MEASURING THE HUMIC ACIDS CONTENT OF COMMERCIAL LIGNITES AND AGRICULTURAL TOP SOILS IN THE NATIONAL SOIL PROJECT

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ABSTRACT

Radiocarbon dating studies have demonstrated that soil organic matter (OM) consists of two pools: a labile, short-lived pool that is an energy source for microbes, and a much longer-lived humic substances (HS) pool that is protected from microbial attack and represents the sequestered carbon in a soil. The longer-lived pool has three operationally-defined fractions: fulvic acids (FA, soluble at all pH), humic acids (HA, insoluble below pH ≈ 2) and humins (HU, insoluble at all pH). HA and FA can be extracted from soils and low-rank coals with aqueous bases and fractionated by acidification of the basic solutions. Several other procedures have been published but, to our knowledge, none have been shown to determine quantitatively the HA content of lignites and soils. This paper describes a gravimetric protocol that measures the HA content of four lignites used as commercial sources of HS products and 24 agricultural top soil samples from 13 counties in southern Idaho. No HU was found in the samples. The lignites and soil samples contain from 2-41 %HA and 0.31-9.8 %HA, respectively. Analytical precision limits are attributed to sample heterogeneity. Gravimetric HA measurements can facilitate rapid soil assessment, carbon cycling research and commercial HA products certification.

Keywords: Agricultural top soils, lignites, humic acid contents, sequestered soil carbon pools

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1. INTRODUCTION

The world's arable lands are being lost to development and erosion, degraded through overuse of inorganic fertilizers and are losing their ability to sequester carbon [1-4]. Remedies include no-till agriculture [5], plowing in crop residues (e.g. [6]), sewage sludge applications (e.g. [7]) and soil replenishment with organic products derived from low-rank coals in a growing 'humics' industry (e.g. [8,9]).

Soil organic matter (OM) contributes to every attribute of a healthy, productive soil, including structural stability, water permeability and retention, erosion resistance, nutrient storage and supply, and influence on pollutant fate [10]. Classic radiocarbon dating research [11] indicates that OM consists of two main pools with very different half-lives: a labile, relatively short-lived pool derived from crop residues is an energy source for soil microbes [6], and a much older, "refractory, recalcitrant" (≥400 yr old) pool collectively called humic substances (HS) that is protected from microbial attack and represents the baseline OM of a soil. The ^{14}C and other data conclusively demonstrate that HS are long-lived [11-15]. The long-lived HS pool is the *sequestered* carbon in a soil [1] and has three fractions operationally-based on aqueous solubility: fulvic acids (FA, soluble at all pH), humic acids (HA, insoluble below pH ≈ 2) and humins (HU, insoluble at all pH). HA often dominate the sequestered carbon, especially in top soils, which is the region of plant growth [16,17].

Aqueous acid-base chemistry generally gives the highest yields of HA from a given sample [18]. Thus, HA and FA can be extracted from soils and low-rank coals with aqueous bases and fractionated by acidification of the basic solutions [19]. Several procedures have been published (e.g., [20-23]). A recent study [15] demonstrates the precision of HA extraction from five peat samples but, to our knowledge, none of the published methods have been demonstrated to measure quantitatively the HA contents of a range of soils and other environmental samples.

The soil fractionation approach used by Campbell et al. [11] (Scheme 1) has three main steps: a) pre-

treatment with 0.1 *M* HCl at 90°C for 3 hr, centrifuging, then "repeat treatment till test for Fe negative;" b) shaking for 20 hr with 0.5 *M* NaOH, centrifuging, then "wash with NaOH till supernatants clear" (note: humate solutions are brown); and c) hydrolysis of solid residues with 6 *M* HCl at 105°C for 10 – 16 hr to give HU and HA hydrolysates. Campbell et al. [11] mention that omitting pre-treatment with 0.1 *M* HCl reduces the yield of HA fractions, consistent with slow dissociation of humate-bound metals (Fe(III), Cu(II), Ni(II), Eu(III)) over hours and days with rates that increase with decreasing pH [24-29]. Such metal humates have low solubility that decreases the HA yield. The Campbell et al. protocol (Scheme 1) [11] is harsh by current standards and specifies no time-span of crucial steps a) and b). The important point is that mean residence times (mrt) of the isolated solid fractions from ^{14}C dating range from 465 yr to 1235 yr except for the mrt of the HA hydrolysate (25 ± 50 yr) in Table 1 [11]. The mrt uncertainty of ± 50-60 yr is due to the long half-life of ^{14}C (5730 yr); the last entry in Table 1 demonstrates that recognizable biomolecules in soil are much more accessible as energy sources to microbes than are HS [30-32].

