

Evaluating the BCR Sequential Extraction Procedure for Carbonate-Rich Sediments and Soils

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Objective

The Bureau of Community Reference (BCR) sequential extraction procedure is a harmonized method for evaluating the distribution of trace metals in sediments and soils, assigning metals into three operationally-defined geochemical fractions: acid-extractable, reducible, and oxidizable. The validity of sequential extraction procedures has been questioned, with concerns centering on the non-selectivity of extracting reagents, the redistribution of trace metals between phases during an extraction, the possible formation of new phases during an extraction, and the possibility of incomplete extractions. The objective of this study is to probe these limitations, particularly as they apply to carbonate-rich sediments and soils.

Background

Sediments and soils are complex mixtures of inorganic and organic phases. When a trace metal enters into a sediment or soil it may be present in any of these phases as a loosely bound surface adsorbate or complex, as a coprecipitate, or as a distinct mineral phase. A trace metal's lability—and thus its susceptibility to release—depends on its speciation.

A popular method for evaluating the distribution of trace metals in sediments and soils is a sequential extraction using a series of increasingly reactive reagents. The distribution of trace metals within the sediment or soil is operationally defined by the reagent, although nominal target phases often are identified. The BCR sequential extraction procedure (Table 1) is one of several standard sequential extraction schemes, and the only one that has been validated with respect to interlaboratory reproducibility.

Reagent (per g sediment)	Operational Definition	Nominal Target Phases
Step 1 40 mL 0.11 M CH ₃ COOH; extract for 16 h	exchangeables	exchangeable cations
Step 2 40 mL 0.5 M NH ₂ OH·HCl adjusted to pH of 1.5 with HNO ₃ ; extract for 16 h	acid-extractables	carbonate minerals
Step 3 10 mL 8.8 M H ₂ O ₂ ; extract for 1 h at room temperature and 1 h at 85 °C	oxidizables	Fe/Mn oxides and hydroxides
10 mL 8.8 M H ₂ O ₂ ; extract for 1 h at 85 °C		organic matter
50 mL 1.0 M CH ₃ COONa; extract for 16 h		sulfide minerals

The validity of sequential extraction schemes, particularly the utility of operational definitions, has been questioned in a number of experimental studies using synthetic sediments and soils. Table 2 outlines the most important potential limitations. For example, using model synthetic sediments Kheobian and Bauer have shown significant redistribution of Cu, Pb, and Zn from the exchangeable and acid-extractable phase to other phases.² Because synthetic sediments and soils use phases that are not in equilibrium with each other, it is unclear whether the conclusions of these studies can be extended to real sediments and soils.³

Table 2: Potential Limitations to Sequential Extraction Procedures

- redistribution of trace metals to other phases
- non-selectivity of extracting reagents
- incomplete extractions
- formation of new phases during extraction

In this project we explore the utility of using the BCR sequential extraction procedure to study natural sediments and soils, particularly those containing significant amounts of carbonate minerals. The results presented here use natural lake sediments from several Indiana lakes, and a model system consisting of a carbonate-free soil mixed with CaCO₃.

Experimental Details

Sediments, from another study, were collected using a core sampler from three lakes in northern Indiana. After returning to the lab, cores were sectioned into 1-cm increments and allowed to air dry. For this study, unused increments were combined and homogenized before use. Analysis of the homogenized samples showed no evidence of heterogeneity at the sampling level used in this work.

Model soils were made using SRM 2710 (National Institute of Standards and Technology), and reagent-grade CaCO₃. SRM-2710 is a standard reference material consisting of a soil collected from the top 10 cm of pasture land along Silver Bow Creek near Butte, MT. The soil contains high concentrations of Fe, Cu, Mn, Pb, and Zn due to periodic flooding of the creek, which drained settling ponds associated with the Anaconda mine.

All extractions were carried out following the standard BCR conditions. All chemicals were ACS reagent grade or better. The concentration of metals in the extracting reagent was determined by flame atomic absorption spectroscopy using a Varian 220FS SpectraAA equipped with an SPS-5 autosampler, and a SIPS sample introduction pump system. Concentrations were determined using external standardizations.

