

**DETERMINATION OF SULFUR AND TOXIC METALS  
CONTENT OF DISTILLATES AND RESIDUAL OIL IN  
THE STATE OF NEW YORK**

**FINAL REPORT 10-31  
DECEMBER 2010**

**NEW YORK STATE  
ENERGY RESEARCH AND  
DEVELOPMENT AUTHORITY**

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Final Report

Prepared for the  
**NEW YORK STATE  
ENERGY RESEARCH AND  
DEVELOPMENT AUTHORITY**



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## ABSTRACT AND KEYWORDS

Trace elements, including mercury, lead and arsenic, pose significant public health risk due to inhalation toxicity or carcinogenicity of certain compounds containing these elements. Recent studies of crude oil in North American markets have shown mercury levels to be substantially lower than those used in emission factors for distillate and residual oils. While mercury emissions may be lower than previously estimated, nickel and vanadium from oil combustion are rising in concern. Recent research is suggesting an association between nickel and vanadium concentrations in fine particulate matter and average daily mortality risk.

This work was undertaken to determine whether or not available emission factors for oil are appropriate for use to develop trace elemental emissions inventories in New York State. The substantial market for both oils in the Northeast, particularly in the New York City area, supports a measurement campaign to better understand the emissions potential for mercury and other trace elements that may be of concern. Trace elemental profiles from in-use oils could also prove useful to scientists performing source apportionment analysis of fine particulates (PM<sub>2.5</sub>).

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 sulfur content and trace elements. The elemental analysis (vanadium, manganese, cobalt, nickel, zinc, arsenic, antimony, selenium, lead, mercury) employed a standard instrumental technique capable of detecting trace elements down to a few parts per billion in a sample. Even so, a number of samples contained mercury below the detection limits of the instrument, so a subset of samples were analyzed for mercury using a more sensitive technique. In general, the trace elemental composition of light distillates appears to be somewhat lower than standard emission factors given in compilations by the U.S. Environmental Protection Agency. 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 in New York State to better understand the relative importance of different sources of trace elements in the overall emissions inventory.

**Keywords:** heating oil, distillate oil, residual oil, biodiesel, ultra-low-sulfur diesel, mercury, nickel, vanadium, sulfur, trace elements, metals, emission inventory

## **ACKNOWLEDGEMENTS**

For their many contributions in developing the scope of this project, NESCAUM thanks Ray Albrecht, P.E. (NYSERDA-retired), Ned Bulmer (Irving Oil), Bernie Kelly (Global Companies, LLC), and Steven Levy (Sprague Energy Corp.). We particularly thank the fuel oil distributors Global Companies LLC, Irving Oil, and Sprague Energy Corp. for providing support and fuel oil samples for elemental analysis. NESCAUM also thanks the New England Fuel Institute and the National Oilheat Research Alliance for helpful comments and advice in developing the project design.

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## EXECUTIVE SUMMARY

Policy-makers rely on air emission inventories as a primary tool for air quality management. The quality of their decisions, however, is a direct reflection of the quality of the underlying inventories. Therefore, maintaining high-quality emissions inventories represents a major priority for informed decision making. Research results presented in this report provide up-to-date trace elemental composition of fuel oils currently used in New York State as well as the northeastern United States. This information improves the understanding of the relative importance of oil combustion in regional emissions inventories for the analyzed elements, which are mercury, lead, arsenic, nickel, vanadium, cobalt, manganese, zinc, antimony, and selenium, along with fuel oil sulfur content.

### **Fuel Oil Consumption and the Public Health Context**

About 6.4 million households in the northeastern United States rely on home heating oil for heating needs, representing about 80% of the total U.S. households dependent upon home heating oil as their primary heating fuel, which is much higher than the 2005 national average of 7% (EIA 2010a). According to the Energy Information Administration (EIA), 82% of all residential fuel oil sales in 2008 occurred in the Northeast,<sup>1</sup> comprising about 3.8 billion gallons of heating oil sold to residential consumers (EIA 2010b). Note that this does not include heating oil sales to apartment and other large multi-family buildings; the EIA attributes heating oil sales to these residential buildings under the commercial rather than residential sector.

The top consuming state for home heating oil in the United States is New York State (23.5% of the sales), followed by its neighboring states Massachusetts, Pennsylvania, Connecticut and New Jersey (EIA 2009). In 2008, New York consumers bought a little over one billion gallons of home heating oil (No. 2 distillate fuel oil), or over one-fifth of all home heating oil sold for residential use in the entire United States (EIA 2009).