Table 1 Mean residence times (mrt) of carbon in the Melfort soil. Adapted from ref. [11]

Fraction	mrt (yr)
Humin II	1140 ± 50
Nonhydrolyzable Humin II	1230 ± 60
Humin II-hydrolysate	465 ± 50
Humic Acids II ("total")	1235 ± 60
Nonhydrolyzable Humic Acids II	1400 ± 60
Humic Acids II-hydrolysate	25 ± 50

Clapp and Hayes [33] and Senesi and Loffredo [18] reviewed the characteristics of HS fractions extracted with different methods that include, for example, using ion-exchange resins [27,34] and organic reagents (e.g. dimethylsulfoxide). As noted above, simple acid-base chemistry gives the highest yield of HA from a given sample and avoids organic extractants (compounds, columns or resins) that might react with or sorb the HA analyte. The long lifetimes of solid fractions isolated with aqueous acid-base chemistry as in Scheme 1 and the highest yields from this approach commend the chemistry in Scheme 1 or an amended version as the method of choice in measuring the amounts of sequestered carbon in environmental samples.

This paper addresses the following questions: 1) What proportion of the total organic carbon in an agricultural top soil is sequestered? That is, how much of the carbon inventory is long-lived? and 2) What is the HA measurement precision? We propose and describe a gravimetric protocol that generates the HA contents of commercial lignite sources of humic products and a variety of agricultural top soil samples and we report the precision of the obtained data. Recently, Lamar and Talbot [35] proposed a spectro-photometric method with absorbance measurements at 650 nm for the analysis of HA in alkaline solutions, where they are present as humate salts. The method depends on the use, as a standard, of HA isolated from the same source as the HA analyte. Gravimetric measurements, as in this study, require use of no HA standard, which is an analytical advantage.

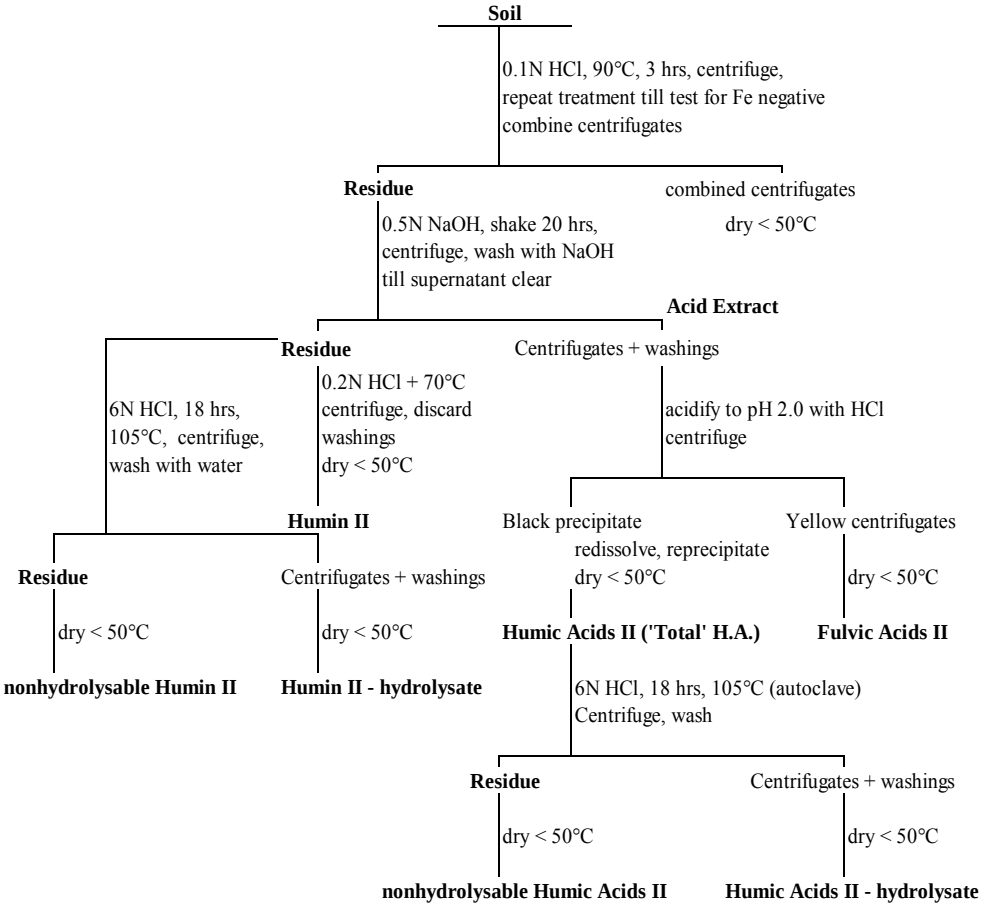
Gravimetric data will be useful in rapid soil assessment, and in precision agriculture that applies minimal amounts of mineral fertilizers and lessens pollutant run-off. HA content data also are useful for season-to-season soil assessment from loss on ignition (LOI) data when the %HA is known and in carbon cycling research, where the amounts in labile and sequestered C pools need to be specified [36]. Lastly, the HA content of a commercial humic product must be known reliably for its certification, regulation and efficacious use [37].