Studies Using Indiana Lake Sediments

To evaluate the utility of the BCR sequential extraction procedure for Indiana lake sediments, we measured the release of iron and manganese as a function of time throughout the 16 h extraction with 0.11 M CH₃COOH. The result for Mn (Figure 1) show the expected steady increase over time, reaching a steady-state value of approximately 350 mg/g sediment after 12 h. The results for Fe, however, show an initial rapid release of metal, followed by a steady decrease in concentration suggesting that the released iron reenters the sediment due to readsorption or precipitation.

Because the sediments are approximately 50% CaCO₃—based on the loss of mass following an exhaustive acid-extraction—the standard BCR conditions cannot dissolve all the carbonate minerals. As a result, the pH of the extracting reagent increases over time and correlates with the change in iron's concentration (Figure 2). The source of the released iron—exchangeable iron or acid-soluble amorphous iron hydroxides—is unknown, as is the form of the reincorporated iron.

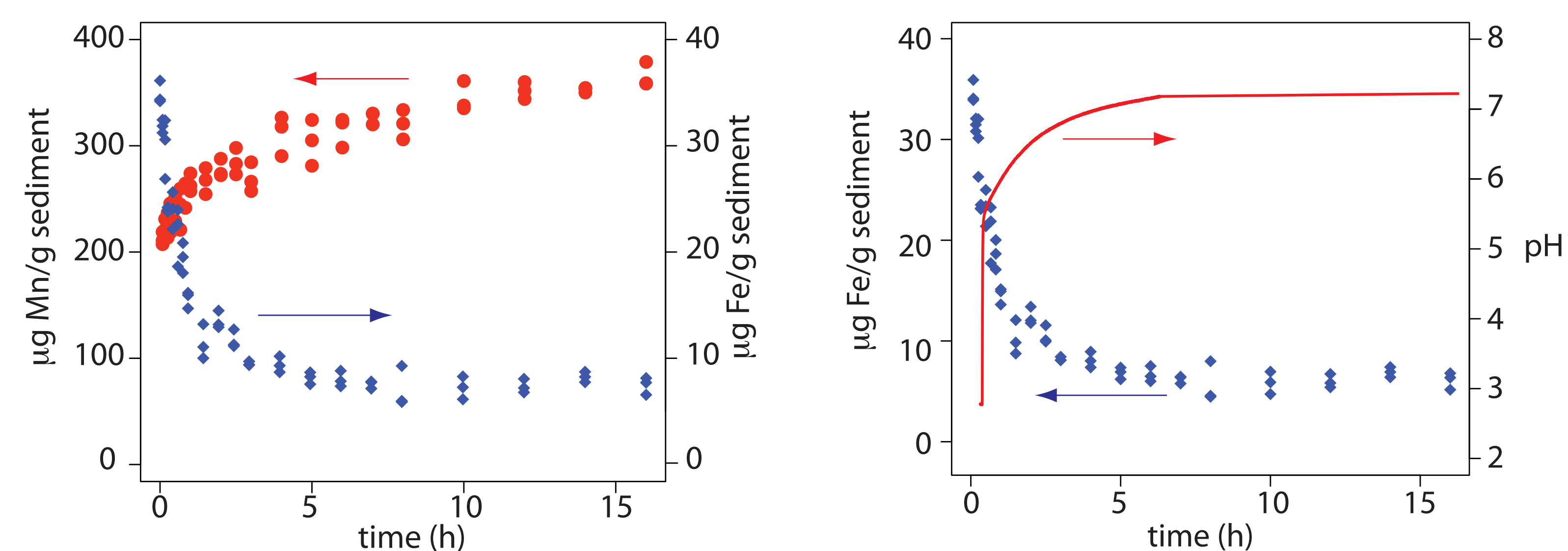


Figure 1. Release of Mn (●) and Fe (◆) as a function of time when extracting a lake sediment with 0.11 M CH₃COOH. Although Mn is continuously released during the extraction, Fe shows evidence of being released and then reentering the sediment.