### ***Sulfur***

Sulfate formed in the atmosphere from sulfur dioxide (SO<sub>2</sub>) emissions when heating oil and other fossil fuels are burned is an important contributor to ambient fine particulate matter (PM<sub>2.5</sub> – particulate matter with a diameter less than 2.5 microns). These small particles can penetrate deeply into the lungs, thus potentially serving as a vector for delivering toxic metals and other hazardous air pollutants into the body. Adverse health impacts due to PM<sub>2.5</sub> inhalation range from minor irritation to chronic disease, to even death.

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<sup>1</sup> For purposes of this comparison, the Northeast region includes the District of Columbia and the states of Connecticut, Delaware, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island, and Vermont.

The overall mass of PM<sub>2.5</sub> in New York, New Jersey, and the New England states is typically comprised of at least 40% sulfate, but sulfate can make up to two-thirds of the total mass on the highest PM<sub>2.5</sub> days (NESCAUM 2006). Due to the linear relationship between the sulfur content of fuel oil and SO<sub>2</sub> emissions, lowering the sulfur content of fuel oil can have significant impacts on SO<sub>2</sub> emissions and PM<sub>2.5</sub> formation.

### ***Mercury in Oil***

Deserving special mention is mercury emitted from fuel oil combustion. Once in the atmosphere, mercury 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, mercury can be converted to methylmercury, a particularly toxic form of mercury. Methylated mercury in the aquatic food chain bioaccumulates in fish tissue to concentrations markedly higher than in the surrounding water.

Mercury is a potent neurotoxin in humans that is particularly damaging to the fetus and young child. A major route of exposure to mercury is through the eating of fish. Women of child bearing age are of special concern as methylmercury ingested by a mother can transport across the placenta into the brain of a developing fetus. In young children and fetuses, methylmercury inhibits the normal development of the nervous system, an effect that may occur even at low exposure levels. This damage frequently 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 (USEPA 1997). Women in the Northeast have the highest mercury exposure in the U.S., with 19% exceeding blood organic mercury level considered safe for fetuses (Mahaffey et al. 2009).

Most of the mercury present in water bodies – and the fish within them – in New York State and the Northeast is deposited from the atmosphere (NESCAUM 2008). Atmospheric emissions of mercury come mainly from combustion sources including electric utility, industrial, commercial, and institutional boilers and municipal waste and sewage sludge incinerators. The mercury in combusted fossil fuels originates primarily from petroleum and coal. The U.S. Environmental Protection Agency (USEPA) Mercury Study Report to Congress (USEPA 1997) determined that the coal combustion in utility boilers constituted the largest source category for atmospheric mercury and also indicated there were, at the time, insufficient data and information available to estimate the amount of mercury emissions that result from the combustion of liquid fossil fuels, such as home heating oil and diesel.

To address mercury in the environment and its threat to human health, New York State and surrounding states have established a regional Total Maximum Daily Load (TMDL) for mercury under the federal Clean Water Act. The regional mercury TMDL was set at a level that would decrease mercury levels in fish tissue low enough for states to lift their fish consumption advisories. To achieve the regional TMDL, it is projected that atmospheric deposition must be reduced up to 98% from 1998 levels (NEIWPCC 2007). This

demonstrates a specific need to identify the major mercury air emission sources contributing to deposition in New York State and the surrounding region so that public health and air quality planners can efficiently expend limited resources to target the highest priority source sectors.

Inventory analysis identified residential fuel oil combustion as an important contributor to the mercury emissions in the region (NESCAUM 2005). When added to estimated mercury 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 USEPA AP-42 database (USEPA 1998). Emerging research on the mercury content of crude oil suggests much lower emissions from petroleum fuels. This indicates a need to update the mercury emission factors for fuel oils in New York State and the Northeast to provide a firmer basis for informed decision making. The work presented in this report seeks to address this information need.

### ***Other Trace Metals in Oil***

The sampling and analysis done to improve the level of knowledge for mercury in New York State's fuel oils also provides an opportunity to improve understanding of other important trace metals in fuel oils. Combustion of heating oil by necessity is co-located with residential areas. Human exposure to toxic metals emitted during oil combustion will be relatively greater in areas where large amounts of heating oil are burned, such as in New York State and other areas of the Northeast. The uncertainty in emissions of toxic metals from oil combustion, however, can hinder assessments of public exposure to these air pollutants.

