



# Determination of Mercury and Other Trace Elements in Home Heating Oil Used in New York State

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## S Supporting Information

**ABSTRACT:** A 2002 mercury emissions inventory developed by the Northeast States for Coordinated Air Use Management using standard fuel oil mercury (Hg) emission factors from the U.S. Environmental Protection Agency (known as US EPA “AP-42” factors) identified residential fuel oil combustion as an important contributor to Hg air emissions in the northeastern United States. Published literature values, however, suggest much lower mercury content in heating oil than inferred from the US EPA factors. To better characterize mercury (along with other trace element) content in heating oil sold in the Northeast, we conducted a two-phase sampling and analysis study of commercially available fuel oil sold in the northeastern U.S., with a focus on New York State. Changes between the two study periods and relationships between trace element and sulfur levels were evaluated. The study found that concentrations of mercury and other trace elements sampled during both study phases were within typical ranges reported in the literature. Although the average sulfur level in the samples dropped by 2 orders of magnitude between the two phases because of new government regulations limiting sulfur content in fuel oil after the first sampling phase, we observed no significant relationship between sulfur content and the other trace elements. In addition, derived emission factors for almost all trace elements showed lower values than the tabulated US EPA AP-42 factors. The lower mercury content measured in the samples indicate that heating oil combustion is a much lower source of mercury emitted to the air in the northeastern U.S. than would be inferred from an emission inventory developed using US EPA emission factors.

## INTRODUCTION

Approximately 6 million households in the northeastern U.S. rely on home heating oil for heating needs, representing approximately 84% of the total households in the U.S. that are dependent upon home heating oil as their primary heating fuel.<sup>1</sup> The top consuming state for home heating oil is New York State (NYS), followed by Pennsylvania, Massachusetts, Connecticut, and Maine. In 2015, NYS consumers bought a little over 890 million gallons of home heating oil, or over 22% of all heating oil sold in the entire U.S.<sup>2</sup> In addition, some institutional and commercial buildings use heating oil for space and water heating. According to the EIA, 92% of all residential and 40% of all industrial and residential distillate fuel oil sales in 2015 occurred on the East Coast, comprising approximately 3.7 and 1.9 billion gallons of heating oil sold to residential and commercial consumers, respectively.<sup>2</sup>

With the relatively large preponderance of heating oil consumption in the northeastern United States, we conducted a two-phase sampling and analysis study to better characterize the trace element content in heating oil (commonly referred to as No. 2 fuel oil or distillate). This study, which focuses on New York State, improves the understanding of the relative importance of heating oil combustion in regional emissions inventories for the analyzed elements. The elements included are mercury (Hg), vanadium (V), manganese (Mn), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), antimony (Sb), selenium (Se), and lead (Pb).

Our study placed special emphasis on Hg, a toxic metal found in residential heating oil (and other fuel oils) that is emitted to the air when the oil is burned. Once in the atmosphere, Hg can be deposited locally or transported over long distances before falling back to the surface. When released into the environment and deposited or carried into water bodies, Hg can be converted to methylmercury (MeHg), a particularly toxic form of Hg. Methylated Hg in the aquatic food chain can bioaccumulate in fish tissue to concentrations markedly higher than that in the surrounding water.

A major route of exposure to Hg is through the consumption of fish. Women of childbearing age are of special concern as MeHg ingested by a mother can transport across the placenta into the brain of a developing fetus. In young children and fetuses, MeHg inhibits the normal development of the nervous system, an effect that may occur even at low exposure levels. Often this damage is not apparent until later in the developmental process, when motor and verbal skills are found to be delayed or abnormal. Developmental effects have been found in children exposed in utero, even though their mothers did not experience any symptoms of adult toxicity.<sup>3</sup> Women in the Northeast have the highest Hg exposure in the U.S., with 19% having blood organic Hg level exceeding what is considered safe for fetuses.<sup>4</sup>

Received: August 16, 2017

Revised: December 1, 2017

Published: December 4, 2017

Most of the Hg present in water bodies—and the fish within them—in NYS and the Northeast is deposited from the atmosphere.<sup>5,6</sup> To address Hg in the environment and its threat to human health, NYS and surrounding states have pursued a number of initiatives aimed at the virtual elimination of Hg releases into the environment. In December 2007, the U.S. Environmental Protection Agency (USEPA) approved a request from NYS and the six New England states to establish a regional Total Maximum Daily Load (TMDL) for Hg under the federal Clean Water Act. The regional Hg TMDL was set at a level that would decrease Hg levels in fish tissue low enough for states to lift their fish consumption advisories.<sup>7</sup> Subsequently, in 2009, New Jersey also received approval from the USEPA for a Hg TMDL for 122 impaired bodies of water within the state. The New Jersey TMDL was set at a comparable level to the regional Hg TMDL previously established by NYS and the six New England states.<sup>8</sup>

There have been a number of relatively recent programs in the U.S. to reduce Hg air emissions, most notably, new state and federal rules aim to reduce or eliminate Hg emissions from municipal waste combustion, medical waste incineration, and coal-fired electric power plants.<sup>9,10</sup> Studies occurring after these Hg reduction measures took effect have documented measurable decreases in Hg concentrations in leaf litterfall in eastern U.S. forests<sup>11</sup> as well as in freshwater fish tissue collected in the northeastern U.S.<sup>12,13</sup> and in important commercial marine fish from the Atlantic Ocean off the eastern U.S. coast.<sup>14,15</sup> As the large Hg source sectors reduce or eliminate their emissions, other source sectors, such as residential heating oil combustion, can become relatively more important for efforts to reduce the public's exposure to Hg being deposited from the air onto land and into water bodies.

An analysis by the Northeast States for Coordinated Air Use Management<sup>16</sup> using fuel oil Hg emission factors taken from the USEPA AP-42 database<sup>17,18</sup> identified residential fuel oil combustion as an important source sector in a 2002 regional Hg air emissions inventory of eight northeastern states (Connecticut, Maine, Massachusetts, New Hampshire, New Jersey, New York, Rhode Island, Vermont). 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 Hg inventory total.

