

**STUDY TITLE:** Trace Metal Quality Control Analyses (100 Samples)

**REPORT TITLE:** Final Report on the Quality Control of Trace Metal Analysis for the MAFLA Baseline Environmental Survey

**CONTRACT NUMBER:** BLM: 08550-CT4-15

**SPONSORING OCS REGION:** Gulf of Mexico

**APPLICABLE PLANNING AREAS:** Eastern Gulf of Mexico; Central Gulf of Mexico

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**KEY WORDS:** Eastern Gulf; Central Gulf; chemistry; trace metals; sediment; water column; fauna; zooplankton; invertebrates; benthos; quality assurance; interlaboratory comparison; spectrophotometry; Mississippi; Alabama; Florida; Gulf of Mexico Region

**BACKGROUND:** The importance of understanding and quantifying the baseline chemical composition of water, sediments, and fauna of an area is well recognized, particularly as it relates to assessing potential impacts associated with offshore oil and gas development activities. Because large baseline environmental study programs have often involved chemical analyses by several independent laboratories, quality control procedures must be established to insure that analytical results are comparable between analytical facilities. To accomplish this objective, the present study effort was initiated in support of the Mississippi-Alabama-Florida (MAFLA) Outer Continental Shelf (OCS) Baseline Study to provide appropriate quality control of the trace metals aspects of the program.

**OBJECTIVE:** To establish a comprehensive quality control program in support of the trace metal phase of the MAFLA OCS Baseline Study program.

**DESCRIPTION:** Five types of marine environmental samples, chosen at random from samples analyzed by the prime chemical analysis contractor, were submitted for quality control verification. Sample types included surficial bottom sediments, dissolved and suspended metals in the water column, and faunal samples (i.e., zooplankton, benthic

invertebrates). A total of 35 sediment samples, 15 filtered water samples, 15 suspended particulate-matter samples, 15 zooplankton samples, and 20 benthic invertebrate samples were tested.

A total of eight different metals or trace metals were determined. Measured metals or trace metals included barium (Ba), cadmium (Cd), lead (Pb), vanadium (V), nickel (Ni), copper (Cu), chromium (Cr), and iron (Fe). Samples were analyzed by flame and/or flameless atomic absorption spectrophotometry.

**SIGNIFICANT CONCLUSIONS:** The metals present in the greatest quantity in the MAFLA sediments included calcium (20%), magnesium (3%), iron (0.7%), aluminum (0.5%), sodium (0.5%), and potassium (0.15%). Average heavy metal concentrations in the sediments were 4,877 ppm for iron; 22.7 ppm for barium; 15.4 ppm for chromium; 11.4 ppm for vanadium; 6.1 ppm for nickel; 4.7 ppm for lead; 1.8 ppm for copper; and 0.086 ppm for cadmium. Percent recovery was lowest in samples analyzed by flameless atomic absorption spectrophotometry techniques. Good recoveries were obtained for chromium, copper, lead, nickel, and vanadium.

Iron was present in the highest concentration in seawater samples analyzed. By comparison, nickel was highest in suspended particulate matter. The lowest concentrations were measured for cadmium and chromium in these latter two types of samples, respectively. Iron was also highest in benthic invertebrates, occurring at an average concentration of over 15,000 ppb. Lead was present at the lowest average concentration of 23 ppb. Similar trends were observed for metals in zooplankton.

**STUDY RESULTS:** In sediment samples collected from the MAFLA survey area, the analysis for barium content was impossible to perform by flame atomic absorption spectrophotometry due to interference from calcium. Therefore, analysis was performed by graphite furnace atomic absorption techniques. Even this technique resulted in some loss of barium due to a need to dry and char the sample for longer periods of time to eliminate interference from smoking of the sample during testing. Vanadium was easily determined by flame atomic absorption spectrophotometry. A 20% average difference was observed between aqueous versus matrix-matched standards. Cadmium was analyzed by flameless graphite furnace because the detection limit by flame atomic absorption spectrophotometry was exceeded. A 25% loss was observed during dry and char steps. Lead was measured by flame atomic absorption spectrophotometry. Comparison of data found no difference between aqueous and matrix-matched standards. Analyses for nickel required a matrix correction and a nonabsorbing wavelength reading. The difference between aqueous and matrix-matched calibration was approximately 10%. Copper determinations required matrix-matching of standards having a 15 to 20% increase in copper compared to aqueous standard calibration. For chromium, values obtained with matrix-matched standards were 10% lower than for aqueous standards. Average heavy metal concentrations in the sediments were 4,877 ppm for iron; 22.7 ppm for barium; 15.4 ppm for chromium; 11.4 ppm for vanadium; 6.1 ppm for nickel; 4.7 ppm for lead; 1.8 ppm for copper; and 0.086 ppm for cadmium. The presence of iron in greater than trace amounts proved to be the only difficulty encountered for sediment analysis of this

element. Large dilutions were necessary in order to use the linear portion of the calibration curve.

With regards to quality control, it was determined that the analyses for cadmium, chromium, copper, lead, nickel, and vanadium were "in control". Iron analyses were not classified (i.e., "in control" versus "out of control") since iron is not a trace component of sediments. It was not possible to apply such decisions to barium since 60% of the barium was lost during flameless atomic absorption spectrophotometry. Recovery of metals in spiked samples ranged from 50.8 to 138.1% for the various elements. Barium gave the lowest recovery, with 99.7% recovery measured for chromium in a matrix-matched sample. Statistical analyses indicated that duplicate analyses were performed with good reproducibility. An average variability of 27.9% was obtained. The highest variability was with cadmium (61.2%) and the lowest with iron (9.9%).

The order of decreasing dissolved metal content was Fe>Ba>V=Pb>Cr>Cu>Ni>Cd for the 15 water samples analyzed. The trace metal content for sediments was Fe>Ba>Cr>V>Ni>Pb>Cu>Cd. Chromium and lead showed the most significant difference between the two groups. For suspended particulate matter, metals concentrations in descending order were Ni>Fe>Cu>Ba>Pb>Cd>Cr. The average concentration of vanadium was less than the detection limit of 5 ppb. Significant concentrations of nickel were measured for the suspended particulate matter as compared to dissolved nickel. Copper averaged 23.0 ppb in suspended particulate matter versus 2.6 ppb in seawater.

Because sample weight and digestion volume were not available for the analysis, a rigorous interpretation of benthic invertebrate data was not feasible. Large amounts of iron, nickel, and vanadium were found in these samples while lead content was low. The order of elements in these samples, ranging from high to low concentrations, was Fe>Ni>V>Ba>Cu>Cd>Cr>Pb. Copper concentrations in zooplankton were similar to those for benthic invertebrates. Iron was present at the highest levels of the eight trace metals, while lead was lowest. Barium was higher than that found in the benthic organisms.

**STUDY PRODUCT:** Gulf South Research Institute. 1975. Final Report on the Quality Control of Trace Metal Analysis for the MAFLA Baseline Environmental Survey. A final report for the U.S. Department of the Interior, Bureau of Land Management Gulf of Mexico OCS Office, New Orleans, LA. Contract No. 08550-CT4-15. xvi + 171 pp.