2. MATERIALS AND METHODS

2.1. Description of the Sample Origins

Dots in Figure 1 identify Idaho counties that have contributed a variety of complex clay-silt-sand-loam agricultural top soils to the National Soil Project (Table 2). The north Payette and south Payette County samples are mixtures of 16 and 18 separate soils, respectively (Table 3), in approximately equal-mass amounts, representing a good test of a gravimetric analytical method. The area covered is 19,698 sq mi, about 24 % of the total land area of Idaho.

Four west Texas lignite samples labeled A1, A2, A3 and A4 used as sources of humic products were provided by Arctech, Inc. (Chantilly, VA). Twenty-four agricultural top soil samples (0-30 cm, location selected by the sample donor) were collected, evaluated and catalogued by the Elmore County Extension Educator for 13 counties in southern Idaho.



Scheme 1 The fractionation scheme used by Campbell et al. [11].

Figure 1 Idaho State County map. Dots indicate the number of samples from a given County.

Table 2 Locations, characteristics and HA contents of southern Idaho County soil samples.

	County	Latitude	Longitude	Soil Type	Texture	%HA	Av. (rd) [cv][b]
1	Ada	42.9563	-115.9444	125 Elmore	Loamy Fine Sand to Loam	1.5, 0.73	1.1 (0.4) [0.4]
2	Bingham	43.2506	-112.4167	Bannock Bock	Loam	2.6	2.6
3	Blaine	43.3293	-114.3199		Sandy Loam to Loamy Fine Sand	1.7, 1.4, 1.5	1.5 (0.1) [0.07]
4	Blaine	42.7326	-113.3767			0.78, 1.1, 0.84, 1.1	0.96 (0.14) [0.15]
5	Camas	43.2091	-114.5611	17 Camas	Loam	10.1, 9.4	9.8 (0.3) [0.03]
6	Camas	43.2016	-114.6654	53 Camas	Loam	2.3, 2.5, 2.4, 2.5	2.4 (0.1) [0.04]
7	Cassia	42.3576	-113.8036	20 Drax 40 heavily Taulville 68 Weeks	Silt Loam Clay Loam Loam	0.95, 0.63	0.79 (0.16) [0.2]
8	Cassia	42.5751	-113.9312	36 Sluka 37 Sluka	Silt Loam Silt Loam	2.9, 3.3	3.1 (0.2) [0.06]
9	Elmore	42.5661	-115.2772	Timmerman	Sandy Loam	2.2, 1.4	1.8 (0.4) [0.2]
10	Gooding	42.7829	-114.7908	194 Gooding	Very Fine Sandy Loam	0.79, 0.65	0.72 (0.07) [0.1]
11	Gooding	42.6884	-114.6355	58 Gooding	Loamy Fine Sand	1.1, 1.0, 0.88, 1.3	1.1 (0.1) [0.1]
12	Gooding	42.9182	-114.7326	149 Gooding	Very Fine Sandy Loam	0.39, 0.43, 0.45	0.42 (0.02) [0.05]
13	Jerome	42.8148	-114.4633	99 Twin Falls	Silt Loam	0.50, 0.55	0.53 (0.03) [0.06]
14	Jerome	42.6231	-114.4727	60 Twin Falls	Loamy Fine Sand	0.58, 0.67	0.63 (0.05) [0.08]
15	Lincoln	43.1201	-114.3584	17 Gooding	Silt Loam	2.2, 2.0	2.1 (0.1) [0.05]
16	Lincoln	42.8276	-113.7778			2.5, 2.4	2.45 (0.05) [0.02]
17	Minidoka	42.5919	-113.9104	18 Minveno	Silt Loam	1.8, 1.5	1.7 (0.2) [0.12]
18	Minidoka	42.7281	-113.5289	Portneuf	Silt Loam	2.3, 2.4	2.35 (0.05) [0.02]
19	Owyhee	42.9767	-116.1194	79 Elmore	Loamy Sand	0.31, 0.31	0.31
20	Twin Falls	42.8808	-112.4254			2.2	2.2
21	Twin Falls	42.4203	-114.5721	120 Twin Falls	Silt Loam	2.8, 2.8, 3.3	3.0 (0.2) [0.07]
22	Twin Falls	42.6068	-114.4958	67 Twin Falls	Silt Loam	2.0, 2.4, 2.3	2.2 (0.2) [0.09]
23	North Payette[a]	44.1563 to 43.9083	-116.6448 to -116.9634		Terrace Escarpments (texture varies widely)	1.2	1.2
24	South Payette[a]	43.9752 to 43.8695	-116.7705 to -116.9631		Terrace Escarpments (texture varies widely)	1.8, 2.5	2.2 (0.3) [0.14]

[a] Latitudes and longitudes are ranges; [b] av is average value, (rd) is the relative deviation and [cv] is the coefficient of variance.