We note that USEPA AP-42 emission factors are developed mainly for national inventory purposes and may not be suitable for a particular source or location. In addition, comparing the results of elemental fuel analysis and USEPA AP-42 emission factors should be made with the consideration that the AP-42 emission factors are based on the emitted elements after combustion. While the amount of trace elements entering the combustion chamber only depends on the fuel composition, the amount emitted postcombustion depends on combustion temperature, fuel feed mechanism, and particulate matter (PM) treatment technology, in addition to the fuel composition.<sup>18</sup> For example, lower flame temperature would result in less metal volatilization from the fuel and less subsequent condensation and enrichment on fine PM, thus lowering the amount of volatilized elements in the stack exhaust gas. On the other hand, erosion of metal components or mercury re-entrainment from “cold spots” after combustion may add small amounts of metal emissions to the stack gas. Apart from these latter factors, metal emissions in the stack gas cannot be greater

than assuming all metal content of the fuel is volatilized through the stack after fuel combustion. This is particularly salient for our study's focus on Hg, which is more volatile relative to other trace elements analyzed in this study, and is chiefly emitted in the gas phase during combustion.

Since the early 1980s, several estimates of Hg in No. 2 distillate oil have been published, describing a wide range of concentrations. The USEPA estimated the concentration of Hg in No. 2 distillate oil as 400  $\mu\text{g}/\text{kg}$ ,<sup>19</sup> and with a later adjustment to <120  $\mu\text{g}/\text{kg}$ .<sup>20</sup> Several studies have been released reporting levels well below these estimates. Liang et al.<sup>21</sup> and Rising et al.<sup>22</sup> reported values below 1  $\mu\text{g}/\text{kg}$  (0.59 and <0.2  $\mu\text{g}/\text{kg}$ , respectively). Bloom<sup>23</sup> found a mean Hg concentration of 1.32  $\mu\text{g}/\text{kg}$  across all light distillates. In addition, total Hg levels in diesel fuel (i.e., distillate) have been reported as high as 3.0  $\mu\text{g}/\text{kg}$  to as low as 0.034  $\mu\text{g}/\text{kg}$ , while the levels in gasoline have been found at 0.04–3.2  $\mu\text{g}/\text{kg}$ .<sup>21,24,25</sup> By comparison, Hg content in No. 2 fuel oil would be 60  $\mu\text{g}/\text{kg}$  when inferred from the USEPA AP-42 emission factor,<sup>18</sup> assuming an oil density of 845  $\text{kg}/\text{m}^3$  (7.05  $\text{lb}/\text{gal}$ ) and that all Hg in the fuel oil is released to air during combustion.

With this spread in the reported Hg content of fuel oils, and with the standard USEPA AP-42 emission factor the U.S. states typically use in developing their Hg air emission inventories, there is a need to better characterize the Hg content in heating oil used in NYS and the northeastern United States. Correct identification of the major Hg air emission sources contributing to deposition will help public health and air quality planners better target limited resources toward the highest priority source sectors. While our study focuses on Hg, we also report results for other trace elements we measured in the heating oil samples, such as nickel and vanadium, to provide additional information in assessing the emissions of these toxic constituents from the combustion of heating oil.

Our two-phase study also explored whether there was a relationship between trace element content and fuel sulfur content, which decreased on average from approximately 2000  $\mu\text{g}/\text{kg}$  during the first phase (Phase I) to less than 15  $\mu\text{g}/\text{kg}$  in the second phase (Phase II), as the result of state and federal rules lowering the allowable sulfur content in No. 2 fuel oil. The lowering of fuel sulfur levels in fuel oil created an opportunity to probe whether the additional desulfurizing step at the refinery had an impact on trace element content in the refined product as well.

In Phase I, we collected and analyzed heating oil samples from oil distribution terminals between February 2008 and November 2009. Phase II collected and analyzed samples from October 2015 to September 2016. In addition to much lower sulfur content in heating oil, there was a large, but temporary, increase in Bakken shale oil entering NYS prior to Phase II. This shift also raised the possibility of a change in trace element content between the two sampling phases due to a large new crude oil feedstock arriving at East Coast refineries.

## ■ EXPERIMENTAL SECTION

**Sampling.** Each phase of this study used a different certified and accredited testing laboratory to perform the sample collecting, shipping, and testing. Samples were collected at each analytical laboratory by staff who had received training in industry standard operating procedures prior to sample collection. In Phase I, sample collection began in February 2008 and continued until November 2009. Sample collection sites included fuel oil distribution terminals in Albany, the Bronx, and Long Island, NY; Revere and Quincy, MA; and Elizabeth, NJ (Table 1). The samples included 95 No. 2 heating oil, 7

**Table 1. Sampling Locations for Fuel Oil and Diesel in Phase I**

location	distributor	terminal
No. 2 heating oil		
Albany, NY	Sprague	Sprague – Albany
	Global	Global – Albany
Boston, MA	Global	Global – Revere
	Irving	Irving – Revere
Boston, MA	Sprague	Sprague – Quincy
Long Island, NY	Sprague	Sprague – Oceanside
	Global	Global – Long Island Terminals
Brooklyn, NY	Global	Global – Brooklyn Metro
biodiesel		
New Jersey	Sprague	Sprague – Elizabeth, NJ
ultra-low-sulfur diesel (transportation fuel)		
New York, NY	Sprague	Sprague – Stuyvesant-Bronx
nonroad diesel		
New York, NY	Sprague	Sprague – Stuyvesant-Bronx

high sulfur diesel, 11 ultra-low-sulfur diesel (ULSD), and 8 biodiesel samples. A smaller number of duplicate samples were taken from the same storage tank, but collected, shipped, and analyzed separately.

Phase II focused on fuel oil distribution terminals within NYS that encompassed the State's eight fuel distribution regions. Figure 1 is a

**Figure 1.** Map of fuel oil terminal locations selected for sampling in New York State for Phase II.

map of the NYS terminal locations. Phase II sampling began in October 2015 and continued on a monthly basis until September 2016. No. 2 heating oil represented the majority of samples (134 samples and 4 duplicates), with limited numbers of ULSD (10 samples and 1 duplicate), and biodiesel (B100) (1 sample). Table 2 shows the sampling schedule and terminal information for Phase II of the study.