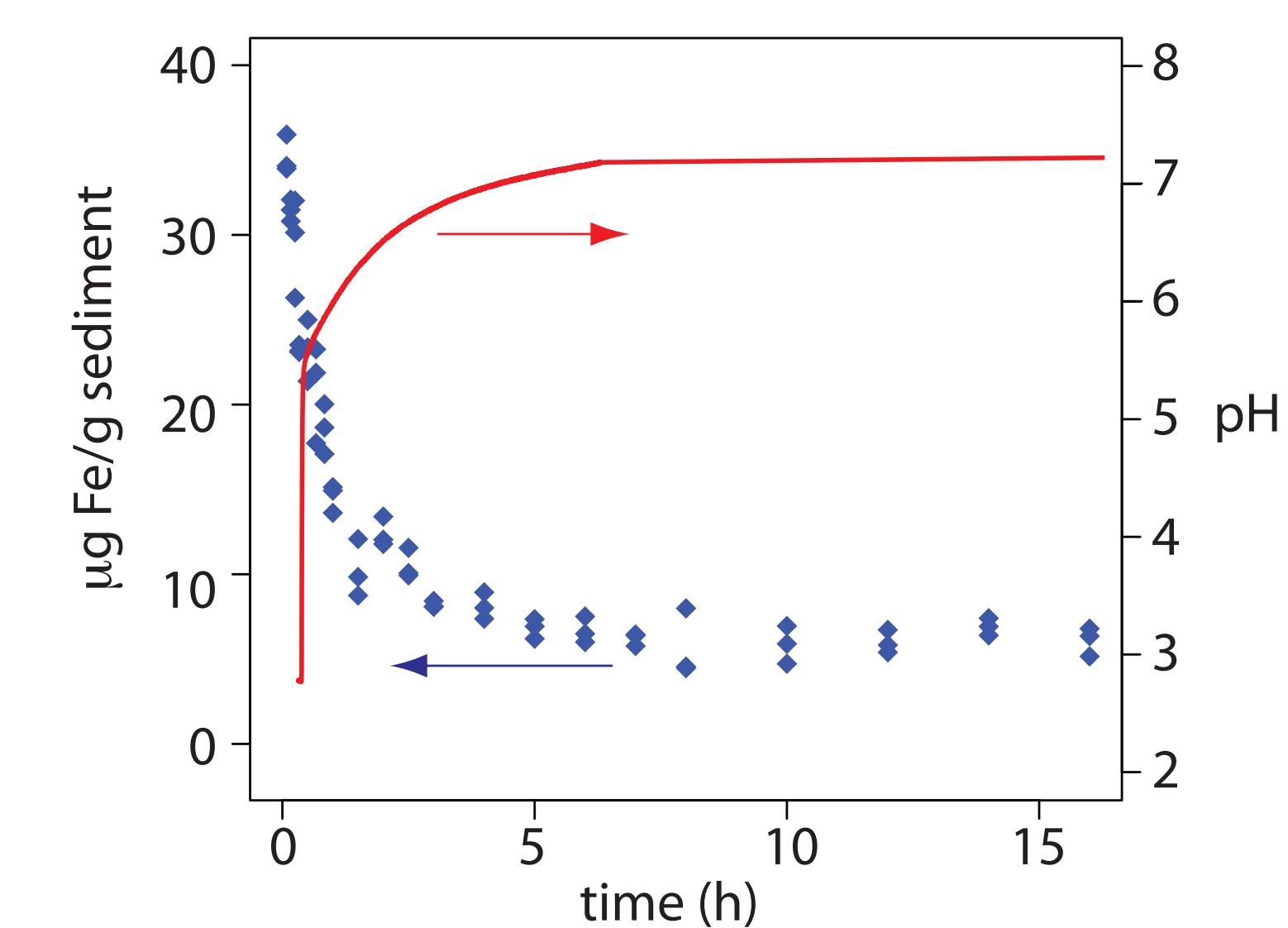


Figure 2. Release of Fe (◆) and pH (—) of extracting reagent as a function of time when extracting a lake sediment with 0.11 M CH₃COOH. Because of the sediment's high concentration of CaCO₃, acetic acid is the limiting reagent and the pH increases rapidly.

