

Soil Contamination of Grass Biomass Hay: Measurements and Implications

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Abstract A large area of unutilized or underutilized marginal land in the northeastern USA, some of which currently produce a mature hay crop for use as mulch, is potentially suitable for bioenergy crop production. Mature-mixed grass hay bales ($n = 1980$) were sampled across New York in late summer and fall of 2011 and 2012 from 65 farms. Chemical analysis of 19 parameters, including gross calorific value, fiber, and elemental analyses, was conducted on the samples. In addition, 156 soil samples, representing 67 soil types, were analyzed for 12 to 14 parameters, using two different extraction procedures. Results indicate that hay composition is extremely variable among bales, and that much of the variation is due to soil contamination. Soil contamination reduced energy content of hay, a reduction best estimated from ash content of the hay. Standard plant analyses of contaminated hay samples determine total elemental content, but the same analyses only partially extract soil elements. A subset of samples showed that fiber analysis of soil-contaminated hay is problematic, with results impacted greatly by soil type and gravimetric filtration method. Aluminum, because of its low plant uptake potential, its high concentration in most soils, and its relatively moderate range in concentration across soil types compared to other soil elemental predictors, is the best indicator of soil contamination of biomass when the soil type is unknown. Evaluation of herbaceous plants for bioenergy parameters should include

ash and Al analysis to assess soil contamination, which could significantly bias other compositional analyses.

Keywords Grass biomass · Marginal land · Soil contamination · Ash · Aluminum

Introduction

Over two million hectares of marginal land in the northeast USA that are no longer used for agriculture are potentially available and may be suitable for production of bioenergy crops [1]. In addition, a large quantity of mature mixed grass hay produced on extensively managed grasslands in the northeast is used for mulch purposes, primarily as a mushroom substrate. The mushroom industry in the USA uses over 350,000 MT of hay annually, and most of this hay is produced in the northeast. Unfertilized or minimally fertilized grasslands are typically harvested once each season as large square bales. Such bales can contain a wide range of grass species, along with a small percentage of forbs, legumes, and occasionally woody species. Inconsistency in physical and chemical properties, due to multiple species, disparate growth, and harvesting conditions, negatively affects both biochemical and thermochemical conversion processes [2].

Although mixed grass biomass from marginal lands requires minimum inputs, it has two major drawbacks: variable composition and modest yields. Marginal lands in south Europe have an estimated 40 % yield reduction compared to typical agricultural land [3]; however, economic returns can still be favorable. Thousands of hectares of fallow or underutilized agricultural lands in Sweden were economically more competitive for bioenergy compared to N-fertilized reed canary grass (*Phalaris arundinacea* L.) [4]. Revenue from managed warm season grasses for biomass in Tennessee was

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less than the cost of harvesting and replacing biomass nutrients removed [5]. Intensified cropping of marginal lands can be risky from an environmental standpoint. For example, it was recommended to return sorghum leaves to the field when growing sorghum for biomass on marginal lands, to reduce nutrient removal and allow for sustainable production [6].

Mixed grasses could be used for anaerobic digestion or combustion [7], but the heterogeneous nature of this feedstock may limit its potential as a bioenergy crop. Densified grass can have a gross calorific value (GCV) similar to premium wood pellets [8] but some compositional factors, such as Cl, K, and N content, will have a significant impact on the combustion process and on emissions. Mixed grass biomass on the less than ideal terrain of marginal lands also has potential for significant soil contamination, similar to that found with agricultural residues. For example, ash content of corn stover ranged from 115 to 282 g kg⁻¹, depending on the harvest system [9].

Contamination

Marginal lands are often less than ideal croplands, with uneven or rough terrain, increasing the possibility of significant soil contamination of hay during the harvesting process. Ash content of grass biomass directly impacts all biomass conversion processes. Potassium, chlorine, and other elements contribute to undesirable reactions in combustion appliances [10], and these elements are found in soil. Ash is composed of endogenous minerals absorbed by the plant, and exogenous minerals are deposited externally on the plant surface from aerosols (detrital contamination) or from soil during harvesting (technogenic contamination) [11]. Aerosols deposited on plants can significantly change the concentrations of elements in plant tissue, compared to plant tissue without aerosol contamination [12], but soil contamination during harvest will have more impact, compared to aerosols. Bonner et al. [9], using a range of equipment for corn stover harvest, measured elevated ash content due to soil contamination from 100 to 400 % higher than typical hand-harvested stover, depending on the harvest equipment used. Soil particles are primarily inorganic in nature and can become a significant component of ash content of biomass.