**Analysis.** In Phase I, the testing focused on determining the levels of Hg, Pb, Ni, V, Zn, Co, As, Se, Mn, Sb, and S. In Phase II, analysis of nitrogen (N) content of the samples was added. Other than for S and N, all samples were analyzed for trace elements by inductively coupled plasma mass spectrometry (ICP-MS), which is highly sensitive and capable of detecting and quantifying a range of metals and several nonmetals at concentrations in the parts per billion ( $\mu\text{g}/\text{kg}$ ) range and below.<sup>26</sup>

Each laboratory used its in-house standard procedures in the handling and analysis of the collected oil samples. The samples were diluted with semiconductor grade xylenes at a minimum dilution of 1:10 for analyzing by ICP-MS. Sample introduction was by self-aspirating perfluoroalkoxy nebulizer. Calibration standards were also prepared in xylenes from organometallic standards. The calibration ranges varied by element and expected result, but were usually in the

0–25  $\mu\text{g}/\text{kg}$  range using a four-point curve, including a calibration blank. The minimum linearity for acceptance was  $r^2 \geq 0.995$ . A check standard was run before and after every sample set with  $\pm 20\%$  of the accepted value required. A sample blank was prepared and run with the samples. The sample blank value had to be less than the method detection limit (MDL) for the data to be used. A minimum of 1 sample per 10 was run in duplicate with the relative standard deviation (RSD) of the duplicate samples required to be less than 20% for any result higher than the MDL. A hydrogen ( $\text{H}_2$ ) reaction cell was used to eliminate interferences from problematic elements.

For samples where the dilution was less than 1:10, the standard additions technique had to be applied. A series of three sample spikes were run with an unspiked sample, all at the desired dilution, and these data were used to generate a standard additions curve and result. The result was cross-checked by converting the standard curve to an external calibration, which was then applied to a spiked sample with the calculated spike recovery required to be 70–130% for acceptance. If multiple samples were run with the same curve, each sample was run with a spiked sample so that recoveries could be used to qualify the additions curve as acceptable for other samples in the set. If the spike recovery was inadequate, a separate additions curve had to be generated using that specific sample.

Sulfur concentrations in No. 2 heating oil and off-road diesel were obtained by energy-dispersive X-ray fluorescence spectrometry according to ASTM Method D5453-12.<sup>27</sup> This method is typically applied to a concentration range of 0.0150–5.00 mass % sulfur in fuel oils. Ultra-low-sulfur diesel (on-road diesel and biodiesel) was analyzed using wavelength dispersive X-ray fluorescence spectrometry according to ASTM Method D2622.<sup>28</sup> In Phase II, the nitrogen content of the No. 2 fuel oil samples was analyzed using oxidative combustion and chemiluminescence detection according to ASTM Method D4629.<sup>29</sup>

Because two different laboratories performed the analysis for the separate sampling phases of this study, the MDLs of the trace elements differed somewhat due to differences in calibration methods, with MDLs typically at 10  $\mu\text{g}/\text{kg}$  or lower, except for sulfur and nitrogen, which had higher MDLs in recognition of their typically much higher concentrations in No. 2 heating oil. The MDLs for each sampling phase are shown in Table 3.

In order to validate the analysis results, quality assurance and quality control (QA/QC) checks must be followed. Each laboratory followed procedures to test and verify the performance of their laboratory instrumentation. In addition, duplicate samples were collected to verify the collection and storage procedures. In Phase I, a total of 35 duplicate samples (34 No. 2 heating oil and 1 ULSD) were drawn from the same storage tank but collected, shipped, and analyzed separately from the original samples. In Phase II, a total of 5 duplicate samples (4 No. 2 heating oil and 1 ULSD) were collected and analyzed for QA/QC purposes. Table 4 shows the comparison of the trace element concentrations of the duplicate samples (distillate and diesel) with the corresponding original sample.

Many of the trace element concentrations in the distillate oil and diesel samples were below the MDLs listed in Table 3. In all samples used in the Phase I duplicate comparison, the trace element concentrations of Co and Pb were below the MDL. Therefore, the percent difference between the Co and Pb concentrations for each duplicate and original sample is 0%. On the other end, all 35 pairs of samples had detectable amounts of sulfur, with an average percent difference between duplicate and original samples of 1.1%. Zinc has the highest average percent difference for the duplicate samples at 30.7%. Overall, the duplicate samples indicate that the trace element concentrations are reproducible. The slight differences shown here are expected given some inhomogeneity of the storage tanks. Phase II duplicate analysis is very limited because only 4 pairs in total were collected and measured. Only the Sb content in all samples had levels above the MDL, for which the average difference between the duplicate and original samples was 78.9%.

Table 2. Sampling Locations and Schedule for Fuel Oil and Diesel in Phase II

terminal name	sampling schedule	distributor
No. 2 heating oil		
Buckeye-Buffalo	monthly	Buckeye Partners LLC-Buffalo
Global-Albany	winter months only	Global Companies LLC
Sprague-Albany	monthly	Sprague Operating Resources LLC-Rensselaer
Buckeye-Brewerton	monthly	Buckeye Partners LLC-Brewerton
Global-Original	monthly	Global Companies LLC
Global-North	winter months only	Global Companies LLC
Global-Oyster Bay	monthly	Global Commander Terminal
Global-Inwood	monthly	Global Companies LLC
Buckeye-Brooklyn	winter months only	Buckeye Partners LLC-Brooklyn
Sprague-Bronx	monthly	Sprague Operating Resources LLC-Bronx
Buckeye-Rochester	monthly	Buckeye Partners LLC-Rochester I
Buckeye-Rochester South	winter months only	Buckeye Partners LLC-Rochester II
Buckeye-Vestal	monthly	Buckeye Partners LLC-Vestal
Buckeye-Utica	monthly	Buckeye Partners LLC-Utica
ultra-low-sulfur diesel (transportation fuel)		
Global-Original	summer months only	Global Companies LLC
Buckeye-Buffalo	summer months only	Buckeye Partners LLC-Buffalo
Buckeye-Rochester South	summer bimonthly	Buckeye Partners LLC-Rochester II
B100 biodiesel		
Sprague-Albany	august only	Sprague Operating Resources LLC-Rensselaer

Table 3. Method Detection Limit (MDL) for Trace Elements, Sulfur, and Nitrogen in No. 2 Fuel Oil ( $\mu\text{g}/\text{kg}$ )

Element	Phase I	Phase II
	No. 2 heating oil	No. 2 heating oil
As	1	10
Co	6	10
Hg	2	10
Mn	5	10
Ni	3	10
Pb	4	10
Sb	10	10
Se	5	10
V	4	10
Zn	6	10
S	1000	1000
N	n.a.	1000

## RESULTS AND DISCUSSION

**Initial Assessment.** The amount of Hg and other trace elements in crude oil varies considerably and is dependent on its geologic source location.<sup>30</sup> Published literature (Table 5) for Hg content in various refined petroleum products provide a range from 0.005 to 40  $\mu\text{g}/\text{kg}$  (with one study reporting “<120  $\mu\text{g}/\text{kg}$ ”). Table 6 summarizes other reported trace elements measured in different petroleum-derived fuels.