Studies Using a Model System: SRM-2170 and CaCO₃

Although not widely recognized as a problem, the difficulty of applying a sequential extraction procedure to carbonate-rich sediments and soils has been addressed in a small number of studies. Methods for modifying the first step of the BCR procedure include using a higher liquid/solid ratio, running the extraction under pH-stat conditions, increasing the concentration of acetic acid, or repeating the extraction several times.⁴

Because it is impossible when using a carbonate-rich sediment or soil to obtain benchmark values in the absence of carbonate, we are using a model system consisting of a carbonate-free reference soil mixed with CaCO₃. SRM-2710 was chosen as a model carbonate-free reference soil because other studies have obtained consistent results when using the BCR procedure. Our analysis of SRM-2710 for Cu, Zn, Pb, Mn, and Fe gave results (not shown) that are consistent with these studies.

For our initial studies we chose to explore the effect of increasing the concentration of acetic acid. Table 3 shows the experimental design. All samples are equivalent to the standard BCR ratio of 40 mL reagent/g sample. Sand was chosen as an inert filler to maintain a consistent total mass of 0.50 g. Analysis of the sand showed it contained no extractable trace metals.

Table 3: Experimental Design for Model System

Samples
• 0.25 g SRM-2710 (±0.0008 g)
• 0.00, 0.05, 0.10, 0.15, 0.20, or 0.25 g CaCO ₃ (±0.0018 g)
• sand to give total mass of 0.50 g (±0.0035 g)
Extraction
• 20 mL of 0.11 M, 0.22 M, 0.33 M, 0.44 M, or 0.55 M CH ₃ COOH
• extraction for 16 h at room temperature
Replicates
• n = 5 for each combination of %CaCO ₃ and [CH ₃ COOH]
Analysis
• samples analyzed for Fe, Mn, Cu, Pb, and Zn by FAAS
• pH measured at end of extraction

The release of metals are presented in Figure 3 as recovery plots showing the percent recovery relative to the amount of metal released when using 0.11 M CH₃COOH and 0% CaCO₃. A recovery between 85–115% was judged acceptable based on the relative uncertainty in BCR results. The diagonal lines show the minimum concentration of CH₃COOH needed to neutralize the CaCO₃, and the minimum concentration of CH₃COOH needed to neutralize the CaCO₃ and to establish the BCR condition of 40 mL CH₃COOH/g sample. Also shown is the pH at the end of the extraction.

Adding sufficient CH₃COOH to neutralize the CaCO₃ and to establish the BCR condition provides acceptable recoveries for Fe, Zn, and Cu. At 80%, the recovery for Mn under these conditions fall just outside the range of acceptable recoveries. Conditions for extracting Mn and Zn are robust as substantially higher concentration of CH₃COOH do not lead to a significant increase in their recoveries. Fe, and to a lesser extent, Cu, are susceptible to excessively high recoveries if the concentration of CH₃COOH is too high. Amorphous iron oxides are known to be partially soluble in acetic acid, and the copper may be associated with the iron.

The results for Pb suggest that its recovery is strongly influenced by the concentration of acetate, CH₃COO⁻, with recoveries increasing for higher concentrations of CH₃COOH and for larger %CaCO₃. This observation may explain why literature results for Pb vary significantly between different extraction procedures, which often use different concentrations of CH₃COOH.