Table 3 Compositions of the north Payette and south Payette County soil samples.

County	Latitude	Longitude	Soil Type	Texture
23 north Payette	44.0291	-116.8451	Mo Moulton	Fine Sandy Loam
	43.9083	-116.7938	EcC Elijah-Chilcott	Silt Loam
	44.1131	-116.6448	NcB Newell	Clay Loam
	44.0747	-116.7759	HiC Haw	Loam
	44.0653	-116.8651	PeC Power-Elijah	Silt Loam
	44-0254	-116.9051	CIB Clems Fine	Sandy Loam
	43.9964	-116.8939	GeA Greenleaf	Silt Loam
	43.9918	-116.8523	GeA Greenleaf	Silt Loam
	44.0183	-116.8912	GeB Greenleaf	Silt Loam
	44.0648	-116.9634	Lf Letha	Fine Sandy Loam
	44.1124	-116.8988	CaB Cashmere	Sandy Loam
	44.1504	-116.8781	HaB Harpt	Loam
	44.1563	-116.8911	15 Baldock	Silt Loam
	44.0648	-116.9231	Mo Moulton	Fine Sandy Loam
	44.0409	-116.9181	Ba Baldock	Silt Loam
	43.9999	-116.9309	CIB Clems	Fine Sandy Loam
24 south Payette	43.8695	-116.7705	JeA Jerness	Loam
	43.8811	-116.9631	NyE Nyssaton	Silt Loam
	43.8833	-116.8939	LbE Lankbush-Purdam	Complex Sandy Loam
	43.9093	-116.9239	OwE2 Owyhee	Silt Loam
	43.9166	-116.8128	EcC Elizah-Chilcott	Silt Loam
	43.9186	-116.8941	LbE Lankbush-Purdam	Complex Sandy Loam
	43.9244	-116.7726	EeB Elijah-Sebree	Silt Loam
	43.9382	-116.9483	CIB Clems	Fine Sandy Loam
	43.9384	-116.8336	LbE Lankbush-Purdam	Complex Sandy Loam
	43.9460	-116.8748	PeC Power-Elijah	Silt Loam
	43.9491	-116.8937	GeC2 Greenleaf	Silt Loam
	43.9526	-116.7732	GeB Greenleaf	Silt Loam
	43.9601	-116.8661	NyB Nyssaton	Silt Loam
	43.9675	-116.9544	Bd Baldock	Silt Loam
	43.9721	-116.8939	GeA Greenleaf	Silt Loam
	43.9727	-116.8141	NyA Nyssaton	Silt Loam
	43.9751	-116.8527	GeA Greenleaf	Silt Loam
	43.9752	-116.9226	Te Terrace Escarpments	

The lignite and soil samples were dried to constant mass at 105°C, ground with an agate mortar and pestle, and sieved to ≤2 mm dimensions before extraction. All other substances used were analytical reagent grade and doubly-deionized water was used throughout. A Sorvall RC-2B refrigerated centrifuge fitted with an SGA rotor was used for separations at 11,000 rpm and 4°C. Separations at 2,000 rpm were conducted with a Daemon/IEC centrifuge at room temperature. Fourier transform infra-red (FTIR) spectra of HA products (1 mg sample in 100 mg KBr) were obtained with a Bruker Vertex 70 spectrometer equipped with a Pike Technologies diffuse reflectance stage and a nitrogen-cooled MCT detector. The pHs of solutions were measured with a Hanna Model 8417 meter calibrated with NIST certified buffers. Loss on ignition data (LOI = total OM) [38] and HA ash contents were obtained by combustion of precisely-weighed, dried samples in a Hythermco muffle furnace at 650°C for 24 hr [35] with good precision under these conditions. The ashes, which ranged from colorless through brown to red, were archived.