After completion of Phase I, two major events occurred that warranted revisiting fuel trace element content in NYS. First, the New York State Department of Environmental Conservation amended a rule that took effect in 2013 to lower the allowable sulfur content in No. 2 heating oil to 15  $\mu\text{g}/\text{kg}$  statewide. The new sulfur limit is more than 100 times lower than the average sulfur content measured in heating oil during Phase I (results presented below).

Second, there was a temporary, but large, shift in the source region for the crude oil shipped to East Coast refineries. Crude oil from the North Dakota Bakken shale fields increased around 2013 and dropped again during 2016. This oil typically went through NYS by rail to the Port of Albany, where it was transferred to barges for shipment to refineries on the East Coast. An oil industry analyst predicted that, in 2014, approximately 800 000 barrels per day of Bakken oil shale crude were shipped to East Coast refineries,<sup>39</sup> equivalent to approximately 60% of the region's total refinery capacity. The overwhelming majority of crude oil inputs to the East Coast region at the time of Phase I study were imported from abroad. However, after 2011, the region started to increase its crude oil input from Bakken shale production through rail shipment. By the end of 2013, Bakken crude by rail was supplying at least 400 000 barrels per day to East Coast refineries. Information from the U.S. Energy Information Administration suggested that crude transported by rail—the majority of it from the Bakken—accounted for as much as 52% of crude oil processed in East Coast refineries, or about 452 000 barrels per day, by

Table 4. Test Results of Duplicate Distillate and Diesel Samples (BDL = Below Detection Limit)

	Mn	Co	Hg	Ni	Se	Sb	Pb	V	As	Zn	N	S
Phase I												
average difference	6.2%	BDL	11.0%	8.0%	10.1%	BDL	BDL	0.0%	18.7%	30.7%	BDL	1.1%
pairs with measurable conc.	5		1	15	19			7	26	19		35
Phase II												
average difference	1.3%	BDL	BDL	67.2%	5.7%	78.9%	BDL	BDL	3.1%	5.0%	3.2%	4.2%
pairs with measurable conc.	1			2	2	4			2	2	1	3

Table 5. Total Mercury in Refined Petroleum Products

reference	year	fuel type	number of samples	mean ( $\mu\text{g}/\text{kg}$ )
Liang et al. <sup>21</sup>	1996	heating oil	1	0.59
Bloom <sup>23</sup>	2000	light distillates	14	1.32
Rising et al. <sup>22</sup>	2004	gas turbine fuel (No. 2)	13	<0.2
USEPA <sup>20</sup>	1997	residual fuel oil		4
Bloom <sup>23</sup>	2000	utility fuel oil	21	0.67
Kelly et al. <sup>24</sup>	2003	diesel (U.S.)	5	3.46
Liang et al. <sup>21</sup>	1996	diesel	1	0.4
Liang et al. <sup>21</sup>	1996	diesel	1	2.97
Hoyer et al. <sup>31</sup>	2004	diesel	1	0.005
Kelly et al. <sup>24</sup>	2003	diesel	6	0.034
Conaway et al. <sup>25</sup>	2005	diesel	19	0.15
Won et al. <sup>32</sup>	2007	diesel		0.219
Liang et al. <sup>21</sup>	1996	gasoline (U.S.)	5	0.22–1.43
Liang et al. <sup>21</sup>	1996	gasoline (Monaco)	2	0.72–0.96
Liang et al. <sup>21</sup>	1996	gasoline (Slovenia)	1	1.2
Liang et al. <sup>21</sup>	1996	gasoline (Algeria)	1	3.2
Hoyer et al. <sup>31</sup>	2004	gasoline	3	0.071–0.259
Conaway et al. <sup>25</sup>	2005	gasoline	20	0.5
Won et al. <sup>32</sup>	2007	gasoline		0.781
Liang et al. <sup>21</sup>	1996	kerosene	1	0.04
Olsen et al. <sup>33</sup>	1997	kerosene	4	0.15
Tao et al. <sup>34</sup>	1998	naphtha	3	40

Table 6. Non-mercury Trace Elements in Petroleum-Derived Fuels<sup>a</sup>

reference	year	fuel type	As	Pb	Mn	Ni	Zn	V	Se
Ugarković and Premerl (Croatia) <sup>35</sup>	1987	light gas oil				2.0 (mg/kg)		0.15 (mg/kg)	
Ugarković and Premerl (Croatia) <sup>35</sup>	1987	heavy gas oil				1.8 (mg/kg)		0.3 (mg/kg)	
Olajire and Oderinde (Nigeria) <sup>36</sup>	1993	heavy distillate	<0.2	10–1120	2.4–3.8 (mg/kg)	5.5–11 (mg/kg)	<10	14–99 (mg/kg)	
Heathcote et al. (U.S.) <sup>37</sup>	2000	diesel		0.3–5.3	<2.0	<2.0	5.1–12.7	0.7–6.5	1.4
Rising et al. <sup>22</sup>	2004	No. 2 fuel oil	<0.9	15	5.5	28.9			<5

<sup>a</sup>Note: Concentrations shown in table are in  $\mu\text{g}/\text{kg}$  unless indicated otherwise.

