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In-Situ Differentiation of Acidic and Non-Acidic Tundra *via* Portable X-ray Fluorescence (PXRF) Spectrometry

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ABSTRACT

Frozen soils or those with permafrost cover large areas of the earth's surface and support unique vegetative ecosystems. Plants growing in such harsh conditions have adapted to small niches, which allow them to survive. In northern Alaska, USA, both moist acidic and non-acidic tundra occur, yet determination of frozen soil pHs currently requires thawing of the soil so that electrometric pH methods can be utilized. Contrariwise, a portable X-ray fluorescence (PXRF) spectrometer was used in this study to assess elemental abundances and relate those characteristics to soil pH through predictive multiple linear regressions. Two operational modes, Soil Mode and Geochem Mode, were utilized to scan frozen soils *in-situ* and under laboratory conditions, respectively, after soil samples were dried and ground. Results showed that lab scanning produced optimal results with adjusted coefficient of determination (R^2) of 0.88 and 0.33 and root mean squared errors (RMSEs) of 0.87 and 0.34 between elemental data and lab-determined pH for Soil Mode and Geochem Mode, respectively. Even though the presence of ice attenuated fluoresced radiation under field conditions, adjusted R^2 and RMSEs between the datasets still provided reasonable model generalization (*e.g.*, 0.73 and 0.49 for field Geochem Mode). Principal component analysis qualitatively separated multiple sampling sites based on elemental data provided by PXRF, reflecting differences in the chemical composition of the soils studied. Summarily, PXRF can be used for *in-situ* determination of soil pH in arctic environments without the need for sample modification and thawing. Furthermore, use of PXRF for determination of soil pH may provide higher sample throughput than traditional eletrometric-based methods, while generating elemental data useful for the prediction of multiple soil parameters.

Key Words: frozen soil, Gelisols, Geochem Mode, proximal sensing, Soil Mode, soil pH determination

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INTRODUCTION

Gelisols, as defined by US Soil Taxonomy (Soil Survey Staff, 1999), are soils affected by permafrost, which occupy large areas of the United States (8.68%) and worldwide (8.61%). Permafrost is a permanently frozen condition at or below 0 °C in the soil profile. Gelisols are very cold soils with gelic materials underlain by permafrost, which acts as a barrier for water movement downward. The upper profile of Gelisols freezes and thaws seasonally, while the lower profile is permafrost and thus stays frozen continuously. Similarly, cold soils are recognized in the World Reference Base for Soil Resources as the reference soil group of Cryosols (IUSS Working Group WRB, 2014). Furthermore, several other soil orders have pergelic or cryic temperature regimes in which soil is periodically frozen throughout the year. Given the extremes of these environments, highly adapted and unique ecosystems have evolved to exploit small niches. For example, tundra ecosystems are largely devoid of trees and support only dwarf or prostrate shrubs, herbs, sedges and grasses. However, different vegetative communities have formed in response to differences in soil reaction (pH) (Walker *et al.*, 1998). Working in many of the same areas as our study, Gough *et al.* (2000) noted that soil pH was significantly positively correlated to species richness ($R^2 = 0.82$) and species density ($R^2 = 0.61$) according

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to the results of coefficient of determination (R^2). Specifically, moist non-acidic tundra (MNT) may feature *Carex aquatilis, Salix arctica, Salix reticulate, Eriophorum vaginatum, Dryas integrifolia, Arctostaphylos rubra* and various mosses with mineral soil pH of 7.0–7.6 (Walker *et al.*, 2001). Conversely, moist acidic tundra (MAT) features different species such as *Ledum decumbens, Racomitrium lan, Betula nana, Vaccinium vitis-ideae, Cassiope tetragonae, Polygonum viviparum, Dactylina arctica, Cetraria cucullata, Cladonia stygia, Hylocomium splendens, Sphagnum* spp. and *Peltigera* spp., where pH of the mineral soil can be 5.0–6.7 (Walker *et al.*, 1998, 2001). In tundra, soil pH is associated with ecosystem function at nearly all levels up through ecosystem trace gas flux (Walker *et al.*, 1998). Differences in soil pH come from two distinct sources: 1) calcareous loess and alluvium originally inherited from the Brooks range limestone, where base salinity is higher and thus contributes to more alkaline soil pH (Walker and Everett, 1991) and 2) prevalence of organics in soil profiles (*e.g.*, Oi, Oijj, Oe, Oejj, Oa or Oajj horizons), whereby soil surface peaty horizons are sources of degrading organics, and thus effectively increase humic and fulvic acid within the soil, lowering soil pH through time (Ping *et al.*, 2005). Given that many tundra soils are highly cryoturbated, surface-accumulated organics have a propensity to work themselves deeply into the subsoil, resulting in a soil profile vastly departing from the traditional concept of decreasing soil C content with depth for most upland soils. In areas such as the Sagwon Hills of Northern Alaska, USA, rolling hills and microtopographical features, such as hummocks and nonsorted circles at the surface and permafrost soil encased organic matter in the profile, can cause considerable soil variabilities even across small spatial areas (Ping *et al.*, 1998; Michaelson *et al.*, 2008). However, a key problem presents itself: with soil pH as such a critical component of ecological dynamics in these areas, how can it be measured *in-situ* in frozen soils?