In general, entrained soil on the surface of the biomass will increase ash content and decrease gross energy. Soil contamination impacts the cellulosic components of biomass feedstocks as well as the energy content. There also are direct negative effects of soil on wear of biomass processing equipment. The significance of contamination depends on the component to be determined, the degree of contamination, and the relative amounts of the component in soil versus an uncontaminated sample. A relatively small amount of soil contamination on plant samples can significantly impact trace element analyses [13, 14], but will not significantly affect the major plant components. Soil contamination of forage

samples can influence fiber concentrations, depending on the filtration system used [15].

There have been many attempts to estimate soil contamination of forage crops, to better assess crop quality. If sufficient data concerning the normal concentrations of a constituent found in clean plants and in soil are available, an estimation of the degree of contamination is possible [16]. Indirect estimation of contamination has been proposed, based on total silica or aluminum [16], acid-insoluble ash [17], titanium [18, 19], or by dry ashing [20]. Elements present in large quantities in soil, such as Al and Fe, can be useful for evaluating soil contamination of plant samples. While Ti concentrations are not as high in soils compared to Al and Fe, plant uptake of Ti is negligible, making Ti concentration in plant samples another potential indicator of soil contamination.

Standard soil analysis techniques involve partial digestions, theoretically designed to extract nutrients potentially available to plants. Plant analyses, on the other hand, are essentially total digestions of plant tissue to determine total concentrations of elements. Therefore, a standard soil analysis will likely not be a reasonable indicator of elemental content changes due to soil contamination of plant tissue.

Washing procedures used on fresh plant samples can remove some of the surface soil [16]. However, no economic treatment process exists to remove soil contamination from hay biomass at or after harvest, so pre-treatment to remove soil contamination of plant samples in a laboratory prior to analyses will result in incorrect estimates of quality, nutrient content, and caloric value. There is no practical method of separating endogenous from exogenous sources of a given element in a grass hay sample.

Recognizing Contamination

Soil contamination affects plant composition both by directly increasing concentrations of certain parameters, and through dilution effects on all other parameters. Many herbaceous biomass studies involve analysis of sugars and/or fiber components, without any analysis of parameters that would indicate the presence or absence of soil contamination. Consequences of not taking soil contamination into consideration when making decisions about feedstock use and suitability can be great. Tao et al. [21] evaluated biomass properties in a wide range of plant species and included one comment on soil: “It may be possible that the influence of Si, Fe, Na, and Al (negative scores in PC1) could be based on sample contamination with soil elements, which was ignored in certain publications.” Shen et al. [22] suggested that high levels of Fe in manure might be explained by soil particles in the manure.

While the words “soil” or “contamination” were not used in a recent biomass characterization study [23], their five grass biomass sources contained from 585 to 11,613 mg kg⁻¹ Al. Monti et al. [24] reported Al concentrations in the leaves of six

biomass species ranged from 328 to 1781 mg kg⁻¹, but the possibility of contamination was not mentioned. Grass plants grown hydroponically in solutions containing Al showed visible signs of Al toxicity when plant Al concentration exceeded 50 mg kg⁻¹ [25], so the elevated Al content in all of the grass biomass sources in the studies mentioned above [23, 24] most likely indicates significant soil contamination.

Biomass composition of mixed grass stands on marginal lands is influenced by both variability in species composition and by soil contamination. Soil contamination of harvested grass biomass is inevitable, but often ignored in biomass evaluations. Soil contamination of plant samples makes the behavior of a fuel during conversion less predictable, and the importance of soil contamination will depend on the level of contamination and on the specific biomass energy conversion process. Our objective was to quantify the range in composition of mature mixed grass hay on marginal lands in New York State, evaluate the impact of soil contamination on composition and analysis of grass biomass, and identify indicators that can be used to identify when a biomass feedstock is contaminated by soil.