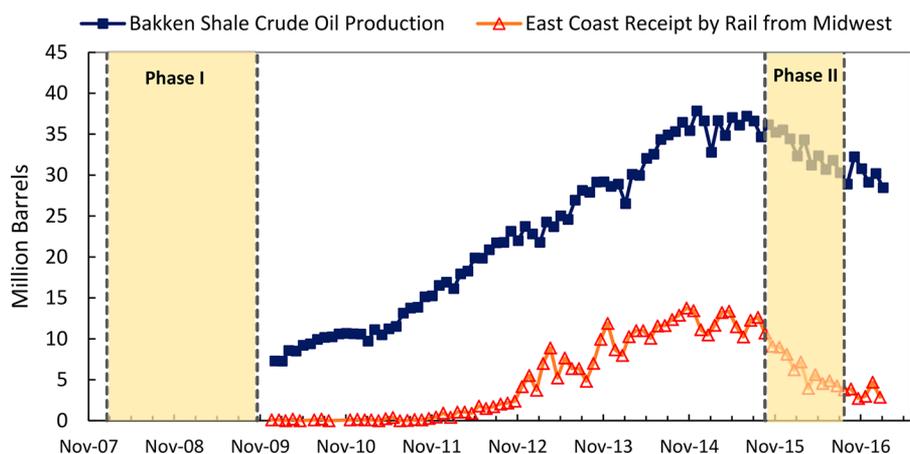


Figure 2. Bakken shale daily production and East Coast receipt of crude oil by rail from the Midwest region.<sup>38</sup>

early 2015.<sup>40</sup> Figure 2 shows the expansion in crude oil production from the Bakken formation since 2010 to early 2015, after which it begins declining. Although Bakken shale production started to decrease after June 2015, its continuing much higher production level relative to the Phase I sampling period created the opportunity for a real-world experiment to examine if this later increase in Bakken shale oil shipped to East

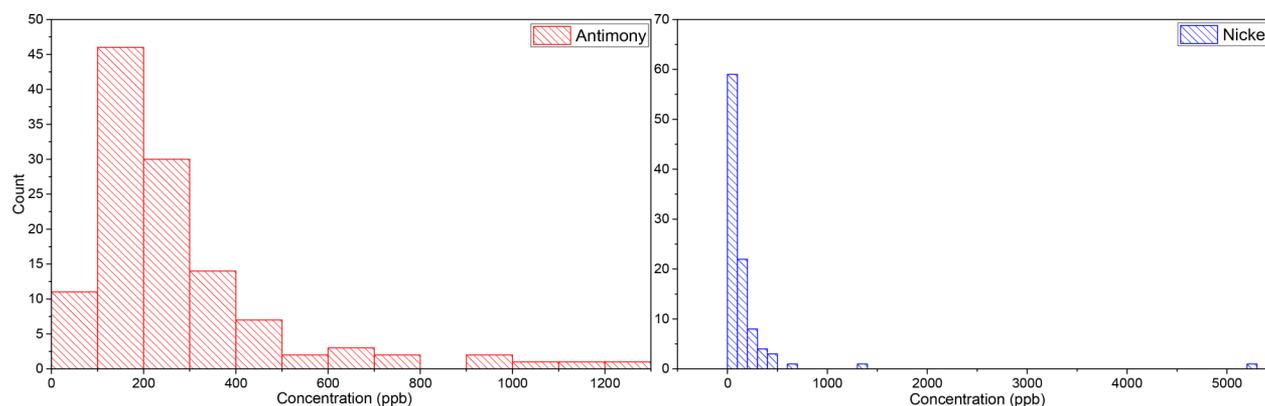
Coast refineries significantly affected the trace element content of refined fuel oils combusted in NYS.

**Non-sulfur Trace Element Content.** The analytical results for the trace element content in No. 2 heating oil samples in both phases of the research are summarized in Table 7 (for analytical results of No. 6 residual oil, see the Supporting Information). Because no nitrogen testing was performed in

Table 7. Summary of Test Results in No. 2 Fuel Oil Samples<sup>a</sup>

Phase II - No. 2 heating oil												
constituent	Co	As	Hg	Se	Sb	Mn	Ni	Pb	V	Zn	S	N
maximum	26	57	ND	181	1206	121	5239	61	525	295	11	50
minimum	<10 (112)	<10 (81)	<10 (134)	<10 (89)	<10 (11)	<10 (101)	<10 (30)	<10 (116)	<10 (119)	<10 (74)	7 (0)	<1 (3)
average	<10	13.0	<10	12.6	246.7	<10	134.7	<10	13.9	29.8	7.9	13.3
median	<10	<10	<10	<10	188.0	<10	44.0	<10	<10	<10	8.0	11.0
% samples below MDL	84%	60%	100%	66%	8%	75%	22%	87%	89%	55%	0%	2%
Phase I - No. 2 heating oil												
constituent	Co	As	Hg	Se	Sb	Mn	Ni	Pb	V	Zn	S	N
maximum	ND	10	13	11	ND	114	9	144	20	66	2899	ND
minimum	<6 (102)	<1 (25)	<2 (72)	<5 (18)	<10 (27)	<5 (55)	<3 (54)	<6 (99)	<4 (85)	<6 (35)	807 (0)	ND
average	2.1	2	2	4.3	2	2	3.2	14.8	14.8	1998	1920	ND
median	2	2	<2	7	<2	7	<3	17	17	1920	1920	ND
% samples below MDL	100%	29%	71%	35%	100%	83%	55%	98%	84%	35%	1%	ND
Phase II - No. 2 ULSD												
constituent	Co	As	Hg	Se	Sb	Mn	Ni	Pb	V	Zn	S	N
maximum	14	ND	1493	38	1208	ND	593	36	ND	102	10	28
minimum	<10 (5)	<10 (10)	<10 (8)	<10 (7)	<10 (2)	<10 (10)	<10 (3)	<10 (8)	<10 (10)	<10 (6)	8 (0)	<1 (1)
average	<10	<10	272.5	11.5	277.2	<10	126.8	<10	<10	36.0	8.7	14.5
median	<10	<10	<10	<10	126.0	<10	89.5	<10	<10	<10	8.0	5.0
% samples below MDL	50%	100%	80%	70%	20%	100%	30%	80%	100%	60%	0%	20%
Phase I - No. 2 ULSD												
constituent	Co	As	Hg	Se	Sb	Mn	Ni	Pb	V	Zn	S	N
maximum	ND	ND	4	5 (1)	ND	5	6	ND	ND	64	8	ND
minimum	<6 (11)	<1 (11)	<2 (9)	<5 (8)	<10 (2)	<5 (10)	<3 (8)	<4 (11)	<4 (11)	6 (0)	<3 (1)	ND
average	<6	<1	<2	<5	<10	<5	<3	<4	<4	24	5.6	ND
median	<6	<1	<2	<5	<10	<5	<3	<4	<4	19	5	ND
% samples below MDL	100%	100%	82%	73%	100%	91%	73%	100%	100%	11%	22%	ND

<sup>a</sup>Note: Units are in  $\mu\text{g}/\text{kg}$  for all trace elements and in  $\text{mg}/\text{kg}$  for sulfur (S) and nitrogen (N). Parentheticals in the table are the number of samples below the given MDL. Elements not detected in any samples are listed as ND in the maximum row.