Traditional methods of soil pH determination include colorimetric, titration and electrode (electrometric) approaches (Schofield and Taylor, 1955; McLean, 1982; Soil Survey Staff, 2014). However, all of the aforementioned methods require the use of reagents/chemicals and/or require the preparation of soil in a paste or at fixed soil:water ratio. Moreover, these approaches are precluded from being conducted *in-situ* on frozen and solid soil. Thus, to determine pH, the soil must be thawed, and then mixed with highly variable moisture content, which inherently ranges from 5%–250%. Recently, Sharma *et al.* (2014) successfully used portable X-ray fluorescence (PXRF) spectrometry to evaluate a wide variety of soil pH (4.17–8.70) using elemental data as a proxy for predicting soil pH. Their results were compelling, with R^2 and a root mean squared error (RMSE) of 0.77 and 0.685, respectively, when comparing lab-determined pH with PXRF-predicted pH. The advantage of the PXRF technique is that it is field portable and rapid (60–90 s) and most importantly, it is a proximal sensing technique which does not disturb the soil and can be applied *in-situ*. Sharma *et al.* (2014) noted the appeal of proximal sensing for pH determination in specific circumstances, specifically noting its potential for evaluation of permafrost-affected soils. Furthermore, PXRF scanning provides simultaneous quantification of a wide range of elements, of which data has already been used in various predictive algorithms to determine soil gypsum content (Weindorf *et al.*, 2009, 2013), texture (Zhu *et al.*, 2011), salinity (Swanhart *et al.*, 2014), cation exchange capacity (Sharma *et al.*, 2015), pollution (Carr *et al.*, 2008; Peinado *et al.*, 2010; Clark and Knudsen, 2014) and horizon boundaries (Weindorf *et al.*, 2012). Furthermore, McLaren *et al.* (2012) have extended the utility of PXRF to four plant species, scanning corn, cotton, soybean and wheat for measuring Ca, Co, Cr, Fe, K, Mn, Ni, P, S, Si and Zn content. An overview of contemporary advances in PXRF spectrometry for environmental, agronomic and pedological applications is provided by Weindorf *et al.* (2014a). Admittedly, PXRF does have some limitations which must be duly noted and considered: specifically, moisture content, sample heterogeneity and variable sensitivity for different elements (USEPA, 2007; Weindorf *et al.*, 2011; McLaren *et al.*, 2012; Weindorf and Chakraborty, 2016). Weindorf *et al.* (2011) conducted a study whereby PXRF readings were compared to those determined by inductively coupled plasma atomic emission spectroscopy and found that the correlation improves if moisture content is considered. Accordingly, drying is recommended for soil samples with moisture content $> 20\%$ (Kalnicky and Singhvi, 2001; Zhu *et al.*, 2011). Applied in arctic ecosystems, the variable morphology of ice within frozen soils is also problematic (French and Shur, 2010; Ping *et al.*, 2014b). Weindorf *et al.* (2014b) conducted a study to examine the effect of ice in Alaskan soils on the performance of PXRF. They found that the correlation between the frozen sample scans and the dried sample scans was significant ($R^2 = 0.81$). Notwithstanding the aforementioned limitations, PXRF data acquisition, which is rapid and inexpensive, has the potential to overcome the problem of pH determina-