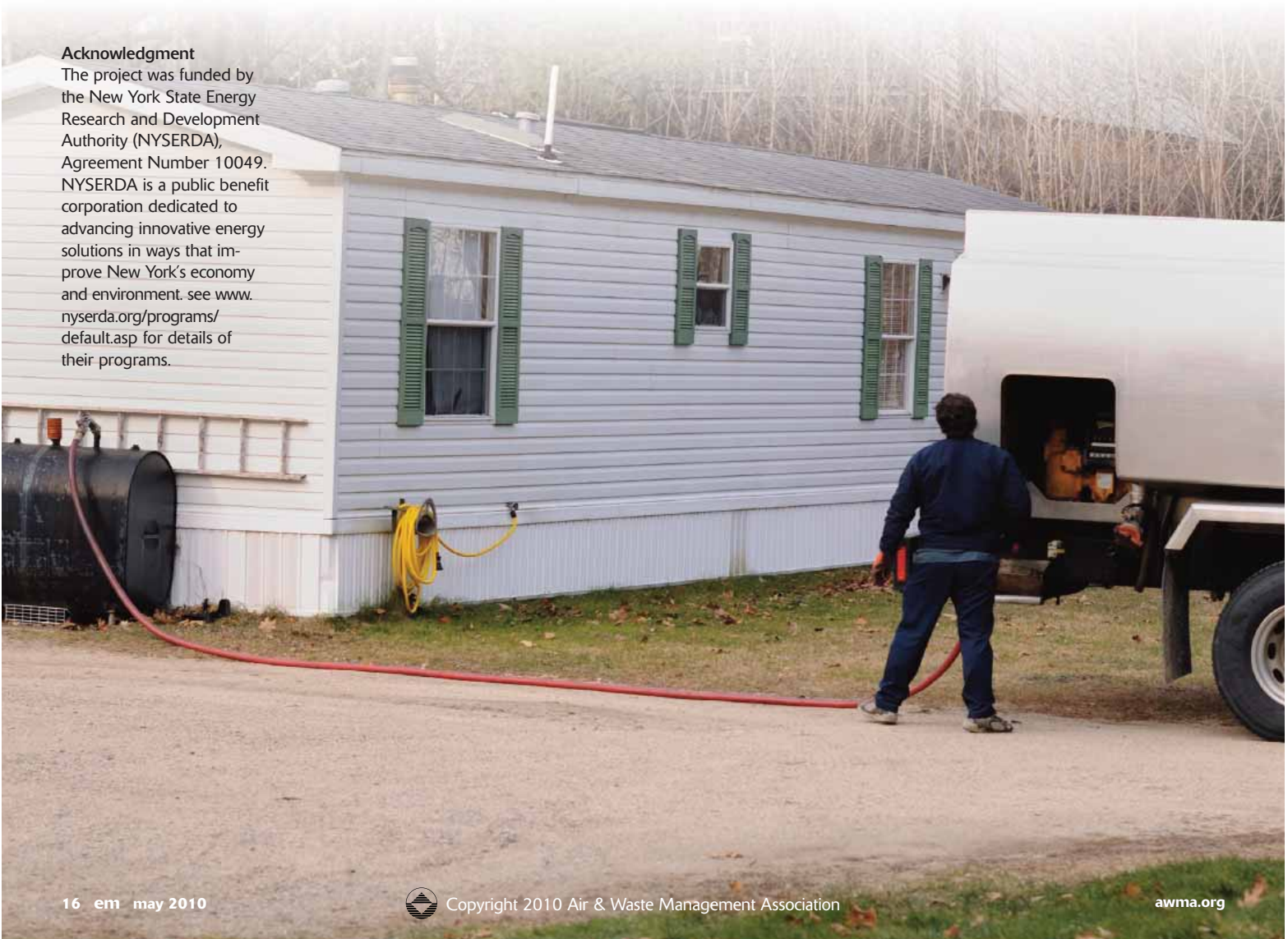by John Graham

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Select Trace Elemental Composition of Fuel Oil used in the Northeastern United States

Policy-makers rely on emissions inventories as a primary tool for air quality management.[1-3] The quality of their decisions, however, are a direct reflection of the quality of the underlying inventories. Therefore, maintaining high-quality emissions inventories represents a major priority for managers. Research results presented here will provide up-to-date trace elemental composition of fuel oils currently used in the northeastern United States. This information improves the understanding of the relative importance of oil combustion in regional emissions inventories for the analyzed elements.