**Figure 3.** Distribution of the detected nickel and antimony contents in No. 2 heating oil in Phase II.

Phase I, there are no results to compare for this element. In Table 7, the average values were calculated by substituting half-MDL values for samples with levels below the MDL. For No. 2 heating oil samples, the average values are reported as  $<10 \mu\text{g}/\text{kg}$  for averages below MDL when substituting half-MDL values. Elements not detected in any sample are listed as ND (not detected) in the maximum row. Generally, the trace element contents of most samples were below the MDL except for nickel and antimony in Phase II. In Phase II, fewer than 15% of the No. 2 heating oil samples had detectable amounts of lead. Additionally, no heating oil samples recorded Hg levels above the instrument MDL.

All samples of Phase II No. 2 heating oil had Hg content below the  $10 \mu\text{g}/\text{kg}$  MDL, which is consistent with the Phase I results. This finding is also consistent with Wilhelm et al.,<sup>41</sup> who reported a  $1.4\text{--}11.3 \mu\text{g}/\text{kg}$  range for Hg content from 42 crude oil samples obtained in 10 states, with an average of  $4.3 \mu\text{g}/\text{kg}$ . Similarly, a 2007 Environment Canada study found a Hg concentration range of  $0.1\text{--}50 \mu\text{g}/\text{kg}$  in 109 crude oil samples collected at Canadian refineries, with an average of  $2.6 \pm 0.5 \mu\text{g}/\text{kg}$ .<sup>42</sup> Other studies<sup>21–23</sup> reported Hg content values at approximately  $1 \mu\text{g}/\text{kg}$  or below. In contrast, earlier USEPA studies<sup>3,19,20</sup> estimated the concentration of Hg in No. 2 heating oil as  $<200$  to  $400 \mu\text{g}/\text{kg}$ . It should be noted that none of these ranges approach the anomalously high Hg concentrations ( $>1000 \mu\text{g}/\text{kg}$ ) reported for the two No. 2 ULSD samples collected in May 2016, which leads the authors to lack confidence in those laboratory results.

Among all the trace elements measured in Phase II No. 2 heating oil, antimony and nickel were the only ones detected above the MDL in most samples. However, the detected values showed some outliers based on common statistical tests. The distribution of the detected values of nickel and antimony from all samples with concentrations above the MDL is shown in Figure 3. The nickel histogram shows a large gap between the majority of measured values and a few high outliers, while the gap is smaller for antimony.

In determining possible outliers in these results, the outlier detection method developed by Tukey<sup>43</sup> is helpful because it makes no assumptions about the underlying distribution and does not depend on a mean or standard deviation that can be distorted by extreme outliers. Tukey's method establishes a range based on the first and third quintiles to detect outside values. The method was applied to both data sets (antimony and nickel), with six outliers identified for antimony and four outliers for nickel. On the basis of these results, statistics for

Sb\* and Ni\* (i.e., outliers removed) were calculated and are shown in Table 8.

**Table 8.** Statistics for Antimony (Sb\*) and Nickel (Ni\*) in Phase II No. 2 Heating Oil after Removing Outliers

constituent	Sb	Sb*	Ni	Ni*
number of samples above MDL	121	115	102	96
maximum ( $\mu\text{g}/\text{kg}$ )	1206	797	5239	444
average ( $\mu\text{g}/\text{kg}$ )	246	215	136	84
median ( $\mu\text{g}/\text{kg}$ )	218	200	85.5	69

Compared to the Phase I results, the No. 2 ULSD analysis results show generally higher levels of trace elements where they were detectable, although a meaningful comparison is difficult due to the limited number of measurements.

None of the trace elements in No. 2 heating oil showed a distinct geographical pattern across NYS, with samples collected statewide typically showing similar concentrations. With regard to seasonal variability of trace elements in No. 2 heating oil, there did appear to be a 4-month window from December 2015 to March 2016 (in Phase II) in which there were a higher number of samples with measured concentrations of some trace elements, but not all, above the MDL of  $10 \mu\text{g}/\text{kg}$ . During this 4-month period, arsenic levels were detected above the MDL in about 90% of all No. 2 heating oil samples (50 out of 55 samples), and all terminals sampled statewide had at least 2 months with detectable arsenic levels in the collected samples. Measurable levels of arsenic ranged from  $10 \mu\text{g}/\text{kg}$  to almost  $60 \mu\text{g}/\text{kg}$ , with the majority of samples in the range of  $10\text{--}30 \mu\text{g}/\text{kg}$ . For the rest of the sampling months (October–November 2015 and April–September 2016), only 2 of 77 samples had detectable arsenic levels, and both were below  $20 \mu\text{g}/\text{kg}$ . Zinc also was detected more frequently above the MDL during the same 4 months, with 40 out of 55 samples having detectable zinc levels in a range from  $11 \mu\text{g}/\text{kg}$  to  $190 \mu\text{g}/\text{kg}$ . Selenium and manganese levels were above the MDL during the sampling months of December 2015 and January 2016, with measurable selenium in 26 out of 28 samples and measurable manganese in all 30 samples statewide. For both trace elements, measured concentrations ranged from 10 to  $30 \mu\text{g}/\text{kg}$  during these 2 months. As discussed above, antimony and nickel strongly spiked in June and July 2016, but our analysis indicates these 2 months are dominated by a subset of sample results that appear to be outliers. There is less variability across sampling months when those potential outliers were excluded. The large majority of Co, Hg, Pb, and V results were

below the 10  $\mu\text{g}/\text{kg}$  MDL across the entire 12-month sampling period; therefore, we were unable to discern any potential seasonal or spatial variability with these trace elements. We were also not able to assess seasonal or spatial differences in No. 6 residual oil trace element content due to the more limited number of samples collected. In 8 of the 12 sampling months, either no or only one No. 6 residual oil sample was collected per month.

