineralized tissues of Equisetaceae; (b) spheroidal aggregates of ZnS attached to plant tissue by microbial biofilm (SEM SE); (c) TEM HAADF image of two galena nanocrystals.

The electron-beam techniques (SEM, TEM/STEM, EMPA) reveal impurities, substitutions, solid solutions, and multi-sulfide submicrometre aggregates to occur in wetland sediments in addition to single-metal sulfide minerals. Traces (up to a few wt%) of As, Se, Cu, Cd, Fe, and Ni were documented in authigenic ZnS (Sonke et al., 2002; Moreau et al., 2013; Myagkaya et al., 2020). Cu was shown to incorporate preferably in galena when only ZnS and PbS are present in organic sediment (Smieja-Król et al., 2015; Smieja-Król et al., 2022b). Due to the nanometer size of individual crystallites, distinguishing between a solid solution and a multi-metal sulfide aggregate is challenging even while using high-resolution TEM. Aggregates of $\sim 10\text{nm}$ particles unresolvable in terms of a solid solution of sphalerite-metacinnabarite or a mixture of pure ZnS and HgS nanoparticles are a good example (Myagkaya et al., 2020). Aggregates of nanoparticles ($<5\text{ nm}$) forming a true Zn-Cd sulfide solid solution in a cubic polytype (sphalerite-hawleyite) over a whole Zn/Cd range were documented using TEM-SAED and STEM-HAADF techniques. An intricate core-shell structure was revealed in which high-Zn outer layers encapsulate Cd-rich sulfide core. PbS inclusions (3-15 nm) occurred between the Cd-rich and Cd poor sulfide within nano sites of increased porosity (Smieja-Król et al., 2022a).

5. Controls of sulfide precipitation in wetlands

The critical requirement for sulfide precipitation at metal polluted sites is the availability of sulfide ions. In the low-temperature range ($< \sim 80^\circ\text{C}$), sulfides are generated through sulfate reduction in a fully biologically mediated process. Due to high activation energy, the abiotic reaction is kinetically inhibited at low temperatures (Cross et al., 2004). Two main biological paths are recognized. The sulfide ions (or hydrogen sulfide) are produced during anaerobic respiration of some types of bacteria and archaea (so-called sulfate-reducing microorganisms; SRM) in excess of biodegradable organic matter serving as an electron donor. The process is known as dissimilatory sulfate reduction. Living organisms also reduce sulfur for incorporation into the principal organic sulfur compounds (e.g., amino acids, coenzymes, vitamins) within cells in a process known as assimilatory sulfate reduction. Assimilatory

sulfate reduction is an energy-requiring process and is assumed to be of lesser importance in terms of sulfide mineral formation (Konhauser, 2007).

Anaerobic condition is a commonly stated pre-requisite for maintaining SRM activity and sulfide mineral formation and persistence (Konhauser, 2007). Some studies even suggest that any oxygen ingress into the anaerobic zone is detrimental to metal sulfide precipitation (e.g., Dvorak et al., 1992; Johnson and Hallberg, 2005). However, wetlands are open systems and stay only mildly reducing, allowing for constant gas exchange with the atmosphere, i.e., ingress of oxygen (e.g., through plant roots), much enhanced during low water table, and liberation of reduced species (H₂S, methane). Sulfide ions and dissolved oxygen co-occur in wetlands porewater (e.g., Smieja-Król et al., 2015). Still, the transformation of oxidized industrial contaminants into authigenic sulfides was detected close (a few cm) to the wetland surface and in wetlands only occasionally waterlogged (Sonke et al., 2002; Smieja-Król et al., 2022a). This can be explained by a diffusion-limited solute exchange in the complex network of wetland pores and the coexistence of diverse groups of microorganisms, which create steep redox gradients between aerated and oxygen-depleted microsites. A close association of the sulfide minerals with decaying vascular plant roots and litter is observed in wetland sediments (Sonke et al., 2002; Smieja-Król et al., 2015; Smieja-Król et al., 2022a).

The organic matter's high affinity to some metals and precipitation of other minerals, mainly Fe hydroxides, controls the chemical composition and mineral assemblage of the sulfides. Especially Cu and Pb ions are agreed to be effectively bound by organic matter, in both solid and dissolved form, limiting the availability of free Pb and Cu ions to react with the sulfide. In contrast, Zn and Cd adsorb rather weakly on organic matter, silicate clays, and oxides at the usual wetland pH, favoring the precipitation of Zn and Cd over Pb and Cu sulfides. Additionally, Fe tends to precipitate as Fe hydroxides (goethite, ferrihydrite) in wetlands with fluctuating water table levels or is stabilized in the ferric form (Fe³⁺) by complexation with organic matter (Syrovetsnik et al., 2007; Bhattacharyya et al., 2018). The preferred preservation of iron in the ferric state in wetlands suppresses the Fe(II) ions activity and allows for the precipitation of the less common sulfides.

5. Implications of sulfide precipitation in wetlands

Trace elements are effectively sequestered into sulfide phases in contaminated wetlands limiting their mobility and toxicity. The wetlands' primary role is to sustain SRM activity by delivering biodegradable organic matter and limiting oxygen penetration. Precipitation inside plant tissues or encapsulation in microbial biofilms increases sulfides resistance to oxidation and mechanical displacement during flooding or short-term water table lowering. Based on thermodynamic data, metal sulfides are extremely insoluble phases, which means they can precipitate at very low ions concentrations in solution (theoretically <1 µg/l), lowering the dissolved metal and sulfide ion concentrations in water well below the environmentally permissible thresholds. On the other hand, the heavily contaminated wetlands constitute a danger of changing from net sinks to net sources of trace elements and sulfate, causing water-quality degradation (Figure 1; Sobolewski 1999; Eimers et al., 2003; Adkinson et al., 2008). The release of the contaminants into water is possible in unfavorable conditions of a prolonged drought, cessation of mine water discharges, or a change of land use. Hardly soluble, sulfides are prone to oxidative dissolution (Barrett and McBride, 2007). Consequently, a safer environment is the ultimate benefit of the in-depth research into the mechanisms that govern sulfide formation and preservation in wetlands, allowing for long-term rational management of the contaminated sites and more efficient designs for artificially constructed wetlands. From a broader perspective, sites extremely polluted by human activities undergo extensive transformation by Earth's surface processes, becoming similar to metal accumulations known from geological records. Vast amounts of metals that transform over time into stable secondary sulfide phases in some wetlands can be considered human-induced ore deposits, adding to the list of significant anthropogenic impacts on Earth's geology, leading recently to the recognition and formalization of the Anthropocene. A concept of human-made deposits has already been introduced by Saryg-ool et al. (2017). Finally, contaminated wetlands can be used to understand the geochemical and biological evolution of the Earth and to reconstruct ancient ore deposits' genesis and mechanisms of formation.

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