As an example, New York University researchers have implicated nickel and vanadium emissions from oil combustion with an increased risk in daily mortality (Lippmann et al. 2006). In the U.S., No. 6 residual oil combustion is the largest source of these emissions, with No. 2 distillate fuel oil having less of an impact. Improved knowledge on fuel content of these and other trace elements helps address and anticipate information needs as the health science of metals from petroleum combustion evolves.

A further area investigated in this work is the potential relationship trace elements may have with differing fuel sulfur contents (e.g., ultra-low-sulfur diesel, biodiesel, No. 6 residual oil). Specifically, as regulatory requirements are implemented to require increasingly lower sulfur levels in petroleum fuels, we seek to answer whether mercury and other trace elements may predictably change (increase or decrease) in response to changes in the refining process to remove sulfur.

### **Summary of Fuel Oil Sampling Results**

Working with major oil distributors in the New York State market, samples of various oil grades were collected, including home heating oil, biodiesel, onroad diesel, and residual oil. Samples were analyzed for

sulfur content and the trace elements mercury (Hg), vanadium (V), manganese (Mn), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), antimony (Sb), selenium (Se), and lead (Pb).

A total of 137 fuel samples were collected and analyzed from fuel oil terminals in Albany, the Bronx, and Long Island, NY; and Revere and Quincy, MA, along with another 36 duplicate samples that were taken from the same storage tank, but collected, shipped, and analyzed separately. The results for distillates (home heating oil and diesels) and heavier residual oil (typically used in electric generating units and large industrial, commercial, and institutional boilers) are displayed in Table ES-1. Also included for comparative purposes are the emission factors and derived fuel oil concentrations of mercury and other trace elements based on U.S. Environmental Protection Agency’s (USEPA’s) “AP-42” emission factors, which are the emission factors compiled by the USEPA and widely used for emissions inventory estimates.

In general, the trace elemental composition of light distillates appears to be 5-to-69 times lower than estimates based on the USEPA’s AP-42 emission factors. The trace elemental composition of residual oil typically 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.

**Table ES-1. Comparison of Emission Factors (EF) and Concentrations of Trace Elements for Distillate and Residual Fuel Oils**

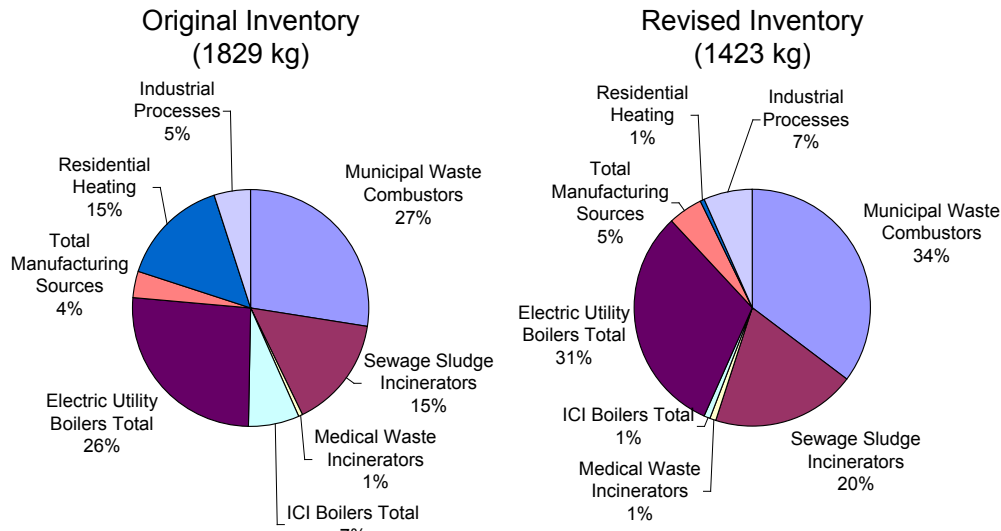
Trace Element	#2 Distillate Oil				#6 Residual Oil			
	NESCAUM		AP-42		NESCAUM		AP-42	
	EF lb/10 <sup>6</sup> gal	Conc. ppb	EF lb/10 <sup>6</sup> gal	Conc. ppb	EF lb/10 <sup>6</sup> gal	Conc. ppb	EF lb/10 <sup>6</sup> gal	Conc. ppb
<b>V</b>			n/a	n/a	23.4	2,967	31.8	4,025
<b>Mn</b>			0.83	120	22.5	2851	3	380
<b>Co</b>			n/a	n/a	8.79	1113	6.02	762
<b>Ni</b>	0.0224	3.2	0.42	60	134	16,988	84.5	10,696
<b>Zn</b>	0.104	14.8	0.56	80	15.5	1,963	29.1	3,684
<b>As</b>	0.0147	2.1	0.56	80	1.36	172	1.32	167
<b>Se</b>	0.0303	4.3	2.08	295	0.945	119	0.683	86
<b>Sb</b>			n/a	n/a	70.1	8,873	5.25	665
<b>Hg</b>	0.014	2.0	0.42	60	0.016	2	0.113	14
<b>Pb</b>			1.25	179	1.49	188	1.51	191

