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Microbially Affected Kupferschiefer Black Shale as an Unrecognized Source of Halogenated Volatile Organic Compounds

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Upper Permian Kupferschiefer is one of the world's three most important formations for sediment-hosted copper (SHC) deposits. The formation extends from Great Britain through the Netherlands and Germany to Poland. The richest deposits are located in the Fore-Sudetic Monocline and North Sudetic Synclinorium (SW Poland), where mining has continued for decades. The mined deposits occur at depths of 200–1400 m. However, in the Leszczyna Syncline, the Kupferschiefer is exposed at the surface as a natural outcrop. Additionally, copper ore processing generates large volumes of post-flotation waste stored in numerous tailings ponds [1]. Previously, lithotrophic and heterotrophic microbial activity and their role in weathering fossil organic matter and sulfides in the Kupferschiefer were demonstrated [2]. These transformations lead to the formation of secondary weathering minerals and the mobilization of organic carbon as numerous organic compounds, including volatile ones. The aim of the present study was to investigate the emissions of halogenated volatile organic compounds (HVOCs). Samples included weathered black shale from underground mines, surface outcrop, and post-flotation waste from a tailings pond. The analyses were conducted using gas chromatography coupled with mass spectrometry and an electron capture detector. HVOCs were detected in all studied sites. Brominated and/or chlorinated C1 compounds were the dominating species, including: bromochloromethane, bromodichloromethane, chloromethane, dichloromethane, tetrachloromethane, and trichloromethane [3]. These findings suggest that SHC deposits may represent an previously undocumented natural source of HVOCs. Considering the large mass of these deposits, they may constitute a potentially significant component of the global HVOCs budget, acting as an important source of atmospheric halogens that contribute to ozone layer depletion and global warming [4]. Further research is planned to elucidate the mechanisms and pathways of HVOCs formation in this environment, with particular emphasis on microbial processes.

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