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Review

The potential for portable X-ray fluorescence determination of soil copper at ancient metallurgy sites, and considerations beyond measurements of total concentrations

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ABSTRACT

Copper (Cu) at ancient metallurgy sites represents the earliest instance of anthropogenically generated metal pollution. Such sites are spread across a wide range of environments from Eurasia to South America, and provide a unique opportunity to investigate the past and present extent and impact of metalworking contamination. Establishing the concentration and extent of soil Cu at archaeometallurgy sites can enhance archaeological interpretations of site use but can also, more fundamentally, provide an initial indication of contamination risk from such sites. Systematic evaluations of total soil Cu concentrations at ancient metalworking sites have not been conducted, due in part to the limitations of conventional laboratory-based protocols. In this paper, we first review what is known about Cu soil concentrations at ancient metallurgy sites. We then assess the benefits and challenges of portable X-ray fluorescence spectrometry (pXRF) as an alternative, rapid technique for the assessment of background and contaminant levels of Cu in soils. We conclude that pXRF is an effective tool for identifying potential contamination. Finally, we provide an overview of some major considerations beyond total Cu concentrations, such as bioavailability assessments, that will need to be considered at such sites to move toward a complete assessment of environmental and human risk.

Contents

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1. Introduction

The production and use of metal objects is a key component of social complexity and emerges ~8000 BCE with an initial focus on Cu (Killick and Fenn, 2012). Copper production also contributes Cu as a significant environmental pollutant, which, from limited studies to date, may potentially be found in extremely high concentrations at such sites around the world (Nagajyoti et al., 2010). This review focuses on examples of Cu contamination at metallurgy sites spanning the Neolithic (~8000 BCE) to the mid first millennium BCE. More specifically, we focus on production sites (Cu smelting and metalworking) rather than mining sites.

Current earliest evidence for Cu working and the first instance of anthropogenic heavy metal pollution is at Neolithic sites (Grattan et al., 2016). The mining of native Cu and fabrication of Cu items rapidly expanded in the Chalcolithic (Copper Age) and by the Early Bronze Age production of Cu-based alloys included conditioning elements such as As and Sn (Harper, 1987; Killick and Fenn, 2012). From the Bronze Age, metallurgical practices involved sustained effort and increasingly complex and large scale operations (Killick and Fenn, 2012).

Ancient smelting sites are not typically situated within naturally mineralized zones (i.e. areas with naturally elevated background concentrations of heavy metals (Pryce et al., 2010)), although they may be within close proximity. This separation allows ready differentiation between natural and anthropogenic heavy metal contamination at these sites as such sites do not have an unknown degree of elevated 'background' contamination from mineralization. Examining Cu in particular at ancient smelting sites could provide insights into the longest term human-induced pollution.

Contemporary assessment of soil contamination from Cu typically focuses on soils that were contaminated over a relatively short time frame (years to decades, and in a very few studies, a few hundred years (e.g. Carr et al., 2008)). Assessment of contamination via total metal concentrations is an essential precursor (see Fig. 1) to more detailed investigations into element mobility, potential biological availability, and actual transfer into biota and foodchain at these sites to determine site specific risk of contamination (NEPC, 2013; Tighe et al., 2013). However, even this preliminary analysis is rarely undertaken (Frahm and Doonan, 2013).

Given the absence of these key baseline data on total soil Cu concentrations specifically at archaeometallurgy sites, we review what is known of total soil Cu at such sites, and explore the potential of portable X-ray Fluorescence spectrometry (pXRF) as a tool to address this shortcoming. We outline the major considerations in the application of this technology in this context with specific reference to practical considerations in quantifying Cu with this method. Assessing total soil Cu will provide new insights into the unintended consequences of metallurgically produced pollution on past societies, and can also enable preliminary assessment of the contemporary contamination risk such sites still pose. These baseline Cu data can additionally inform possible long term behaviour of a given level of contemporary contamination in similar environments.

2. The contamination legacy of ancient Cu smelting

2.1. Copper in the environment

Copper is a naturally occurring element which can be found in fauna, flora, rocks, volcanic dust and soil (Adrees et al., 2015; Ginocchio et al., 2006). Worldwide background values in soils range up to 110 mg kg^{-1} depending on parent material and soil texture, with an average of 14 mg kg^{-1} (Kabata-Pendias and Szteke, 2015). Copper forms strong bonds with sulfur, creating a range of Cu sulfide minerals such as covellite (CuS) and bornite (Cu_5FeS_4) (Kabata-Pendias and Szteke, 2015). When subjected to weathering, these minerals can combine with carbonate and oxides to generate new mineral phases such as malachite ($Cu_2CO_3(OH)_2$) (Kabata-Pendias and Szteke, 2015).

Changes in atmospheric Cu pollution correlate with changes in Cu mining and smelting over time (Nriagu, 1996). Ice cores and bogs provide comparatively stable environmental archival sources of this correlation. The timing of anthropogenic Cu production in the northern hemisphere generally corresponds in ice cores from Greenland, peat bogs from Scotland, shell middens and sediments from the Iberian Peninsula, and lagoon sediment cores from Egypt (Hong et al., 1996a; Küttner et al., 2014; Martínez Cortizas et al., 2016; Véron et al., 2013).

From its initial definitive appearance in the Chalcolithic (~5000 BCE), Cu production increased significantly during the Roman Period (~250 BCE – 350 CE) due to its use in coinage, expanded again due to numerous activities during the Sung Dynasty of China (960-1279 CE), and again with the onset of the Industrial

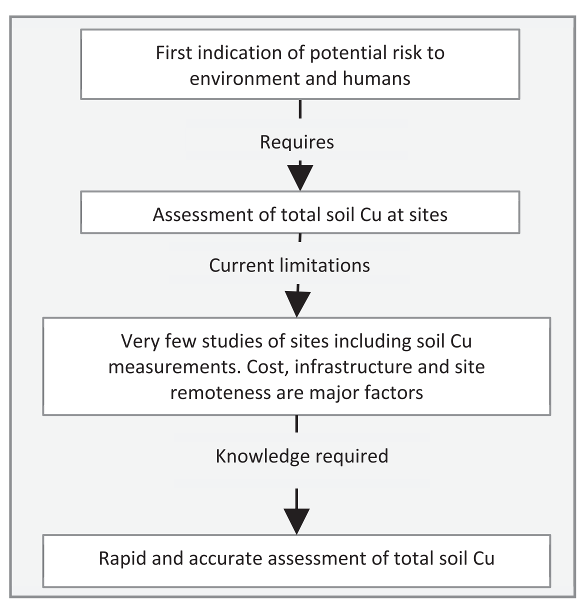

Fig. 1. The requirements and current limitations in assessing total Cu at ancient archaeometallurgy sites framed in terms of the initial sampling and analysis component of recommended contaminated site assessment (NEPC, 2013; Tighe et al., 2013).