*Note:* The blank entries indicate where samples had no detectable levels above the minimum detection limit.

### Mercury

The mercury levels found in this study are substantially below those in previous inventory estimates in New York State. A comparison of emission factors and concentrations from this study and the USEPA AP-42 factors for #2 and #6 fuel oils are given in Table ES-1. Based on this study’s findings, the mercury emissions estimates for these source categories in New York State could be overestimated by a factor of 30 for #2 distillate oil (e.g., home heating oil) and by a factor of seven for #6 residual oil.

In order to illustrate the impact that the results from this work have on emissions inventory data, we revisited the 2002 mercury inventory for New York State. NESCAUM previously updated a baseline 1996 anthropogenic mercury emissions inventory for the State of New York to the year 2002 (NESCAUM 2005). In the 2002 inventory, the USEPA AP-42 emission factors were employed to estimate the emissions from the oil combustion source categories, including industrial/commercial/institutional (ICI) oil-fired boilers, electric utility oil-fired boilers, and residential heating from distillate heating oil. Figure ES-1 presents the previous and revised 2002 New York State mercury emissions contributions by sector that reflects the change in fuel oil mercury emissions obtained from the fuel oil sampling results.



**Figure ES-1. General Source Category Contributions to the 2002 New York State Anthropogenic Mercury Emissions Inventory.**

When adjusting the 2002 New York State inventory estimates using the emission factors determined in this work, the contributions of residential heating and ICI boilers to the overall state-wide mercury emissions drop from 15% and 7%, respectively, to only 1%. These adjustments make the contributions from the other source categories relatively more significant; for example, the emissions from sewage sludge incineration after revision represent 20% of the entire inventory rather than 15% in the original inventory. Municipal waste combustors continue to contribute the largest share of mercury air emissions in New York State, increasing from 27% to 34% of total state-wide emissions when the fuel oil combustion contributions are adjusted to reflect the observed lower mercury content in fuel oil. Note that although the emission estimate of oil-fired electric utility boilers was adjusted, the majority of mercury emissions from electric utility boilers in New York State are from coal-fired boilers, so the total contribution from all electric utility boilers actually becomes relatively more significant after the revisions.

### **Sulfur**

In this study, testing results found average concentrations of sulfur from the set of obtained home heating oil samples to be 2000 parts per million (ppm) and residual oil 50% greater (Table ES-2). Ultra-low-sulfur

measurements were approximately six ppm and biodiesel somewhat higher at 27 ppm, consistent with previously reported values.

The fuel oil testing results found no strong relationship between the concentration of any trace element and the sulfur content of the fuel sample. On a more macroscopic scale, the trace element concentrations in residual fuel oil are generally at least an order of magnitude higher than in distillate heating oil and diesel. Mercury is the exception, as it appears to be at comparable and relatively low levels in #2 distillate and #6 residual oils.

**Table ES-2. Sulfur (S) Content in Fuel Oil Samples**

Type (n)	Metric	S Content (ppm)
<b>Home Heating/ Diesel (102)</b>	maximum	2899
	minimum	807
	average	1998
	median	1920
<b>Residual (16)</b>	maximum	3860
	minimum	2780
	average	3020
	median	2970
<b>Ultra-low Sulfur (11)</b>	maximum	8
	minimum	<3 (1)
	average	5.6
	median	5
<b>Bio-diesel (8)</b>	maximum	84
	minimum	4
	average	27.3*
	median	30.5

Note: Parentheticals in the table represent the number of samples obtained or that were used to calculate a particular value.

