

ERDC Dredging Operations Technical Support Program (DOTS)

U.S. ARMY CORPS OF ENGINEERS

BUILDING STRONG®

Response Summary:

The Alaska District contacted the ERDC Environmental Laboratory Chemistry Branch to confirm the concentrations of selenium in dredged material determined by a Department of Defense Environmental Laboratory Accreditation Program (DoD ELAP) approved commercial laboratory using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Recent concentrations reported by the commercial laboratory were ~3 times higher than data generated several years prior, and suggested rapid increases in sediment selenium concentrations. ERDC researchers reviewed the contract laboratory data and quickly suspected analytical interferences were responsible for the discrepancies. District personnel sent newly created sediment composite samples to ERDC for investigation, where researchers conclusively confirmed the presence of Rare Earth Elements (REEs) in the sediments.

ERDC used a combination of Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS) and ICP-MS, the latter operated in standard and reaction cell modes, to detect the interferences and confirm the concentration of selenium (and REEs) in the sediment samples. They demonstrated that the REEs produced the erroneously high selenium results due to specific Gadolinium and Dysprosium 'double charged' ions that are indistinguishable from the selenium isotope used for analysis by the specific ICP-MS method performed at the contract laboratory. The ERDC techniques were able to circumvent or overcome these issues and produced data that was an accurate measurement of selenium concentration and characterization of the observed interferences. The value ranges were also in general agreement with prior analyses in the area by other laboratories using different techniques.

A similar issue was encountered by the Philadelphia District previously. In that case, erroneous arsenic concentrations were detected in groundwater at confined disposal facilities (CDFs), resulting in regulatory concerns and uncertain future use of the CDFs. The ERDC team solved that issue through the application of our advanced analytical methods demonstrating the arsenic detections were false and the result of REE interferences, allowing continued District use of the CDFs.

Period of Performance:

October, 2022.

Benefits of the Response to the USACE Dredging/Navigation Program:

Accurate determination of target analytes in dredged material is critical to decisions about ultimate disposal of the material, including any plans for beneficial use. The results of this study confirm that even use of a DoD accredited laboratory does not guarantee accurate data. Rare Earth Elements are a potential interference on both arsenic and selenium in ICP-MS analyses (as well as other elements when the REEs interfere with ICP-MS internal standards), necessitating that care is taken in applying this method to complex natural matrices.

Deliverable:

The ERDC provided confirmatory selenium analysis in sediments by multiple analytical methods, including GF-AAS and ICP-MS. Furthermore, they demonstrated the presence of REEs in the subject sediment samples and described the mechanism of how these elements interfered with ICP-MS analyses performed by the original commercial laboratory, yielding erroneous elevated selenium concentrations. The accurate data allowed the District to proceed with the project without negative environmental impact. This work was completed within approximately 2 weeks of the initial contact from the District, and within 4 days of ERDC receiving the samples for testing.

Providing environmental and engineering technical support to the U.S. Army Corps of Engineers Operations and Maintenance navigation and dredging missions

POC: Anthony J. Bednar ERDC Environmental Laboratory Name • Anthony.J.Bednar@usace.army.mil DOTS ID: 23-R03