Materials and Methods

Bale Sample Collection

A total of 1980 bales were sampled from 198 lots of hay over 2 years located on 65 different farms in 13 New York counties in late summer and fall of 2011 and 2012. Lots of hay ranged in size from a minimum of 10 bales to over 300 bales, harvested under a wide range of soil conditions using the range of equipment typically found on farms. Some lots of hay were from a single field, while other lots came from multiple fields. Most were large square bales, which can vary in weight from about 350 to 900 kg each, but some round bales and a few small square bales were included in the 1980 bales as well. Ten random bales were sampled per lot of hay, using a gas-powered drill and a Colorado hay probe, model 2004 (UDY Corp., Fort Collins, CO). The probe was 1.9 cm in diameter and 45.7 cm long, with a collection chamber for multiple cores. At least four cores were taken from each bale. Bales within each lot of hay were composited, and a total of 198 composite samples were analyzed. In addition, 200 individual bale samples from 10 random lots for each year were analyzed.

Bale Chemical Analyses

Bale core samples were oven dried (60 °C) and ground to pass a 1-mm screen, and the 10 individual samples in each lot were combined by weight to form a composite sample for each lot. Gross calorific value was determined using a Parr 6200 bomb

calorimeter (Parr instrument Co., Moline, IL). Samples were analyzed by Dairyland Laboratories, Inc. (Arcadia, WI), for elemental composition using microwave nitric acid digestion and inductively coupled plasma spectroscopy (AOAC Method 985.01). Nitrogen content was determined using NIRS techniques and expressed as crude protein (CP) (N * 6.25). Neutral detergent fiber, acid detergent fiber (ADF), and acid detergent lignin (ADL) were determined sequentially as described by Cherney et al. [26] using ANKOM techniques (Macedon, NY). Sodium sulfite was eliminated from the aNDF procedure. Total ash content was determined by heating samples to 510 °C for 4 hours. The regression analysis for Fig. 1 was conducted using PROC REG [27].

Soil Extractions

Most soil contamination of biomass occurs at harvest, influenced by type of harvesting equipment, and field and soil conditions. Samples collected directly from small plots of grass biomass [28] will not reflect the reality of soil contamination. To evaluate the range in soil composition, soil samples (67 soil types, $n = 156$) representative of five of the six basic soil management groups (SMG) [29] were selected from agricultural fields across New York and analyzed using both soil and plant analysis techniques. These samples ranged from fine-textured soils in SMG-1 to very coarse textured soils in SMG-5. Soils from the organic or muck soil category (SMG-6) were not included in the analysis; grass hay typically would not be produced on these soils. Soil samples were extracted using the Morgan sodium acetate extraction, the recommended soil test for agronomic guidelines in New York [30]. In addition, all soil samples were extracted using the same microwave nitric acid digestion technique as used to determine total elemental composition of plant samples (Dairyland Laboratories, Inc., Arcadia, WI).

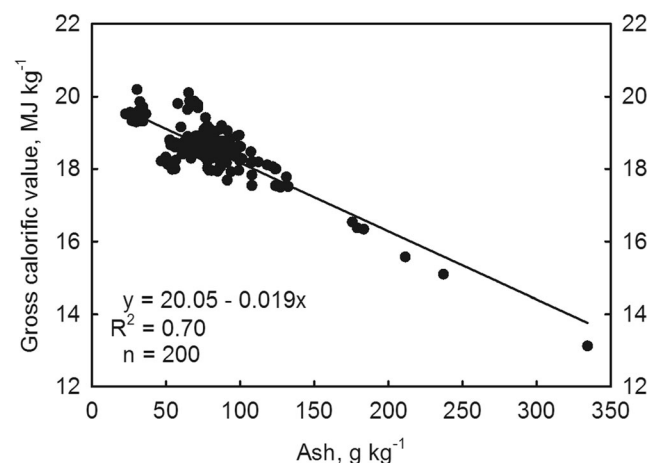


Fig. 1 Relationship between ash content and energy content for individual hay bales

Three soil samples representing the range of soil types were selected to evaluate the effect of different ANKOM (Macedon, NY) fiber bags on retention of soil during neutral and acid detergent extraction. Soils were a Claverack sand (sandy over clayey, mixed, superactive, nonacid, mesic Aquic Udorthents), a Mino loam (coarse-loamy, mixed, active, nonacid, frigid Aeric Endoaquepts), and a Kingsbury silty clay (very fine, mixed, active, mesic Aeric Endoaqualfs). The ANKOM F57 (25- μm pore size) and F58 (8- μm pore size) bags were used for the fiber analyses. Soils were ground to pass a 1-mm screen. Soil (0.1 g per bag) simulated approximately 20 % soil contamination of a 0.5 g sample. Twenty samples of each soil (0.1 g) were weighed into each type of ANKOM bag. Each soil type was analyzed separately in an ANKOM²⁰⁰ fiber digester (capacity of 24 digestion bags), including four blanks. Neutral detergent fiber (aNDF) and ADF were not run sequentially. One blank bag was placed on the bottom tray, one on the top tray, and two in the middle trays, within each ANKOM digestion rack.