\*Averages calculated by substituting half the instrumental minimum detection limit for samples below the limit.

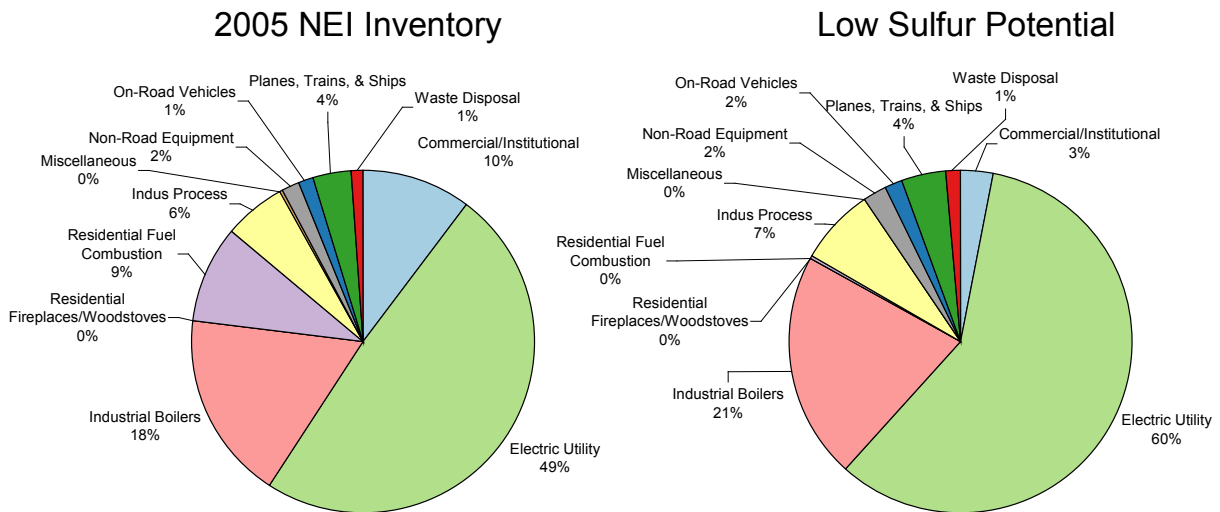
Analysis of biodiesel constitutes one novel result for this study as this fuel represents an emerging market. Based on the results, biofuel appears to have similar composition to ultra-low-sulfur diesel with trace elemental composition at or below that determined for home heating oil. Its sulfur level, however, appears on average to be higher than ultra-low-sulfur diesel, based on these limited samples and findings from other more extensive studies. Current USEPA regulations require all diesel fuel (highway and nonroad) meet a 15 ppm level as of June 2010 (Federal Register 2006). Refined levels in ultra-low-sulfur diesel may need to be as low as five ppm to assure product at the pump meets the 15 ppm requirement. The fuel sampling results in New York State indicate that biodiesel in and of itself may not necessarily be below ultra-low-sulfur diesel regulatory levels if not subject to the same regulatory or certification requirements. Such certification is possible, with the biodiesel industry having developed a voluntary fuel accreditation program called BQ-9000 that includes certification testing for 15 ppm (as well as 500 ppm) sulfur content



in pure (100%) biodiesel (National Biodiesel Board 2008). Accreditation under the BQ-9000 program requires that the fuel must meet the biodiesel certification levels established by the industry standard method ASTM D6751 (ASTM International 2010).

Recently passed legislation in New York State mandates that all No. 2 distillate home heating oil meet the same ultra-low-sulfur fuel standard (15 ppm) as highway and nonroad diesel fuel by July 2012. This law carries significant public health, environmental, and other benefits (Batey and McDonald 2005). SO<sub>2</sub> and PM<sub>2.5</sub> emissions will be drastically reduced; for example, the annual SO<sub>2</sub> emissions from the residential home heating sector in New York are estimated to decrease to about 150 short tons SO<sub>2</sub>, which corresponds to a 99% reduction from 2005 levels. This would diminish the residential sector's share of the statewide SO<sub>2</sub> emissions inventory from 9% in 2005 to well less than 1% after the law is fully implemented.