**Sulfur Content.** Table 7 shows a considerable decrease in the detected sulfur content of No. 2 heating oil between Phase I and Phase II samples. Figure 4 shows the range of the detected

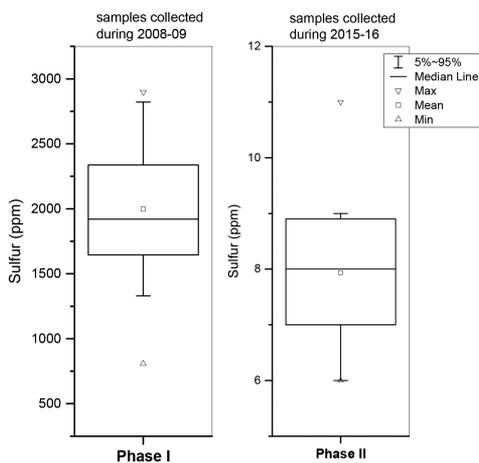


Figure 4. Comparison of sulfur content in No. 2 heating oil samples in Phase I and Phase II.

sulfur content in No. 2 heating oil in the samples collected during 2008–9 (Phase I) and 2015–16 (Phase II). In comparison, the maximum, median, average, and minimum sulfur content in Phase I dropped by more than 99% in Phase II, consistent with the more recent sulfur limits set by NYS.

In investigating whether a correlation exists between sulfur and trace element contents, it should be noted that two distinctly separate clusters of data exist due to the significant change in the sulfur content between the two sampling phases. In addition, other parameters changed between the phases, including the oil source production regions of the refined fuels consumed in NYS and the testing laboratories between the two phases. The laboratories employed different equipment and indicated some differences in MDLs. In this situation, random and fixed effect regression models, collectively called “mixed-effect” models, are more applicable than a standard regression analysis.<sup>44–46</sup> For this study, a mixed-effect model was developed between each trace element content data set (response variable), sulfur content (explanatory variable), and measurement phase (random factor) using formula 1

$$Y_{i,j} = x_{i,j}\alpha + C + u_{i,j}\beta_i + \theta_i + \epsilon_{i,j} \quad (1)$$

where  $Y$  is the response variable (trace element content),  $x$  is the covariate variable (sulfur content),  $\alpha$  and  $C$  are the covariate coefficient and intercept, respectively,  $u$  is the random-effect variable (measurement phase),  $\beta_i$  and  $\theta_i$  are the coefficient and intercept of the random factor, respectively,  $\epsilon$  is the error term, and  $j$  is the sample number in the  $i^{\text{th}}$  phase. In this linear equation, the term  $x_{i,j}\alpha + C$  is the fixed-effect component, while  $u_{i,j}\beta_i + \theta_i$  is the random-effect component of the regression. Therefore, the analysis involved both varying-slope and varying-intercept models for the random-effect component.

It should be noted that phase does not represent time in the model but represents change in the measurement methodology and oil source in two phases of the study that are not separated in the observation data set. The computed mixed-model for each trace element examines the effect of sulfur content on trace elements and the random effect introduced by changing the measurement laboratories and oil source production regions. The  $p$ -values and  $R^2$  of the mixed-model were calculated, and the results are shown in Table 9. Calculated  $p$ -values for the fixed factor (sulfur) show the correlations between sulfur and Ni, Mn, and Se are significant at a 0.95 interval level (i.e.,  $p$ -value < 0.05). In those cases, however, the correlation is weak. All other trace elements show no statistically significant relationship with sulfur content, when the random effect of the sampling phases is considered.

**Emission Factors.** Tables 10 and 11 compare the estimated emission factors of trace elements for No. 2 heating oil and No.

Table 10. Comparison of the Calculated Emission Factors (EF, in  $\text{lb}/10^6 \text{ gal}$ )<sup>a</sup> for No. 2 Heating Oil from Current Study, USEPA AP-42,<sup>18</sup> and USEPA MATS<sup>47</sup>

trace element	Phase I	Phase II	AP-42	AP-42 EF rating	MATS
Co					2.39
As	0.02	0.09	0.6	E	0.36
Hg	0.01	<0.07	0.4	E	0.02
Se	0.03	0.09	2.0	E	0.28
Sb		1.72			4.62
Sb*		1.50			
Mn			0.8	E	1.32
Ni	0.02	0.95	0.4	E	48.4
Ni*		0.59			
Pb			1	E	1.82
V		0.10			
Zn	0.10	0.21	0.6	E	

<sup>a</sup>Note: Conversions from concentration (ppb) to EF ( $\text{lb}/10^6 \text{ gal}$ ) for the Phase I and II analytical results were made by assuming an oil density of  $845 \text{ kg}/\text{m}^3$  ( $7.05 \text{ lb}/\text{gal}$ ) and a heating value of  $140 \text{ MMBtu}/10^3 \text{ gal}$ . The heating value of  $140 \text{ MMBtu}/10^3 \text{ gal}$  was also used for AP-42 and MATS conversions (taken from pp 1.3–8 of ref 18).

6 residual oil based on the findings in both phases of this study along with their corresponding USEPA AP-42 emission factors<sup>18</sup> and emission factors presented by USEPA in the

Table 9. Mixed-Effect Model Regression Analysis Results

mixed-model parameters		elements (response variable)									
		Co	As	Se	Sb	Mn	Ni	Pb	V	Zn	Hg
random factor (phase)	$p$ -value	0.80	0.020	1.000	0.600	0.040	1.000	0.700	1.000	0.800	0.070
	$R^2$	0.03	0.00	0.037	0.04	0.14	0.03	0.00	0.012	0.02	0.196
fixed factor (sulfur)	$p$ -value	0.589	0.748	0.005	0.510	0.018	0.008	0.933	0.094	0.736	0.600

**Table 11. Comparison of the Calculated Emission Factors (EF, in lb/10<sup>6</sup> gal)<sup>a</sup> for No. 6 Residual Oil from Current Study, USEPA AP-42,<sup>18</sup> and USEPA MATS<sup>47</sup>**

trace element	Phase I	Phase II	AP-42	AP-42 EF rating	MATS
Co	8.79	15.6	6.02	D	2.57
As	1.36	37.9	1.32	C	0.38
Hg	0.02	2.51	0.113	C	0.02
Se	0.95	15.6	0.683	C	0.30
Sb		9.89	5.25	E	4.95
Mn	22.4	7.99	3.00	C	1.41
Ni	134	103	84.5	C	51.9
Pb	1.49	12.8	1.51	C	1.95
V	23.4	49	31.8	D	
Zn	15.5	445	29.1	D	