2.2. Gravimetric Protocol

The analytical method applied to lignite and agri-cultural top soil samples begins with a four-step, 96-hr sequential treatment with 0.1 *M* HCl with the following advantages: 1) it sterilizes the sample; 2) it floats away the labile ('light') organic matter common in top soil samples (the densities of HA gels exceed that of 0.1 *M* HCl); and 3) it accelerates metal removal by cation exchange [39,40]. As previously reported, binding of Ca(II), Fe(III), Cu(II), Mn(II) and Pb(II) by HA lowers their solubility [41] and so reduces HA yields. Also noted above is that bound metal ion dissociation from HA is slow with half-lives of hours or days, hence the need to 1) allow sufficient time for removal of all but the most tightly-held trace metals and 2) replace the HCl-treatment solution to shift equilibria towards metal dissociation.

The lignites and Idaho soils were analyzed with the protocol optimized for analysis of agricultural top soils in the National Soil Project initiated in 2008 at Northeastern University in the following steps: (1 - 4) A precisely-known mass of a dried soil or lignite in the range 3.90-4.10 g was shaken in a horizontally-configured 250 mL centrifuge bottle (Nalgene, polycarbonate co-polymer, catalog no. 3120-0250) with 100 mL of 0.1 *M* HCl in a Labline Orbit Environ-Shaker at 100 rpm and room temperature for 24 hr. The mixture was then centrifuged at 11,000 rpm at 4°C for 30 min and the supernatant was discarded. The sample was treated in the same manner three more times for 24 hr, each time with a fresh charge of 0.1 *M* HCl; (5 and 6) The resulting solid was washed for 24 hr with 100 mL water followed by centrifugation at 11,000 rpm and 4°C for 30 min, discarding the supernatant. This step was repeated with fresh water addition; (7 and 8) The resulting solid was then treated for 24 hr with 100 mL of 0.1 *M* aqueous NaOH by shaking in the same horizontally-configured, closed 250 mL centrifuge bottle at 100 rpm at room temperature. Then the mixture was separated by centrifugation at 11,000 rpm and 4°C for 30 min. The supernatant was transferred to a second 250 mL centrifuge bottle, which was centrifuged at 11,000 rpm and 4°C for 30 min. This 'two bottle' sequence avoids transfer of solids from very dark-colored solutions that would overestimate the HA content of the sample in subsequent steps and it sometimes results in the isolation of brown translucent solid humin. The supernatant was transferred to a 250 mL beaker and its pH was immediately adjusted to 1.6 with conc. HCl. The solids in the first and second 250 mL bottles were combined and treated a second time with 100 mL of 0.1 *M* NaOH for 24 hr in the same manner. The supernatants from the first and second NaOH extractions were combined and the pH was reduced to 1.6 as before. The solid residue from the protocol was discarded; (9 and 10) HA aggregation in the 250 mL undisturbed beaker for 24 hr at room temperature gave a dark brown HA gel and a yellow supernatant taken to be a solution of FA [42], which was decanted and archived in the dark. The HA gel was washed twice with water by centrifugation at 2000 rpm for 20 min, dried at 105°C to constant mass and weighed on a microbalance. Analyses were run in parallel to increase sample throughput and repeated to determine analytical precision. All HA contents are expressed as percent by mass on a dry soil basis.

3. RESULTS AND DISCUSSION

3.1. Sample Recovery

Three thoroughly-purified solid HA samples were used as the input to see if they could be recovered intact at the end of the protocol. These HA labeled NHA, GHA and NYHA were isolated from a New Hampshire bog soil, a German peat and a New York organic farm soil, respectively, with an elaborate protocol used in previous metal binding [41] and nucleic acid constituent adsorption [43] studies. These freeze-dried solid HA had been stored in the dark in

tightly-closed containers at room temperature for 13 years. We expected to see no yellow color of FA in the supernatant [42] at the point where the alkaline extract solution is acidified to pH 1.6 with HCl to precipitate the HA gel. To our surprise, the yellow color was observed, indicating that FA had been produced from dry HA in the dark over many years. Estimates of this FA [44] indicated it to be less than 3% of the mass of the starting HA. In duplicated experiments we found that variable proportions of the initial HA were insoluble in 0.1 *M* NaOH. These materials appear to be highly cross-linked products of long-term storage of dry solid HA in the dark. Neglecting the < 3 % fraction that appeared as FA and combining the masses of the solid HA and the cross-linked solid by-products gave an average recovery of 98 ± 4 % of the HA masses introduced in the protocol from six experiments with NHA, GHA and NYHA. The analytical method thus appears to result in only minor gravimetric loss of HA analytes.

3.2. HA Contents of Commercial Lignites

The analytical method was applied to west Texas lignite samples A1-A4. We found that repeated measurements give good precision over a wide range of HA contents for lignite samples A1 (41 ± 2 %HA), A2 (13 ± 3 %), A3 (2.1 ± 0.1 %) and A4 (26 ± 2 %). These data are encouraging because all but the most dilute lignite-derived alkali humate solutions are so darkly colored that decanting a centrifuged lignite-supernatant mixture in steps 7 and 8 of the protocol runs the risk of transferring some of the solid phase to the pH reduction step and leads to overestimated HA contents. The 'two-bottle' approach (see Materials and Methods) lowers this risk and leads to good analytical precision. Data with good precision for difficult lignite samples led us to investigate gravimetric analysis of agricultural top soil samples.