Results and Discussion

Composition of Mulch Hay Bales—Individual Bales Within a Hay Lot

Soil contamination of grass hay during harvest was highly variable, in part due to variable soil moisture and terrain throughout a field. An extreme example of variation in one lot of bales is shown in Table 1. Crude protein, fiber and lignin concentrations had a relatively small range, while total ash and most elemental concentrations had a very large range over 10 bales.

Total ash content had a fivefold range, but Al, Fe, and Ti all had over a 100-fold range in concentration over 10 bales. Because there is very little plant uptake of Ti or Al, it is clear that all 10 bales had some level of soil contamination. The highest level of soil contamination in this bale set reduced GCV by approximately 30 %. Shen et al. [22] recently evaluated energy content of manures and concluded that some types of manure had higher heating values than others, but did not conclude that these differences may have been primarily due to differences in soil contamination. The correlation between high heating value and ash content was -0.91 for that study [22].

Composition of Mulch Hay Bales—Individual Bales Across Hay Lots

Variation among individual bales across different lots of hay was large (Table 2). The range in CP, fiber, and lignin concentrations across hay lots was much greater than within one lot (Table 1), reflecting a range in soil fertility, grass

Table 1 Variation in composition of individual bales for one lot of hay, $n = 10$

Variable		Mean	Std. dev.	Minimum	Maximum
Crude protein	g kg ⁻¹	96.2	6.65	90.6	108
aNDF	g kg ⁻¹	651	22.8	624	698
ADF	g kg ⁻¹	461	28.7	434	534
ADL	g kg ⁻¹	80.0	5.08	72.7	89.2
Ash	g kg ⁻¹	108	80.3	64.6	334
Ca	g kg ⁻¹	5.18	1.03	3.90	6.70
P	g kg ⁻¹	1.47	0.485	0.80	2.20
Mg	g kg ⁻¹	2.24	0.650	1.40	3.90
K	g kg ⁻¹	12.7	2.43	7.30	15.6
Cl	g kg ⁻¹	2.01	1.36	0.80	5.30
S	g kg ⁻¹	1.64	0.433	1.00	2.30
Na	mg kg ⁻¹	202	149	113	568
Fe	mg kg ⁻¹	1733	4270	113	13,860
Al	mg kg ⁻¹	1865	4582	146	14,890
Ti	mg kg ⁻¹	72.7	174	3.69	566
Mn	mg kg ⁻¹	128	68.4	53.0	260
Zn	mg kg ⁻¹	39.4	18.8	25.0	90.0
Cu	mg kg ⁻¹	12.6	2.99	10.0	19.0
GCV	MJ kg ⁻¹	17.9	1.69	13.1	18.9

aNDF neutral detergent fiber, ADF acid detergent fiber, ADL acid detergent lignin, GCV gross calorific value

Table 2 Variation in composition of individual bales over 20 lots of hay in 2 years, $n = 200$

Variable		Mean	Std. dev.	Minimum	Maximum
Crude protein	g kg ⁻¹	97.6	25.2	33.3	160
aNDF	g kg ⁻¹	682	78.2	545	900
ADF	g kg ⁻¹	480	58.3	345	644
ADL	g kg ⁻¹	88.6	18.4	48.2	148
Ash	g kg ⁻¹	78.2	24.9	22.7	334
Ca	g kg ⁻¹	5.04	1.81	2.00	12.5
P	g kg ⁻¹	1.49	0.53	0.60	3.40
Mg	g kg ⁻¹	1.79	0.78	0.50	4.90
K	g kg ⁻¹	10.0	4.66	0.90	25.4
Cl	g kg ⁻¹	2.15	1.89	0.60	11.2
S	g kg ⁻¹	1.30	0.37	0.50	2.30
Na	mg kg ⁻¹	205	327	77	3265
Fe	mg kg ⁻¹	564	1197	59	13,860
Al	mg kg ⁻¹	580	1284	68	14,890
Ti	mg kg ⁻¹	17.9	47.4	0.62	566
Mn	mg kg ⁻¹	100	85.5	14.0	481
Zn	mg kg ⁻¹	35.6	15.0	15.0	103
Cu	mg kg ⁻¹	11.9	3.96	4.00	36.0
GCV	MJ kg ⁻¹	18.6	0.77	13.1	20.2