Regional Mercury Emissions

In June 1998, the New England Governors and Eastern Canadian Premiers (NEG-ECP) adopted a comprehensive regional Mercury Action Plan (MAP) with aggressive emission reduction and pollution prevention goals that would result in virtual elimination of mercury (Hg) emissions from the region. As a first step in meeting emission reduction milestones in their plan, the NEG-ECP developed and reviewed regional Hg emissions inventories. The review and subsequent regulations prompted emissions reductions from a number of major source categories, including medical waste incinerators and municipal waste combustors.[4]

After addressing the major sources with their relatively well-defined emissions profiles, managers confronted the uncertain task of dealing with the remaining sources. Inventory analysis identified residential fuel oil combustion as an important contributor to the Hg emissions in the region.[5] When added to estimated Hg emissions from oil used to fire boilers in the commercial, industrial, institutional, and electrical generating sectors, emissions derived from oil combustion comprised nearly one-fourth of the regional inventory total.

These estimates were based on emission factors from the U.S. Environmental Protection Agency's (EPA) AP-42 database.[6] Emerging research conducted by EPA[7] and Environment Canada[8] on the Hg content of crude oil suggested much lower emissions from petroleum fuels. That analysis implied a need to update the Hg emission factors for petroleum distillates and was the initial impetus for the study described in this article.
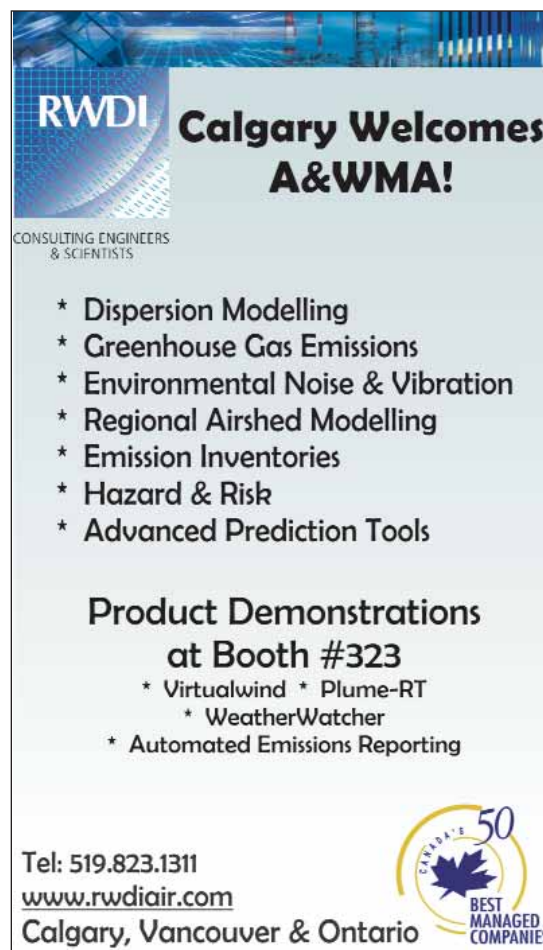
While the MAP represents a regional effort to address environmental pollution, local plans can also promote environmental improvements for a more limited geographic area. In 2007, New York City Mayor Michael R. Bloomberg put forth a comprehensive sustainability plan for the city's future, called PlaNYC.[9] This plan focuses on five interconnected pieces—land, air, water, energy, and transportation—and outlines 10 overarching goals for 2030. The research presented here will provide useful information for a number of the air quality goals outlined in PlaNYC, including reduction of emissions from transportation and buildings through the use of cleaner burning fuels.