3.3. Analysis of Top Soils from Agricultural Fields in Idaho

With Washington and Oregon States, Idaho is in Region 5 of the USDA Census of Agriculture. Its State Soil is the Threebear series, which consists of moderately well-drained soils formed in silty sediments with a thick mantle of volcanic ash. Alfisols, Aridisols, Entisols and Mollisols can be found in the Idaho landscape.

Table 2 lists the locations, soil types and textures of the Idaho soils. Most of the samples were analyzed twice, with some samples analyzed three or four times. Average measured HA contents are given to two significant figures in Table 2 to allow for soil sample heterogeneity (*vide infra*). Figure 2 illustrates the analytical precision for several of the Idaho soils.

The soil samples investigated contain from 0.31 – 9.8 %HA, with a grand average of 1.9 ± 1.1 % av. deviation (55 samples). Neglecting the Camas sample with an average 9.8 %HA, the average for 53 samples drops to 1.6 ± 0.8 %. Twenty-eight samples are below this average and 25 have above-average HA contents. The %HA contents at different locations within a county are not widely different, with the exception of the two samples from Cassia (0.79 %, 3.1 %) and Camas (2.5 %, 9.8 %), the last being by far the highest value recorded in this study. HU was not detected in any of the samples.

The ash contents of five HA samples isolated from Bingham (sample 2 in Table 2), Camas (5), Cassia (7, 8) and Elmore (9) counties were 1.4, 0.97, 1.2, 1.4 and 1.3 %, respectively, with an average 1.2 ± 0.1 %. This result compares favorably with the ash contents of IHSS Standard HA (range 0.88-3.1 %) and Reference HA (0.31-3.4 %) [45].

The degree of heterogeneity of a lignite or soil is reflected in its analytical variability: uniform analyte distributions give good precision. On the basis of the highest coefficients of variance in Table 2, the most heterogeneous soils are samples 1, 4, 7, 9, 10, 17 and 24. No such statement can be made for samples 2, 19, 20 and 23 with only one datum for each. Relative to soil samples, the good precision of the HA contents of Sphagnum-peats [46] ranging with depth from 7.6 ± 0.5 to 22.8 ± 1.1 is consistent with their common plant origin. The variability of the HA content of Sphagnum peat, ranging from 5.2 to 28.3 % of the total bulk peat, is related to the botanical composition of peat and climatic conditions occurring during the last millennia.

The HA content of a given soil sample never exceeds its loss on ignition and often is far less (Figure 3), indicating that LOI data rarely reflect the sequestered carbon attributed to the HA content of a soil sample. The HA contents in Table 2 will be compared in future publications with those of agricultural top soils from across the United States as measured in the National Soil Project.

3.4. Infra-red Characterization of HA Products

Examples of FTIR spectra of HA isolated as described from the lignite and top soil samples are shown in Figure 4.

