Geoderma 308 (2017) 341–349

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Evidence for a naturally occurring post-glacial acid sulfate weathering event in northwestern Indiana, USA

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ARTICLE INFO

Handling Editor: M. Vepraskas

Keywords:
Acid sulfate weathering
Arsenic
Unproductive black soils
Organic soils

ABSTRACT

We review the evidence for a naturally occurring acid sulfate weathering event along the southern shore of Lake Michigan that was initiated ~15,000 years BP (before present) at the close of the Wisconsin Glaciation. The evidence includes: (1) "unproductive black soils" that were encountered when settlers drained the wetlands in the area for agriculture, (2) areas of soils that have anomalously low base saturation and are classified into ultic subgroups in a region where typic subgroups are the norm, (3) unexpectedly high arsenic concentrations in streambed sediments of the Kankakee River, (4) pyrite, jarosite, and gypsum in cobbles from outwash deposits in the areas, and (5) identification of a modern day "unproductive black soil" with a surface soil pH of 2.1. We propose that the acid sulfate weathering event was initiated when the Lake Michigan Lobe of the Wisconsin Glacier eroded pyrite-rich bedrock and deposited it in an outwash fan in front of the Valparaiso Moraine, where sorting by water depleted calcium carbonate-rich fine material relative to pyrite-rich coarse material. Acid sulfate weathering on the higher landscape positions led to well-drained soils depleted of calcium and magnesium and resulted in anomalously low base saturation and soils now classified into ultic subgroups. Calcium, iron and sulfate moved to adjacent wetlands in the lower lying landscape positions, where reduction of iron and sulfate resulted in the precipitation of secondary pyrite in the accumulating organic material. Drainage of these wetlands for agriculture beginning in the late 1800s exposed the secondary pyrite to oxygen and initiated a second cycle of acid sulfate weathering that led to some of the reports of "unproductive black soils." These soils developed extremely low pH upon drainage. Some of these highly acid conditions exist today. Arsenic in the original pyrite is moving through the landscape and is manifested in the unexpectedly high arsenic contents in streambed sediments of the Kankakee River that drains the area. This work shows that a whole landscape approach is necessary to understand how seemingly unrelated observations are all manifestations of a single natural phenomenon.

1. Introduction

The impacts of acid sulfate weathering have been well documented in coastal environments (i.e., van Breemen, 1982) and in areas disturbed by mining (i.e., Barnhisel et al., 1982; Grube et al., 1982; Singh et al., 1982) in which the acid sulfate weathering event is usually initiated by anthropogenic activities such as drainage of coastal marshes, dredging of pyrite-rich sediments, or mining of coal or metals. The sustainable management of these soils and landscapes impacted by acid sulfate weathering remains a significant issue (Sullivan, 2004). The impacts of naturally occurring acid sulfate weathering events are less frequently documented, although they have been described in Maryland (Wagner et al., 1982; Fanning et al., 2010), Texas (Carson et al., 1982), northern Germany (Buurman et al., 1973), and the Murray-–Darling Basin in Australia (Creeper et al., 2015).

Here we present evidence for a natural acid sulfate weathering event that was initiated by weathering of Wisconsin aged glacial deposits derived from pyrite-containing bedrock. We focus on the southern shore of Lake Michigan where the glacial sediments were deposited ~15,000 years BP (Fig. 1), but it is likely that this event influenced, and continues to influence, soils and landscapes over a larger area. We take a historical approach, using multiple lines of evidence to illustrate how a number of seemingly unrelated problems and issues are explained by an acid sulfate weathering event.

2. The problem of unproductive black soils

The relatively low impact approach to land use of the Native Americans who lived in the forests and the prairies of the Midwestern U.S. changed rapidly in the 19th century as European settlers moved in,

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http://dx.doi.org/10.1016/j.geoderma.2017.06.006
Received 18 October 2016; Received in revised form 25 May 2017; Accepted 4 June 2017
Available online 16 June 2017
0016-7061/

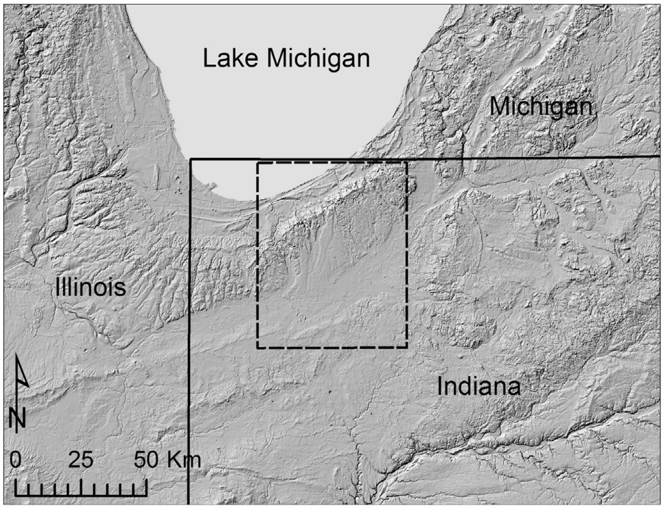

Fig. 1. Location of the study area. The area within the dashed rectangle is illustrated in more detail in Fig. 2. The hillshade base map is based on the U.S. National Elevation Dataset (U.S. Geological Survey, 2017).

clearing forests, plowing prairies, and draining wetlands to introduce their form of cultivated agriculture. The well-drained soils on the more sloping areas or on areas underlain by sand and gravel were cultivated first because they could be farmed immediately by simply plowing the prairie or by girdling the trees and planting between the tree trunks. Wetter soils, such as those on the extensive low relief till plains, required artificial drainage before they could be farmed. The lowest lying areas could be ponded for weeks or months, and some areas were covered by permanent wetlands. King's, 1852 map of Indiana (King, 1852), for example, shows many wetlands and shallow lakes in the northern third of the state that no longer exist. Similar marshes and bogs, some large, some only a hectare or less in size, covered significant areas of Ohio, Michigan, Illinois, and Wisconsin as well. Many of these areas have (or had) soils that today are classified as Histosols or histic subgroups of Mollisols, Alfisols, Inceptisols, and Entisols. In the early literature they are referred to as *muck soils*, *swamp soils*, *bogus soils*, *humus soils*, *peat*, *dark sandy soils*, *black soils*, or other similar terms.