Our research will improve the understanding of the emissions potential for Hg and other trace elements, which is especially important in New York City, as it represents a substantial market for home heating and residual oils in the Northeast. Fuel use data compiled for 2008 by the U.S. Energy Information Administration (EIA) for New England (PADD IA)[10] and the Central Atlantic (PADD IB)[11] shows these areas represent more than 80% of the nationwide market for home heating oil and half of the distillate used in the commercial sector. For all sectors of the economy, including transportation, fuel use in the Northeast represents 20% of the market for distillate fuel oil and nearly 30% for residual fuel oil. Confirmation or revision of the trace elemental composition of these important fuels will be useful for air quality planners.

Other Trace Elements

In addition to Hg, trace elements, including lead (Pb) and arsenic (As), pose significant public health

Table 1. Analytical results of trace metals by ICP-MS.

Type (n)	Metric	S	Ni	Zn	As	Se	Hg
Home Heating/ Diesel (102)	maximum	2899	9	66	10	11	13
	minimum	807	<3 (54)	<6 (35)	<1 (25)	<5 (18)	<2 (72)
	average	1998	3.2[a]	14.8[a]	2.1[a]	4.3[a](75)	2.0[a]
	median	1920	<3	17	2.0	7.0	<2
Residual (16)	maximum	3860	22600	4960	523	197	ND
	minimum	2780	11900	813	<20 (8)	<125 (4)	<25 (16)
	average	3020	16988	1963	172[a]	119[a]	
	median	2970	16650	1810	35	125	
Ultra-low S (11)	maximum	8	6	64	ND	5 (1)	4
	minimum	<3 (1)	<3 (8)	6	<1 (11)	<5 (8)	<2 (9)
	average	5.6		24			
	median	5		19			
Bio-diesel (8)	maximum	84	5	50	1	ND	ND
	minimum	4	<3 (6)	<6 (1)	<1 (7)	<5 (8)	<2 (8)
	average	27.3[a]		22.5[a]			
	median	30.5		27			

Notes: Units are given in ppb except for S, which is in ppm. Composition is summarized by four oil types: home heating oil/diesel (#2), residual oil (#6), ultra-low S diesel, and bio-diesel. The number of samples for each category is listed in parentheses for the each type. Parentheticals in the table represent the number of samples with that measurement or that were used to create the value. For Se in the home heating fuels, the minimum value was the below the minimum detection limit (MDL) of 5 ppb for 18 samples. 75 sample results were averaged for Se, 57 values above the detection limit and 18 included at half MDL. Averages and medians were not determined when a low percentage of samples above the detection limit were recorded. Elements not detected in any samples are listed as ND in the maximum row. [a]Averages calculated with half MDL values for samples with unquantifiable levels.

risk due to inhalation toxicity or carcinogenicity of certain compounds containing these elements. Lippmann[12] suggests an association between nickel (Ni) and vanadium (V) concentrations in fine particulate matter ($PM_{2.5}$) and average daily mortality coefficients—with residual oil identified as a potential major source of these trace elements. Other researchers have also identified exposure to these trace elements in $PM_{2.5}$ as possible risk factors for increased respiratory problems[13] and cardiovascular and respiratory hospitalization.[14]

A study conducted by EPA supports the conclusion that residual oil contributes to the atmospheric burden of trace elements both in New York State and in the continental United States.[15] Researchers at New York University concur, observing the strong winter increase in ambient Ni in $PM_{2.5}$ to be associated with residual oil combustion in New York City.[16] These results are based, in part, on measurements from the Interagency Monitoring of Protected Visual Environments (IMPROVE) and EPA Speciation (STN) monitoring networks. That same dataset shows cobalt (Co) levels are also higher in the Northeast than in other regions of the United States. Trace elemental profiles from in-use oils like those developed in this research may prove useful to scientists performing source apportionment analysis of fine particulates.