aNDF neutral detergent fiber, ADF acid detergent fiber, ADL acid detergent lignin, GCV gross calorific value

species, maturity, and growing conditions prior to harvest. Based on the lowest Al concentration in individual bales (68 mg kg⁻¹), all bales likely contained at least a small amount of soil contamination. Considering individuals bales with low Al content, we estimate that ash concentration in individual bales from diverse lots of hay without any soil contamination (endogenous ash) may range from 23 to 100 g kg⁻¹. While soil contamination is an uncontrollable issue in hay bales, soil contamination can certainly be minimized by clipping a sample from standing forage in the field. Landstrom et al. [31] reported ash concentration in October hand-sampled reed canary grass averaged 53 g kg⁻¹, while autumn hand-sampled reed canary grass averaged 107 g kg⁻¹ in another study [32]. Burval [33] hand-sampled one cultivar of reed canary grass at 14 sites in Sweden and ash concentration ranged from 22 g kg⁻¹ on a humus-rich sandy soil to 101 g kg⁻¹ on clay soil. Since it is not possible to separate endogenous from exogenous ash, it is impossible to accurately determine the exact amount of soil contamination in hay samples containing multiple grass species from diverse soils and growing environments.

For elements where soil contamination has the greatest impact, range in elemental concentrations among 200 bales was not greatly different from the range in concentration in one lot of 10 bales with significant soil contamination. For example, the range in Al among one lot of 10 bales (Table 1) was 14,744 mg kg⁻¹, compared to a range of 14,822 mg kg⁻¹ across 20 lots of hay over 2 years (Table 2). Notable exceptions were Na and Cl, due primarily to

composition of one of the 20 lots of hay that averaged 1179 mg kg⁻¹ Na and 3.93 g kg⁻¹ Cl, while the 20-lot averages were 205 mg kg⁻¹ Na and 2.15 g kg⁻¹ Cl. One bale in this hay lot contained 3265 mg kg⁻¹ Na and 11.2 g kg⁻¹ Cl (Table 2), the largest concentrations of all individual bales analyzed.

Data collected on individual bales were used to evaluate the relationships among parameters most influenced by soil contamination. A correlation matrix (Table 3) showed Al, Fe, and Ti were highly correlated with each other, as well as with ash content and GCV. The relationships of Al to ash and GCV are quadratic; however, both of these comparisons exhibited heteroscedasticity and regression analyses were not reported. Magnesium, Mn, Zn, and Cu were all significantly correlated with Al as well. Aluminum was not correlated with CP, fiber, lignin, P, K, or Cl (data not shown). Gross calorific value was most highly correlated with ash content, with a linear relationship (Fig. 1). This regression passed Levine’s test for constant variance ($P=0.873$). This relationship is very similar to a model that was developed for 62 different types of biomass by Jenkins [34]: $GCV (MJ kg^{-1}) = 20.07 - 0.023 * ash (g kg^{-1})$; $R^2 = 0.71$. As the equation in Fig. 1 is primarily influenced by the level of soil contamination, the similarity between this equation and Jenkins’ equation suggests that Jenkins’ relationship between GCV and ash is also primarily driven by soil contamination.