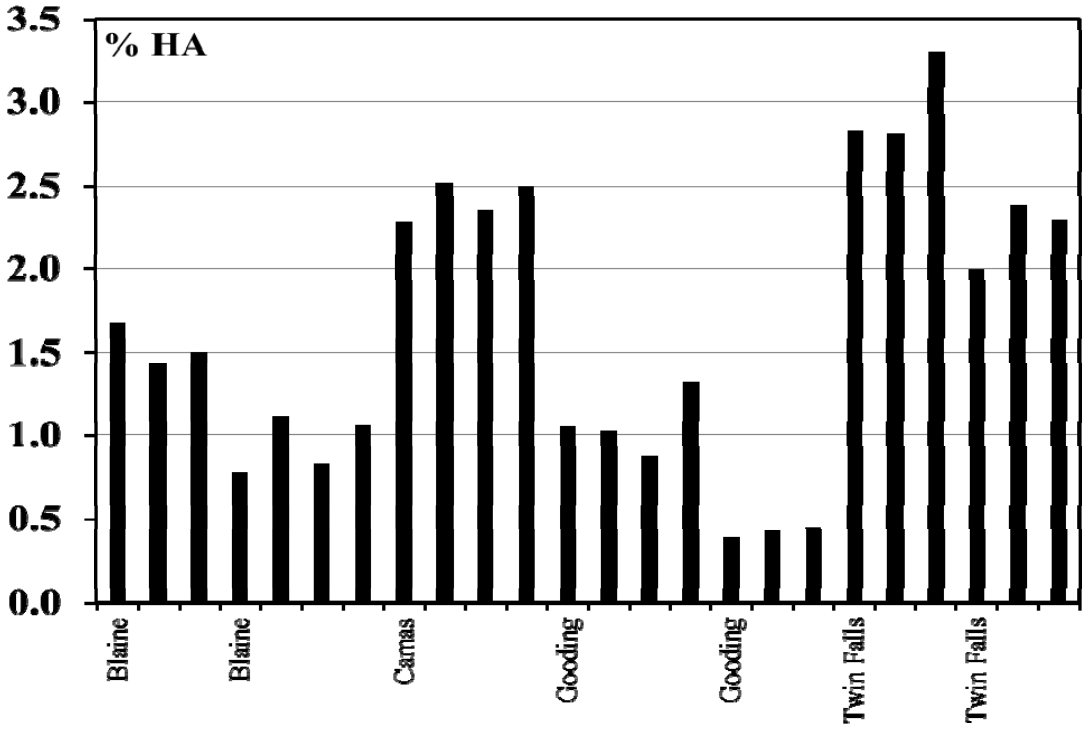


Figure 2 Results of repeated analyses of seven soil samples from four Idaho Counties.

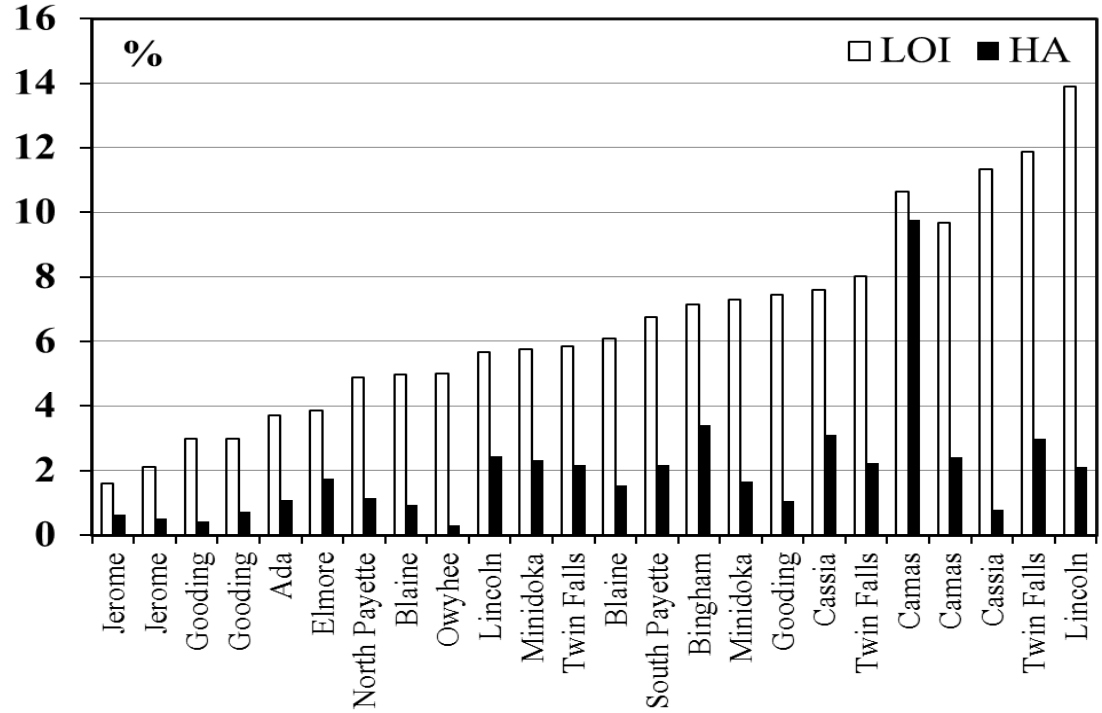


Figure 3 Loss on ignition (LOI, □) and average %HA data (■ , Table 2) in order of increasing LOI for Idaho County soil samples. There is no correlation between the two measurements except for an atypical organic-rich sample from Camas County.