Beyond air toxics, oil combustion contributes to ambient sulfur (S) levels in the Northeast. Measurements of fuel S content will better enable air quality managers to assess the real reduction potential as the region moves forward with its S reduction strategy to improve visibility in Class I[17] areas under a Mid-Atlantic/Northeast Visibility Union (MANE-VU)[18] initiative. Estimates of current and future S levels are based on regulated limits rather than actual in-use levels. A study conducted

Table 2. Analytical results of trace metals by ICP-MS and Hg by CVAA.

Type (n)	Metric	V	Mn	Co	Sb	Pb	Hg
Home Heating/ Diesel (102)	maximum	20	114	ND	ND	144	5.5
	minimum	<4 (85)	<5 (55)	<6 (102)	<10 (27)	<6 (99)	<1 (3)
	average						1.9[a]
	median						2
Residual (16)	maximum	8940	4870	1650	16900	603	2
	minimum	849	1820	697	3880	<10 (2)	1
	average	2967	2851	1113	8873 (6)	188[a]	1.3 (3)
	median	2105	2755	1145	6930	181	1
Ultra-low S (11)	maximum	ND	5	ND	ND	ND	
	minimum	<4 (11)	<5 (10)	<6 (11)	<10 (2)	<4 (11)	<1 (1)
	average						
	median						
Bio-diesel (8)	maximum	ND	8			ND	
	minimum	<4 (8)	<5 (7)	<6 (8)	(0)	<4 (8)	(0)
	average						
	median						

Notes: The five trace elements tabulated were rarely found above the MDL in the light distillate oils. Only 27 of the home heating oil samples were analyzed for Sb. For lead, 99 of the 102 samples were below detection and no Co was detected in any of the 102 samples. [a]Averages calculated with half MDL values for samples with unquantifiable levels. Elements not detected in any samples are listed as ND in the maximum row.

in Idaho[19] references the National Petrochemical & Refiners Association, which claims refined levels in ultra-low S diesel may need to be as low as 5 parts per million (ppm) to assure product at the pump meets the 15-ppm requirement. Compliance survey data collected by EPA for PADD I from 2006 to 2009 corroborates this over-compliance. Consistent with EPA regulations that initially required 80% of highway diesel to meet a 15-ppm requirement by June 2006 with all fuel meeting that level by June 2010, the data reveal a downward trend in average sulfur content to below 10 ppm, with a minimum sulfur level of 3 ppm in some samples.
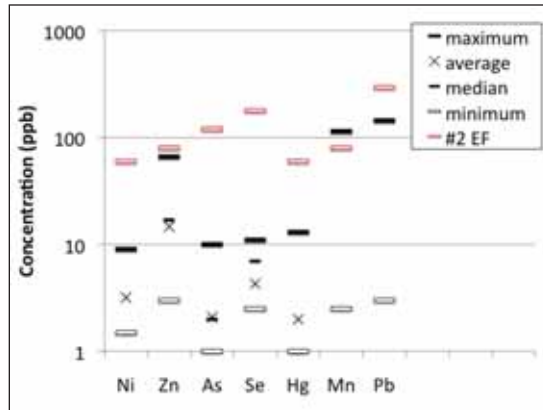
Study Overview

Existing EIA data show the importance of liquid fuel use in the Northeast region. With concerns in the accuracy of current inventories, as the case with Hg, and regionally high levels of air toxics as indicated by ambient data, the New York State Energy Research and Development Authority[20] funded the Northeast States for Coordinated Air Use Management (NESCAUM)[21] to conduct a sampling survey of in-use liquid heating fuels in New York and the surrounding region to assure the validity of existing emissions estimates from oil combustion.