Table 3 Pearson correlation coefficients among parameters that were significantly correlated with Al for individual bales ($n=200$)

Parameter	Fe	Ti	Ash	Mg	Mn	Zn	Cu	GCV
Al	0.99 ***	0.97 ***	0.84 ***	0.19 **	0.33 ***	0.41 ***	0.43 ***	-0.75 ***
Fe		0.96 ***	0.83 ***	0.18 *	0.36 ***	0.44 ***	0.45 ***	-0.75 ***
Ti			0.80 ***	0.24 **	0.32 ***	0.46 ***	0.34 ***	-0.70 ***
Ash				0.11 NS	0.20 ***	0.35 ***	0.50 ***	-0.84 ***
Mg					0.25 **	0.36 ***	0.08 NS	-0.08 NS
Mn						0.53 ***	0.38 ***	-0.02 NS
Zn							0.42 ***	-0.13 NS
Cu								-0.27 ***

GCV gross calorific value
* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

Table 4 Variation in composition of bale composite samples over 2 years, $n=198$

Variable	Mean	Std. dev.	Minimum	Maximum	
Crude protein	g kg ⁻¹	95.7	20.7	36.7	159.3
aNDF	g kg ⁻¹	664	60.6	533	886
ADF	g kg ⁻¹	461	45.5	347	603
ADL	g kg ⁻¹	86.9	15.7	51.2	141
Ash	g kg ⁻¹	65.8	14.8	23.5	117
Ca	g kg ⁻¹	4.92	1.51	1.60	9.80
P	g kg ⁻¹	1.46	0.50	0.20	3.90
Mg	g kg ⁻¹	1.68	0.50	0.50	4.20
K	g kg ⁻¹	11.1	3.80	1.20	24.70
Cl	g kg ⁻¹	2.51	1.59	0.70	9.00
S	g kg ⁻¹	1.33	0.38	0.60	3.20
Na	mg kg ⁻¹	169	141	52.0	1175
Fe	mg kg ⁻¹	245	272	54.0	2487
Al	mg kg ⁻¹	272	317	48.0	3076
Ti	mg kg ⁻¹	6.40	11.0	0.40	114
Mn	mg kg ⁻¹	90.4	66.6	14.0	476
Zn	mg kg ⁻¹	31.9	11.7	2.00	116
Cu	mg kg ⁻¹	9.87	3.10	4.00	23.0
GCV	MJ kg ⁻¹	18.7	0.29	17.6	19.5

aNDF neutral detergent fiber, ADF acid detergent fiber, ADL acid detergent lignin, GCV gross calorific value

Table 5 Soil analysis following a Morgan extraction (M), versus a nitric acid (N) plant extraction, $n = 156$

Variable		Mean	Std. dev.	Minimum	Maximum	Range ^a x -fold
pH		6.06	0.83	3.73	7.68	2
OM	g kg ⁻¹	45.2	17.4	10.0	110	10
Morgan extractable nutrients						
P	mg kg ⁻¹	0.43	0.24	0.09	1.41	16
K	mg kg ⁻¹	10.7	13.6	0.48	126	263
Ca	mg kg ⁻¹	224	146	26.8	1131	42
Mg	mg kg ⁻¹	99.6	81.8	19.1	521	27
Mn	mg kg ⁻¹	42.2	66.5	3.85	334	87
Zn	mg kg ⁻¹	22.4	23.7	2.14	164	77
Fe	mg kg ⁻¹	1672	864	155	5095	33
Al	mg kg ⁻¹	12.5	30.0	0.57	186	326
NO ₃	mg kg ⁻¹	58.5	47.8	0.48	256	533
Nitric acid extractable nutrients						
P	g kg ⁻¹	0.70	0.45	0.10	4.40	44
K	g kg ⁻¹	1.09	1.69	0.10	14.8	148
Ca	g kg ⁻¹	3.49	3.29	0.80	36.4	46
Mg	g kg ⁻¹	2.84	1.44	0.50	9.00	18
S	g kg ⁻¹	0.41	0.93	0.10	11.6	116
B	mg kg ⁻¹	27.4	10.7	8.00	78	10
Mn	mg kg ⁻¹	578	315	80.0	2445	31
Zn	mg kg ⁻¹	65.4	22.9	23.0	138	6
Cu	mg kg ⁻¹	18.7	25.0	2.00	240	120
Fe	mg kg ⁻¹	17,511	6356	4043	56,410	14
Al	mg kg ⁻¹	12,777	4403	2937	30,190	10
Ti	mg kg ⁻¹	137	166	20.3	836	41
Mo	mg kg ⁻¹	0.24	1.15	0.01	9.55	955
Na	mg kg ⁻¹	254	167	1.00	1503	1503

OM organic matter content

^a Column value times minimum value equals maximum value

Composition of Mulch Hay Bales—Composite Samples of each Hay Lot

Variation in the composition of all 198 bale lots over 2 years was large (Table 4). Parameters less impacted by soil contamination have mean values and ranges for composite samples (Table 4) not greatly different from that of individual bales (Table 2). These parameters include CP, fiber, and lignin; however, aNDF, ADF, and lignin were determined gravimetrically using ANKOM F57 filter bags. These filter bags are known to lose small particles due to their 25- μ m pore size [35].

