



Predicting soil arsenic pools by visible near infrared diffuse reflectance spectroscopy



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ARTICLE INFO

Article history:

Received 22 June 2016

Received in revised form 3 January 2017

Accepted 16 February 2017

Available online 27 February 2017

Keywords:

Diffuse reflectance spectroscopy

Landfill

Soil arsenic solid phases

Partial least squares regression

Visible near infrared

ABSTRACT

Rapid and cost-effective analysis of soil solid As phases would be an invaluable tool in studying polluted soils and predicting soil As mobility. Analysis of soil solid As phases has commonly used sequential extraction; however, the approach is time consuming, destructive, and costly. Several studies have established the viability of using visible near infrared diffuse reflectance spectroscopy (VisNIR DRS) for elemental data analysis of soil, sediment, and other matrices. This pilot study used VisNIR DRS spectral data for rapidly predicting total As and five different solid As phases (Mg, PO₄, Ox, HCl and org pools). A total of 200 surface soil (0–15 cm) samples were collected from arable lands surrounding a polluted landfill site and scanned via VisNIR DRS. The raw reflectance spectra were preprocessed using three spectral transformations for predicting soil total As and five extracted pools using partial least squares regression (PLSR). Quantitatively, better accuracy was produced by PO₄ (Validation R² = 0.72, RPIQ = 3.39) and org (Validation R² = 0.93, RPIQ = 4.81) pools along with total As (Validation R² = 0.88, RPIQ = 3.54) using the first derivative of original reflectance values. Both qualitative spectral analysis and PLSR coefficients indicated that prediction of soil As and its phases were dependent on their close association with spectrally active soil organic matter, clay minerals and Fe/Al-oxides.

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1. Introduction

Arsenic (As) is a carcinogenic metalloid and large oral doses (>10 µg/L) of inorganic As can have lethal consequences (ATSDR, 2005). While anthropogenic activities and rapid industrial growth are mainly responsible for As contamination in the environment, the intake of As by humans happens via contaminated water, food and soil. Though groundwater As contamination has already gathered worldwide attention, soil As contamination cannot be discounted due to its substantial health effects (Hemond and Solo-Gabriele, 2004). Soil As contamination threatens the health of tens of millions of people worldwide, especially in Bangladesh and Eastern India (Smedley and Kinniburgh, 2002).

Movement of As from contaminated soils can pollute adjoining water bodies, while this movement is chiefly governed by different solid phases (Bangla and Kaiser, 1996). Oxygen rich environments

greatly influence As adsorption and mineral precipitation mechanisms via aqueous acidity constants of As when it is present as an oxyanion. While the oxidized As species, arsenate [As (V)] occurs as charged H₂AsO₄⁻ in neutral aqueous solutions, the highly toxic reduced species, arsenite [As(III)] occurs predominantly as uncharged H₃AsO₃ (Cullen and Reimer, 1989). Bhumbra and Keefer (1994) postulated that the dynamic between these two As species is crucial owing to comparatively greater mobility and high toxicity of As (III). Furthermore, humic fractions from soil organic matter can bind both As (V) and As (III). Apart from existing with oxides, As (V) can also yield several durable inner-sphere complexes (Stumm and Morgan, 1996). Thus, predicting soil As and exploring its connotations with several soil solid phases are imperative for predicting soil As mobility.

Over decades, environmental soil scientists collected As contaminated soil samples in the field and returned them to the laboratory for multi-step laboratory analyses via atomic absorption or inductively coupled plasma spectroscopy. Moreover, a wide variety of methods like sequential extraction, X-ray spectroscopy, and X-ray crystallography were employed to explore several solid phases of As. These conventional methods, while accurate and well documented, are laborious, expensive, and time intensive.

Abbreviations: RPD, residual prediction deviation; VisNIR DRS, visible near infrared diffuse reflectance spectroscopy; PLSR, partial least squares regression; LOI, loss on ignition; RMSE, root mean squared error; RPIQ, ratio of performance to inter-quartile distance; 1D, first derivative; 2D, second derivative; OSC, orthogonal signal correction.

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Visible near infrared diffuse reflectance spectroscopy (VisNIR DRS) is rapidly evolving as a feasible, fast, and non-invasive method to simultaneously characterize multiple soil properties from reflectance spectra (Brown et al., 2006). The VisNIR DRS approach is portable, cost-effective, promotes high-throughput, and has the potential to be operated both in proximal and remote sensing mode. Typically, an effective chemometric predictive algorithm is established between a host of soil parameters and spectral reflectance values in the VisNIR range (350–2500 nm). Furthermore, the DRS technique has been utilized for estimating heavy metals in agricultural soils (Ren et al., 2009; Wang et al., 2014). Since spectrally active chromophores like Fe/Al oxides, clay minerals, organic matter, and carbonate often absorb or bind metal ions, DRS has already shown its potential for rapidly predicting As and other heavy metals (Wu et al., 2005; Reeves and Smith, 2009; Niazi et al., 2015; Chakraborty et al., 2015). However, to the best of our knowledge, no effort has been made so far to explore predictions of solid phases of As in the VisNIR spectra, thus requiring a critical analysis focused on DRS-based prediction. Therefore, this investigation was designed to assess the potential of VisNIR DRS for rapidly predicting soil solid As phases in conjunction with three different spectral pretreatments and multivariate algorithms. We hypothesized that VisNIR DRS can rapidly predict total As and five different solid As phases.