Working with major oil distributors in the New York market, samples of various oil grades were collected, including home heating oil, biodiesel, onroad diesel, and residual oil. Samples were analyzed for S content and trace elements. The elemental analysis—V, Manganese (Mn), Co, Ni, Zinc (Zn), As, Antimony (Sb), Selenium (Se), Lead (Pb), Hg—relied on Inductively Coupled Plasma Mass Spectrometry (ICP-MS), with a subset of samples analyzed for mercury using cold vapor atomic absorption (CVAA). In general, the trace elemental composition of light distillates appears to be somewhat lower than reported profiles from

AP-42. As expected, the trace elemental composition of residual oil far exceeds that of lighter distillates. These current elemental measurements can be used along with existing fuel use to better understand the relative importance of different sources of trace elements in the overall emissions inventory.

Sampling Approach

The project was envisioned as a two-year effort, collecting samples of residential heating oil over multiple heating seasons. In addition to heating fuels, samples of other commonly used petroleum products were evaluated, including residual fuel, biodiesel, regular diesel, and ultra-low S diesel. Three fuel distributors–Global Partners, Irving Oil, and Sprague Energy–agreed to provide access to their terminals for this effort. An experienced contractor (Intertek Caleb Brett) was hired to collect samples directly from the terminals and process them for analysis in their petroleum laboratory.

The project began sampling in February 2008 and continued collection until November 2009, encompassing, in part, three different heating seasons and one full calendar year. Home heating oil represented the majority of samples, with limited numbers of on-road diesel, biodiesel, and residual fuel samples.

Sample collection sites included terminals in Albany, the Bronx, and Long Island, NY; and Revere and Quincy, MA. A total of 137 fuel samples were analyzed, along with another 36 duplicate samples, where a duplicate sample refers to a sample taken from the same storage tank, but collected, shipped, and analyzed separately. The samples included 95 home heating oil, 7 high S diesel, 11 ultra-low S diesel, 8 biodiesel, and 16 residual oil samples.

Table 3. Emission factors of trace elements for distillate and residual fuel oils (AP-42, 1998).

	#2 Distillate Oil		#6 Residual Oil	
	Emission factor lb/10^6 gallon	Concentration (ppb)	Emission factor lb/10^6 gallon	Concentration (ppb)
As	0.56	80	1.32	167
Pb	1.25	179	1.51	191
Mn	0.83	120	3	380
Ni	0.42	60	84.5	10,696
Zn	0.56	80	29.1	3,684
Co	n/a	n/a	6.02	762
V	n/a	n/a	31.8	4,025
Sb	n/a	n/a	5.25	665
Hg	0.42	60	0.113	14
Se	2.08	295	0.683	86

Notes: The mercury emission factors were used in NESCAUM's development of the 2002 regional Hg inventory. Concentration values are derived from the emission factor, assuming all of the species are emitted. Actual concentration in the oils could be higher than shown here if some elemental portion remains in the combustion device.

Analytical Results

Upon collection, samples were shipped directly to the analytical lab. All samples were analyzed by ICP-MS for V, Mn, Co, Ni, Zn, As, Pb, and Hg. A subset of samples included analysis for Sb and Se. For comparative purposes, 24 samples were analyzed by CVAA for Hg, and S analysis was conducted by X-ray fluorescence.

The analytical results are summarized in Tables 1 and 2, grouped by fuel type. The elements in Table 1 represent those found most frequently in the samples, while the concentration of those in Table 2 were more likely to be below the analytical detection limit. Review of the S levels shows average concentrations in home heating oil to be 2000 ppm and residual oil 50% greater. Ultra-low S measurements were approximately 6 ppm and bio-diesel somewhat higher at 27 ppm, consistent with previously reported values.[19]

Given the emphasis the Northeast has placed on Hg emissions, two analytical approaches were used for this study. The ICP-MS method is less sensitive than the CVAA, and also required more sample handling, which could adversely affect the results. In the light distillates, Hg was detected in just over 25% of the samples. Hg levels were recorded for more than 80% of the light distillates by the CVAA technique. When substituting half the detection limit in for samples reporting below-detection levels, the average concentration of 2 parts per billion (ppb) agrees for both techniques. None of the residual oil samples had detectable levels by ICP-MS, although the sensitivity for that approach was an order of magnitude less than distillate fuel. Three residual samples were analyzed by CVAA, with an average of 1.3 ppb.