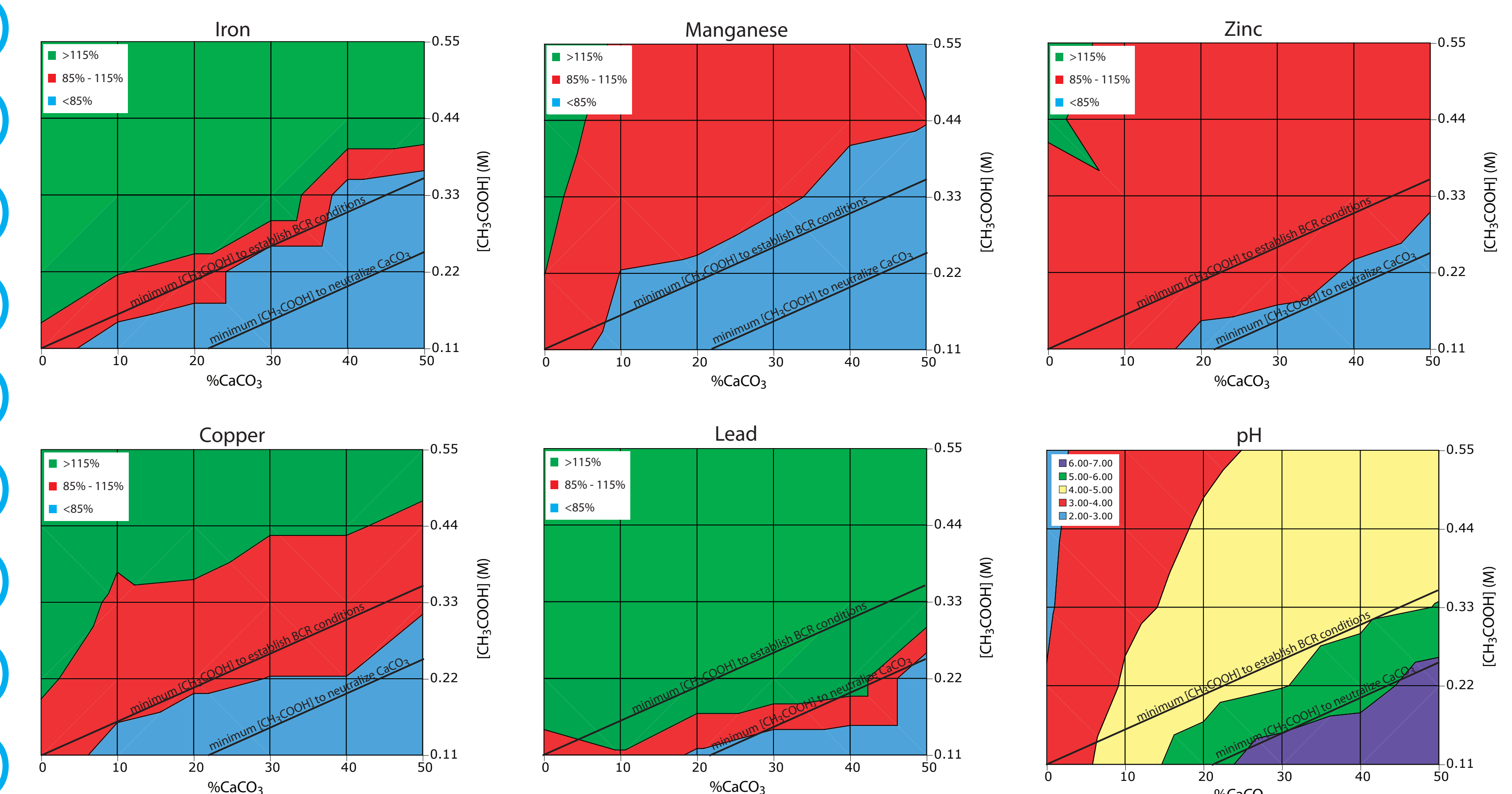


Figure 3. Recovery plots for Fe, Mn, Zn, Cu, and Pb, and the final pH at the end of the 16 h extraction. The diagonal lines show the minimum concentration of CH₃COOH needed to neutralize CaCO₃, and the minimum concentration of CH₃COOH needed to neutralize CaCO₃ and to establish the BCR condition. For the metals, the areas in red represent an acceptable recovery of 85%–115%. The recoveries are too high for conditions shown in green, and too low for conditions shown in blue.

Conclusions

The first step of the BCR sequential extraction of carbonate-rich sediments and soils is subject to significant errors if the concentration of CH₃COOH is insufficient to neutralize the CaCO₃ and to establish the standard BCR conditions. Although the recoveries for Mn and Zn are relatively insensitive to excess CH₃COOH, the recoveries for Fe and Cu show significant increases for higher concentrations of CH₃COOH. In the absence of additional work, using the BCR sequential extraction procedure—or any other sequential extraction procedure—for determining the distribution of Pb in any sediment or soil is questionable.

References

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