Soil Analysis

There was a twofold range in soil pH, a 10-fold range in organic matter (OM) content, and over a 500-fold range in available nitrate among the soils (Table 5). Soil pH and SMG were negatively correlated with OM, while extractable

Table 6 Pearson correlation coefficients among nitric acid-extracted parameters (N), Morgan-extracted parameters (M), soil management group (SMG), soil pH, and soil organic matter (OM) ($n = 156$)

Parameter	Al (N)	Fe (N)	Ti (N)	Al (M)	Fe (M)	pH	OM
SMG	-0.46 ***	-0.36 ***	-0.28 **	0.01 NS	-0.36 ***	0.10 NS	-0.27 **
Al (N)		0.86 ***	0.50 ***	-0.01 NS	0.40 ***	0.05 NS	0.51 ***
Fe (N)			0.22 **	-0.01 NS	0.37 ***	0.08 NS	0.46 ***
Ti (N)				-0.04 NS	0.29 **	0.08 NS	0.28 **
Al (M)					-0.39 ***	-0.66 ***	0.45 ***
Fe (M)						-0.69 ***	0.29 **
pH							-0.28 **

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

Table 7 Neutral detergent and acid detergent non-sequential extraction of three soils using ANKOM bags of differing porosity, on a dry matter basis

	F57 bag			F58 bag		
	Sand	Loam	Clay	Sand	Loam	Clay
aNDF, g kg ⁻¹ (n = 20)	847	388	676	925	818	780
aNDF, St. dev.	28.4	87.0	45.0	11.6	24.1	26.1
aNDF, blank change ^a , g kg ⁻¹	+5.2	+19.0	+9.2	-1.78	-0.45	-0.77
ADF, g kg ⁻¹ (n = 20)	836	315	690	913	782	791
ADF, St. dev.	24.2	68.6	38.6	10.5	21.7	26.3
ADF, blank change, g kg ⁻¹	+0.25	+2.93	+0.44	-2.60	-0.94	-1.63

aNDF neutral detergent fiber, ADF acid detergent fiber

^a Gain or loss of DM in blank bag following neutral or acid detergent extraction

Al, Fe, and Ti were positively correlated with OM (Table 6). Organic matter content was positively correlated with extracted Al, Fe, and Ti, regardless of the extraction method for Al and Fe. Soil pH was highly negatively correlated with Morgan-extractable Al and Fe, but soil pH was not correlated with nitric acid-extracted Al, Fe, or Ti (Table 6). Comparing Table 2 with Table 5, Zn has a similar range in concentration across soils and individual bales using the same plant extraction procedure. All soils contain sufficient Al, Fe, and Ti to greatly increase grass bale concentrations of these elements following contamination with soil. All other nitric acid-extracted elements in Table 2 have the potential to either increase or decrease grass concentrations of these elements following contamination, depending on soil type.

The Morgan solution is sodium acetate, a weak acid extraction, and elements not soluble in weak acid (e.g., Al) are not extracted from soil to any great extent. A nitric acid plant extraction of soil removes much higher concentrations of elements from soil, but still is only a partial extraction of soil. Nitric acid extracted, on average, over 160-fold more Al from soil than a Morgan extraction. As expected, here is no correlation between Morgan and nitric acid extractions for Al (Table 6). Nitric acid extracted less than one third of soil Al, however, compared to a total soil digestion using hydrofluoric (HF) acid [18]. The proportion of any given element in soil particles that is chemically active vs. unavailable during each

specific biomass conversion process is essentially unknown. Since all plant digestion methods except HF release only a portion of each element contained in soil, it is unclear how plant-extracted elements from soil relate to actual amounts of soil elements available during different biomass conversion processes.