The Hg levels determined by this study are substantially below those used previously in inventory development in the Northeast. AP-42 factors for #2 and #6 fuel oils are shown in Table 3. The concentrations of Hg for these two fuels are 60 and 14 ppb, respectively. These levels far exceed those obtained in this work and imply the emissions estimates for these source categories could be overestimated by factors of 30 and 7, which corresponds to over a 1-ton overestimate.

For the other trace elements in home heating oil, Figure 1 shows the emissions factors to greatly exceed the average measured levels in this study, and in many cases, even the maximum recorded concentration in the analyzed samples. Since the maximum emission from combustion of these fuels cannot exceed the concentration in the input fuel, the current emission factors for these trace elements exceed their true values. Note that the reported fuel concentrations based on the emission factor are at best a lower bound, as they assume
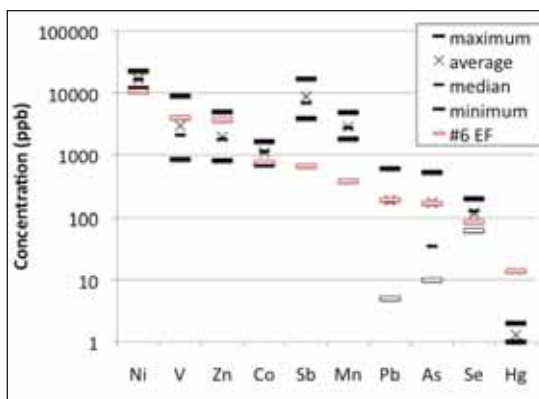

Figure 2. Comparison of the measured elemental concentrations in residual oil and assumed concentrations based on AP-42 emission factors.

Notes: The range of measured values is plotted. For Pb, As, and Se, the minimum measured value represents half of the minimum detection limit for those elements (open bar). The minimum values for the other elements represent actual measurements (solid bar). Note the scale on the y-axis is logarithmic and, in many cases, the emission factor estimate differs from the measured value by an order of magnitude. AP-42 emission factors (red bar).

complete emission of all trace elements from the combusted fuel.

Results for the residual fuel are more complicated and are plotted in Figure 2. A number of results compare quite favorably, especially Pb and As, whose measured average concentration aligns with the emission factor estimate. The relative percent differences for Ni, V, Zn, Co, and Se show reasonable consistency. For those elements, the estimated emission factor concentration falls within the bounds of the measured range. Only Mn and Sb differ by a wide margin, with nearly an order of magnitude greater concentration in the fuel samples analyzed in this work.

Analysis of bio-diesel constitutes one novel result for this study as this fuel represents an emerging market. Based on the results, this fuel appears to have similar composition to ultra-low diesel with trace elemental composition at or below that determined for home heating oil.

Conclusion

The research presented here provides an up-to-date estimate of trace elemental composition of distillate fuels used in the Northeast United States. The fuel composition results for residual oil reasonably agree with existing emission factors, except for Sb, Mn, and Hg. For home heating oil, however, the existing emission factors may exceed the true concentration in the fuel currently used in the Northeast. This confirms the importance of trace elemental emission from residual oil and reveals its relative contribution to be even greater than previously estimated when compared to emissions from home heating oil.

These data can be employed by air quality program managers in their work to develop inventories of emissions for the Northeast. These inventories form the basis for decisions, either by direct analysis or use in air quality modeling exercises and, therefore, require a reasonable degree of accuracy. Results for Hg, in particular, demonstrate the need to continually review and reassess available emission factors and associated emissions estimates. The evaluation process becomes especially critical once the emissions of well-characterized major source categories have been reduced or controlled. **em**

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