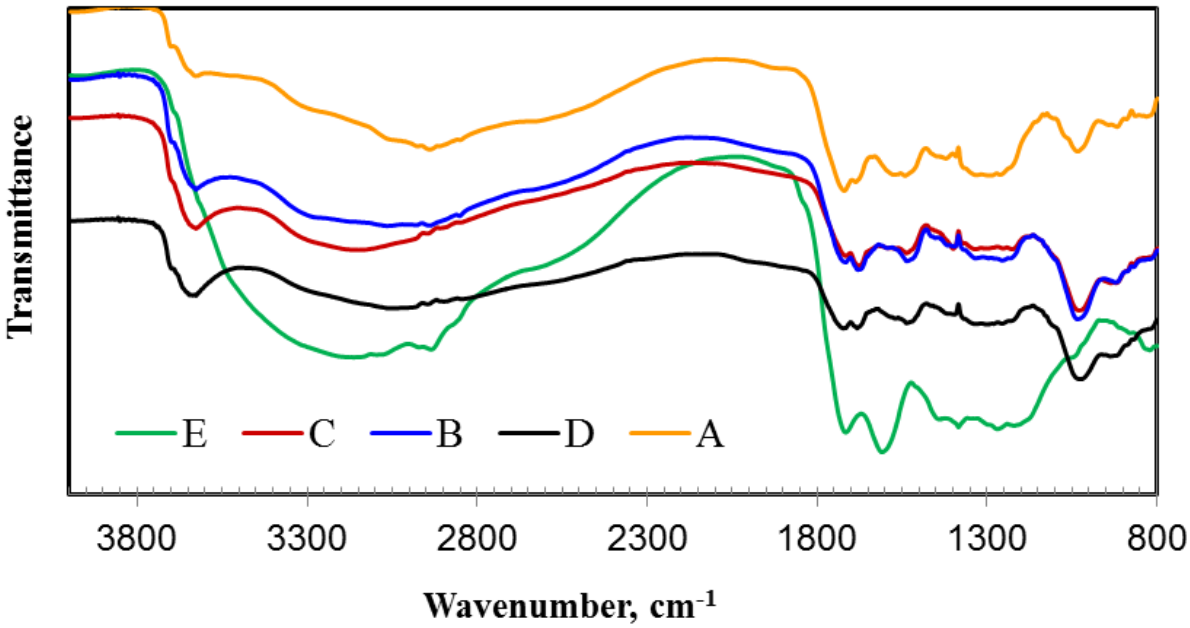


Figure 4 FTIR spectra A-D of HA isolated from samples 3, 11, 15 and 4, respectively in Table 2, and E of HA isolated from lignite sample A2.

The spectra have several common features. Comparison of the data in Figure 4 with the assigned spectrum of a typical HA [47] indicates common features (cm^{-1}) as follows: 3660 (O-H stretch, (contributions from aliphatic OH and water)), 2980 (asymmetrical C-H stretch), 2600-2230 (O-H stretch of COOH), 1720 (C-O stretch of COOH), 1610 (aromatic C=C stretch and/or COO^- asymmetric stretch), 1450 (CH_2 in-plane bending or scissoring), 1350 (-COO^- symmetric stretch and carboxylic O-H bend), and 1070 (aliphatic C-C stretch). This last feature is absent in the HA from lignite spectrum.

3.5. Potential Uses and Benefits of the Results

A concerted effort is underway to develop spectral methods of measuring soil OM remotely and in the field with the advantage of more data in less time [48]. Visible and near infra-red radiation in the range 350 or 400 to 2500 nm is scanned over the soil surface and the reflectance spectrum or *albedo* is recorded. First-derivatives help to pinpoint spectral features [49]. Dark-colored HA in soil are optically absorptive, especially in the visible region [50] and can affect the spectral contribution of almost every soil component (clay, water, etc.) [51]. Less humified organic matter such as straw or corn stover present in the sample is more reflective [52,53]. Knowledge of the HA content of a soil can facilitate interpretation of its diffuse reflectance spectrum. Also as noted, modeling of soil dynamics depends on knowing the contents of each C-pool [36], which will be facilitated by HA data such as those reported here. Lastly, the HA content of a commercial product needs to be known reliably for its certification, regulation and efficacious use [37].

4. CONCLUSIONS

A gravimetric method of analysis with easily available inorganic reagents and common laboratory equipment gives useful measurements of the HA contents of a variety of lignites and agricultural top soil samples. The method is based on the 'acid-precipitation' approach with thorough HCl-pretreatment of the lignite or soil sample to accelerate metal dissociation. Although lengthy from the need for metal removal and increased HA extractability, analyses can be run in parallel to increase sample throughput. The results are a measure of the sequestered carbon in a soil. Knowledge of soil HA assists precision agriculture that applies minimal mineral fertilizers for efficacy and lessens pollutant run-off. Knowledge of sequestered carbon is useful in season-to-season soil

assessment from LOI data when the %HA is known. HA contents can also facilitate rapid soil assessment and modeling of soil carbon dynamics. Lastly, we hope this work will assist the new Humic Products Trade Association since the content of a commercial humic product must be known reliably for certification, regulation and efficacy.

We are measuring the HA contents of agricultural top soils from across the United States in the National Soil Project at Northeastern (www.hagroup.neu.edu). Donated agricultural top soil samples with background information are welcome in this research.

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