2. Materials and methods

2.1. Sample collection

Soil samples examined in this study were collected from the same Dhapa landfill region, India, as mentioned previously in Chakraborty et al. (2015, 2017) (Fig. 1). Soils in this landfill are anthropogenic and highly disturbed. Although no official classification has been established yet for these soils in India, they exhibit similar characteristics of landfill soils found in the United States (e.g., Typic Udorthents) or Europe (e.g., Technosols). Municipal solid wastes of Kolkata and its suburbs (~229 km²) have been uncontrollably dumped in a huge disposal site (~26 km²) over the last 35 years at an average rate of 3000 tons day⁻¹. These anthropogenic activities have resulted in leachate accumulation and leachate runoff in the adjoining water bodies (SCS engineers, 2010). The vast section of land adjoining the core area (~2000 acres) is presently used for vegetable farming and provides the city ~147 t of vegetables per month. The major crops are cauliflower, ridge gourd and corn. The climate is humid tropical with an annual mean temperature of 26.6 °C and mean annual rainfall of 1623 mm.

In this study, we followed the sampling procedure of Keon et al. (2001) with some minor modifications. A total of 200 geo-referenced surface soil (0–15 cm) samples were collected from arable lands. A random sampling scheme was planned in ArcGIS 9.3 (ESRI Inc., USA) and

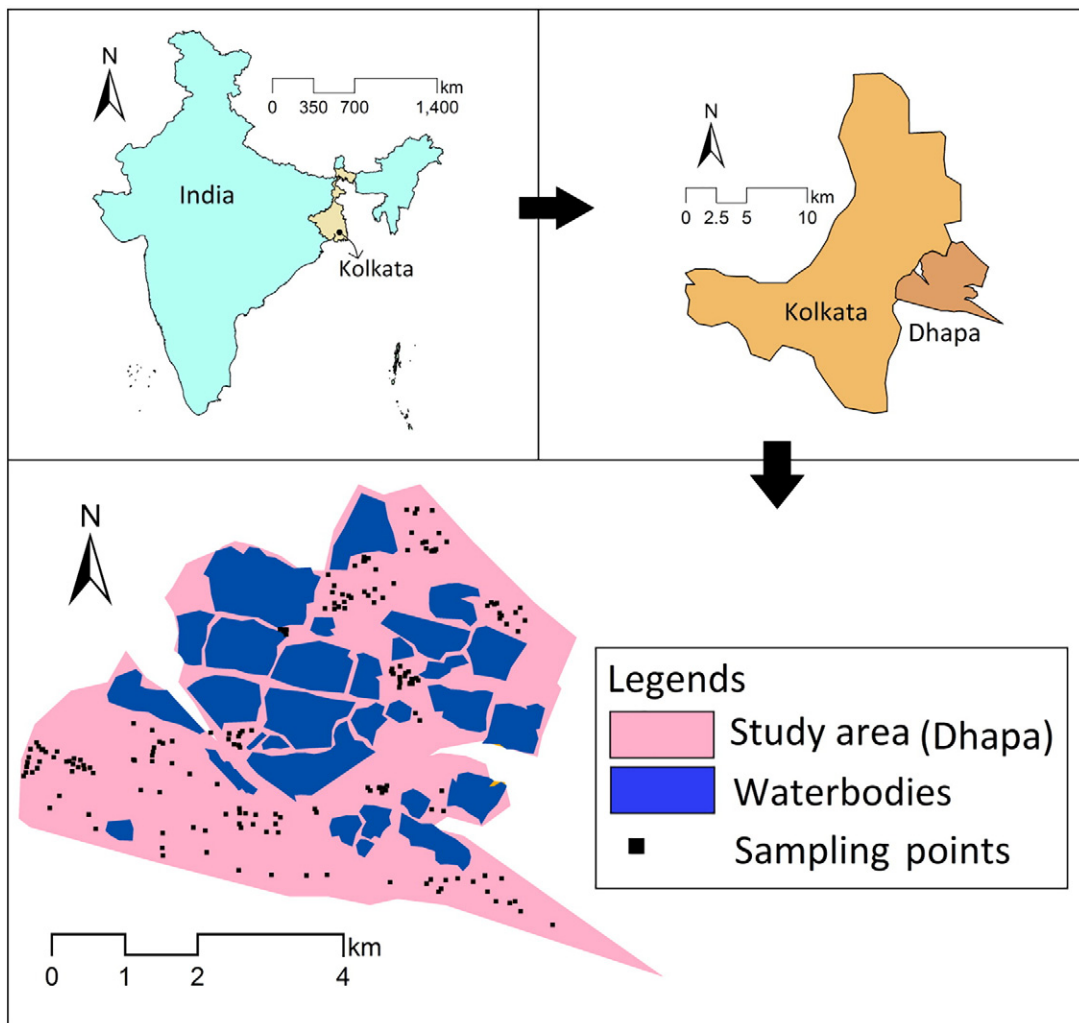


Fig. 1. Map of the study indicating sampling points in West Bengal, India.

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