Farmers initially believed that wetlands were worthless and they left them idle. They soon learned, however, that wet black soils could be highly productive once drained (Conner, 1933). Initially it was thought that drainage was all that was necessary to bring these soils into agricultural production, but it was soon discovered that not all wet black soils were the same and that some did not produce well at all. Neill and Tharp (1907), in their description of the "Peat" mapping unit in the *Soil Survey of Newton County, Indiana*, provide a detailed description of the problems associated with these soils, where "corn" refers to *Zea mays* L.:

> "The cost of constructing the existing drainage systems has been great, so it is most desirable that immediate returns be secured on the capital invested. In some cases the results obtained from growing crops on the Peat have been most gratifying; in others they have been most discouraging. It has been the experience of most of the farmers that the Peat generally produces fairly well for two or three years after being reclaimed, when its productiveness begins to decline, each succeeding crop being poorer than the one preceding. On the other hand, some of the areas improve with cultivation, although the improvement is gradual. There are also areas that have never produced well, the crops being generally small and frequently failing to mature. It has also been observed that the productiveness of the Peat areas is correlated in some way with the state of the organic matter present and that as soon as the marsh sod, leaves, trash, etc., plowed under, become thoroughly decayed or consumed the yields of the crops grown cease to be profitable."

Hopkins (1904) provides a similar description of the problem in Illinois:

> "There are immense areas of peaty swamp lands in the northern and north-central part of Illinois. … These soils are usually very black and very rich in organic matter, and they are frequently drained at great expense with the expectation that they will be very productive and almost inexhaustible, but not infrequently they yield disappointment and financial loss."

The problems associated with the unproductive black soils of the drained wetlands were so great that many of the state agricultural experiment stations in the Great Lakes Region conducted research specifically targeted to the management of these soils. In Indiana, research commenced in the summer of 1892 (Huston, 1895) and for the next 4 decades, there was a steady stream of research publications and extension bulletins (Huston, 1895, 1903; Conner, 1912, 1933; Conner and Abbott, 1912; Abbott et al., 1913). Outside of general soil fertility trials that had been initiated shortly after Purdue University opened in the 1870s, research on unproductive black soils was the first research in Indiana designed to understand a problem that was specific to a particular type of soil. Unproductive black soils were a problem in Illinois (Hopkins, 1904) and Wisconsin (King and Jeffery, 1899; Whitson and Stoddart, 1904), and likely occurred in adjoining states such as Ohio and Michigan that also have large areas of wet, black, organic or organic-matter-rich mineral soils.

Drainage, obviously, was a first prerequisite to bring the wet black soils into production. These soils were well endowed with nitrogen from the mineralization of the organic matter, and they usually contained sufficient phosphorus. Potassium, however, was usually found to be a major limiting nutrient (Kohnke and Ohlrogge, 1975).

It was soon learned, however, that unproductive black soils were not all the same. Near the town of Wanatah, IN, Abbott et al. (1913) note that "… local areas of peaty sand, sandy loam, and fine sand were discovered which did not respond to the usual drainage and potash treatment, or in short to any fertilizer or manure treatment." Much of the area that Abbott et al. (1913) describe was still under native prairie vegetation in the early 20th century. They go on to observe, "It is generally possible to identify this type of soil even in virgin prairie by the inferior native vegetation … dewberries (*Rubus canadensis*), red sorrel (*Rumex acetosella*), pine weed (*Hypericum gentianoides*), wild flax (*Koellia flexuosa*), various mosses, and a few inferior grasses and sedges cover the ground. … In the worst places considerable areas of nearly bare ground are found. … Corn fails to grow normally …. The roots of the dwarfed corn plants which survive present a peculiar gnarled appearance …. Clovers refuse to grow at all." These observations are significant because they document conditions that are probably no longer present today. Aside from a few hundred hectares scattered here and there, all of the native prairie areas in Indiana and Illinois have been plowed and cropped over the past century.

In a series of field, pot, and water culture experiments, Abbott et al. (1913) go on to show very convincingly that aluminum toxicity is the cause of the poor plant growth on these particular unproductive black soils. Liming, along with proper fertilization, was therefore necessary to make this soil productive. Although the Swiss chemist and plant physiologist Nicolas-Théodore de Saussure had shown that aluminum salts were toxic to plants (de Saussure, 1804), the work by Abbott et al. (1913) was the first to show that aluminum toxicity also occurred in the field (Kohnke and Ohlrogge, 1975).

Although Abbott et al. (1913) "solved" the problem of how to make these unproductive soils agriculturally productive, the question that they did not ask is why these soils were so acidic in the first place. The glacial drift in northern Indiana was originally calcareous, and the soils have been weathering for no more than ~15,000 years (i.e., Johnson, 1986). In the great majority of the soils in this area today, carbonates