<sup>a</sup>Note: Conversions from concentration (ppb) to EF (lb/10<sup>6</sup> gal) for the Phase I and II analytical results were made by assuming an oil density of 944 kg/m<sup>3</sup> (7.88 lb/gal) and a heating value of 150 MMBtu/10<sup>3</sup> gal. The heating value of 150 MMBtu/10<sup>3</sup> gal was also used for the MATS conversions (taken from pp 1.3–8 of ref 18).

supporting documentation for its power plant Mercury and Air Toxics Standards (MATS) rule.<sup>47</sup> In the case of No. 2 heating oil, the Hg content of all samples was below the detection limit in Phase II, which suggests the emission factor cannot be greater than 0.07 lb/10<sup>6</sup> gal. This is consistent with Phase I Hg results, and is well below the USEPA AP-42 factor. When emission factors were calculated in Phase I for other trace elements (As, Se, Ni, Zn), the corresponding Phase II results indicated higher concentrations. However, more than 50% of the No. 2 heating oil samples did not have detectable levels of trace elements above the MDL, with the exceptions of Ni and Sb. This finding would distort the emission factor calculations.

Tables 10 and 11 show USEPA AP-42 emission factor ratings, which are engineering judgments indicting the perceived reliability, or robustness, of a factor. An AP-42 rating is based on the quality of the experimental data and theoretical methods used to derive the factor. The highest quality factor is rated as “A”, while the lowest is assigned an “E”.<sup>18</sup> Table 10 shows that all USEPA AP-42 emission factors for No. 2 heating oil are of the E rating, which indicates a low level of reliability. Therefore, it is not surprising that there are large differences between the current study results and the USEPA AP-42 data set.

Table 11 shows that emission factors for No. 6 residual oil are of generally higher quality than the No. 2 heating oil factors. However, all factors have a “C” or lower rating, which also makes differences between the current research results and the USEPA data set not unexpected.

As shown in Table 10 for No. 2 heating oil, all emission factors computed from the Phase II analysis are lower than their corresponding USEPA AP-42 and MATS emission factors, with the exception of nickel, which is about twice the AP-42 factor but an order of magnitude lower than with MATS. The Phase I results for Ni, however, are 20 times lower than the AP-42 factor. In comparison, Rising et al.<sup>22</sup> reported an average of 28.9 ppm of Ni in No. 2 distillate oil samples collected at 13 different gas turbine installations in 10 U.S. states. The Ni in the samples ranged from 0 μg/kg (0.2 μg/kg MDL) to 185 μg/kg. The Phase I and II results are within the range reported by Rising et al.,<sup>22</sup> with the Phase I Ni average at the lower end of the range, and the Phase II Ni average at the higher end. Outliers are not unexpected in field studies and further

sampling and analysis is recommended to better quantify the impact of outliers on the emission factors calculated based on the mean values.

For the No. 6 residual oil emission factors in Table 11, our Phase II results generally are higher than our Phase I results, except for Mn and Ni. The Phase II results are uniformly higher than the USEPA AP-42 and MATS emission factors. While the Phase I results are lower than in Phase II, they also tend to be higher than the USEPA AP-42 and MATS factors, with the exceptions of Hg, Pb, V, and Zn. The general tendency of the Phase I and II emission factors derived from trace element fuel content to be lower than the postcombustion-based USEPA AP-42 and MATS emission factors is consistent with the expectation that other factors occurring during and after combustion can deplete trace element concentrations measured at the stack.

## CONCLUSION

This fuel oil analysis provides an estimate of the trace elemental composition of No. 2 heating oil collected at fuel oil distribution terminals across NYS and surrounding states. The research was conducted in two phases (2008–2009 and 2015–2016) to investigate changes in trace element composition of the fuels in time. The elemental analysis included sulfur content and the trace elements Hg, V, Mn, Co, Ni, Zn, As, Sb, Se, and Pb. In addition, in Phase II of the study, the nitrogen content of the fuel samples was measured. Analytical results were used to calculate values and compare them with USEPA emission factors.

For No. 2 heating oil, the Hg content in all of the analyzed samples in Phase II was below the method detection limit of 10 μg/kg, which is consistent with the low Hg levels measured in Phase I, as well as with what has been reported in other studies. Collectively, these studies consistently find lower Hg levels in No. 2 heating oil than would be estimated using the USEPA AP-42 Hg emission factor for distillate oil. For the other trace elements (As, Se, Ni, Zn) whose emission factors in No. 2 heating oil were calculated in Phase I, fuel oil analysis indicated higher concentrations in Phase II than in Phase I. Of particular note, Ni levels in No. 2 heating oil were higher than Phase I results by greater than an order of magnitude, but we note that results from both phases were within the range of Ni levels measured in No. 2 distillate oil samples collected in 10 U.S. states.<sup>22</sup> All emission factors derived in this study for No. 2 heating oil, except for Phase II Ni, were lower than USEPA AP-42 emission factors. Of important significance is the difference between the USEPA AP-42 mercury emission factor for No. 2 fuel oil and the Hg factor deduced from the two phases of this study. The lower mercury content measured in heating oil used in NYS and the northeastern U.S. indicate that heating oil combustion in the region is a much lower source of mercury emissions to the air than would be inferred from an emission inventory developed using the standard USEPA AP-42 factor for No. 2 fuel oil.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.7b02404.

Tables listing sampling locations for No. 6 residual oil, method detection limit for No. 6 residual oil analysis,

summary of test results in NYS fuel samples for No. 6 residual oil ([PDF](#))

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors thank Jason Rudokas of NESCAUM and Leiran Biton, USEPA, for helpful comments and review of the analysis approach. This research was supported by the New York State Energy Research and Development Authority (NYSERDA) under Agreement Nos. 10049 and 59811. Any opinions expressed in this article do not necessarily reflect those of NYSERDA or the State of New York, and reference to any specific product, service, process, or method does not constitute an implied or expressed recommendation or endorsement of it.

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