Aluminum and titanium are elements that are taken up by plants only in very small quantities. Of these elements, nitric acid-extractable Al is the most appropriate indicator of soil contamination. Nitric acid extraction of soil released less than one half of a percent of total soil Ti [18]. In addition, the range in Ti concentration in the nitric acid extraction was wide (41-fold range) versus a 10-fold range in Al concentration (Table 5); the larger the range in concentration of an element across soil types, the larger the error in estimating soil contamination based on that element, when contamination is from an unknown soil type.

Fiber Analysis Techniques Applied to Soil

Neutral detergent and acid detergent non-sequential extractions were performed on three representative soils, using ANKOM F57 and F58 filter bags (Table 7). To our knowledge, this is the first time that soil was used as the sole substrate for ANKOM fiber extractions. A considerable amount of soil escaped from F57 bags for all three soil types, and some

Table 8 General soil contamination categories based on Al concentration in nitric acid-extracted grass hay or based on total ash concentration in hay, assuming the contaminating soil has average extractable Al content

Al range	Soil contamination based on Al	Ash range	Soil contamination based on ash
<50 ^a	Essentially none	<50 ^b	Insignificant to low
50–100	Insignificant	50–100	Insignificant to low to moderate
101–500	Low	101–120	Moderate to high
501–1000	Moderate	121–150	Very high
1001–5000	High	>150	Excessive
5001–10,000	Very high		
>10,000	Excessive		

^a mg kg⁻¹

^b g kg⁻¹

soil moved into blank bags. The majority of the loam soil escaped through the 25- μm pores of the F57 bags during neutral detergent extraction and passed into and increased the weight of the blank bags by 19 g kg⁻¹. Acid detergent extraction of soil also resulted in soil passing through the bag, but much less soil moved into the blank bags, compared to neutral detergent extraction (Table 7). Fiber content of grass-soil mixtures, after filtering residues through sintered glass or glass wool plus sintered glass, was significantly affected by filtration method [14]. High ash content due to soil contamination can dramatically and unpredictably alter various measures of fiber composition [36].

Estimating the Degree of Soil Contamination

Soil contamination of grass hay samples can be indirectly estimated using either Al or ash content of hay samples (Table 8), although both methods are somewhat problematic. Categories are based on our knowledge of the range in extractable Al in grass and soil, as well as the range in endogenous ash content of grass. Extractable Al in soils and endogenous ash content of grass hay are both relatively variable, while endogenous Al in hay and ash content of soil are relatively consistent. The endogenous ash content of hay is typically unknown, and there is a relatively wide range in concentration of endogenous ash, which is impacted by plant species, soil fertility, plant maturity, and the growing environment. Mature grass hay lots normally contain multiple species, often from multiple fields with different soil types and fertility. This means that ash is a crude indicator of contamination and is not very effective at relatively low ash concentrations (<100 g kg⁻¹). Since Al uptake by cool-season grasses is very limited, it is a better indicator of contamination than ash, although there is a considerable range in extractable Al across soil types (Table 5). Categories in Table 8 are based on average extractable Al content for the contaminating soil.

Conclusions

Soil contamination of harvested grass biomass is highly variable, influenced by the type of harvesting equipment, field terrain, and soil conditions. Gravimetric methods involving filtration for determining fiber components of hay samples with soil contamination will be greatly influenced by the porosity of filters used. Depending on the filter used and the soil type, soil contamination could result in an increase, decrease, or have no effect on fiber concentrations of hay samples. Expressing fiber values on an ash-free basis will not adequately correct soil contamination, due to the variable amount of soil that will pass through filters. Soil contamination will directly decrease energy content of hay, and this decrease can be estimated from ash content. In New York, any given hayfield

often will contain two or more different soil types, and mulch hay lots typically originate from multiple hayfields. This makes it nearly impossible to associate soil contamination in a given hay lot with a particular soil type. Therefore, the soil component most appropriate for evaluating soil contamination of hay is one that has little or no plant uptake, and is the most consistent in extracted concentration across all soil types. Aluminum comes closest to meeting these requirements for indirect estimation of soil contamination. Assuming an average extractable Al content for soil, broad categories of soil contamination have been proposed, based on Al concentration in grass hay. Analysis of herbaceous biomass routinely should include both ash and aluminum to evaluate the potential for soil contamination. Furthermore, given the potential for massive variability in level of soil contamination of hay samples across lots, methods need to be developed to obtain representative samples.

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