Figure ES-2 illustrates the potential impact that using ultra low sulfur fuels in the residential and commercial/institutional sectors has on the overall SO<sub>2</sub> emissions inventory for New York State. This figure shows the 2005 SO<sub>2</sub> emissions by sector from USEPA's National Emissions Inventory (NEI) (left side) and the potential reduction in SO<sub>2</sub> emissions if ultra-low-sulfur fuel was used in the residential and commercial/industrial sectors (right side). Other air pollutants, such as oxides of nitrogen (NO<sub>x</sub>) and carbon dioxide (CO<sub>2</sub>), will decrease as well as the boilers and furnaces will operate more efficiently on ultra-low-sulfur oil. This also has the added benefit of requiring less equipment service, thus lowering the costs for maintenance.



**Figure ES-2. General Source Category Contributions to the 2005 New York State Sulfur Dioxide Emissions Inventory and Low Sulfur Potential.**

### Implications and Future Directions

With the information presented here specific to New York State and the region, air quality program managers can factor into their work improved inventory estimates of mercury and other trace metal emissions. Because these inventories form the basis for decisions, either by direct analysis or use in air

quality modeling exercises, they require a reasonable degree of accuracy. Results for mercury, in particular, demonstrate the need to continually review and reassess available emission factors and associated emissions estimates. Improved estimates can be applied toward prioritization of control strategies as New York State addresses its regional goal of significantly reducing mercury releases and deposition from air into water bodies of the state and region. In addition, the measurements of other trace elements provide a firmer foundation going forward in evaluating potential public exposure and source contributions to these elements as scientific understanding of their public health and ecological impacts evolve (e.g., nickel and vanadium).

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## **SECTION 1**

### **INTRODUCTION**

#### **Purpose of Assessment**

The purpose of this project is to assess the contents of mercury (Hg) and other trace elements including lead (Pb), arsenic (As), nickel (Ni), vanadium (V), cobalt (Co), manganese (Mn), antimony (Sb), selenium (Se), and zinc (Zn) as well as sulfur (S) in fuel oil used in New York State and the neighboring region. This will assist the region in better understanding the relative contributions of the source category to overall trace element emissions. The data can also be useful in assessing exposures to emissions that may have detrimental human health impacts.

About 6.4 million households in the northeastern United States rely on home heating oil for heating needs, representing about 80% of the total U.S. households dependent upon home heating oil as their primary heating fuel. According to the Energy Information Administration (EIA), 82% of all residential fuel oil sales in 2008 occurred in the Northeast, comprising about 3.8 billion gallons of heating oil sold to residential consumers (EIA 2010a). The top consuming state for home heating oil in the United States is New York State, followed by its neighboring states Massachusetts, Pennsylvania, Connecticut and New Jersey. In 2008, New York consumers bought a little over one billion gallons of home heating oil (No. 2 distillate fuel oil), or over one-fifth of all heating oil sold in the entire United States (EIA 2009).

Combustion of heating oil by necessity is co-located with residential areas. As a result, human exposure to toxic metals from oil combustion can be relatively greater in areas where large amounts of heating oil are combusted, such as in New York State and other areas of the Northeast. The uncertainty in emissions of toxic metals from heating oil, however, can hinder assessments of public exposure to these air pollutants. The work described in this report seeks to address these data gaps through representative sampling of heating oil streams at various distribution points in New York State and adjoining areas. A special emphasis is placed on measuring the Hg content in heating oil due to public and ecological health concerns over eating fish that have high Hg levels as a result of atmospheric deposition.

#### **Background on Mercury**

Mercury is 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, a particularly toxic form of Hg. Methylated Hg in the aquatic food chain can bioaccumulate in fish tissue to concentrations markedly higher than in the surrounding water.

Mercury is a potent neurotoxin, particularly damaging to the fetus and young child. A major route of exposure to Hg in humans is through the eating of fish. Women of child bearing age are of special concern as methylmercury ingested by a mother can transport across the placenta into the brain of a developing fetus. In young children and fetuses, methylmercury inhibits the normal development of the nervous system, an effect that may occur even at low exposure levels. This damage frequently 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 (USEPA 1997a).

Women in the Northeast have the highest Hg exposure in the U.S., with 19% exceeding blood organic Hg level considered safe for fetuses (Mahaffey et al. 2009). This translates into over 84,000 newborns in the Northeast at risk for irreversible neurological deficits from exposure to Hg in the womb. Emerging data also suggest a link between Hg exposure and increased risk of adverse cardiovascular effects (Salonen et al. 2000; Mozaffarian and Rimm 2006). Further, previous analyses confirmed that eating mercury-contaminated fish and shellfish is the primary route of accumulating blood organic Hg for most people (Mahaffey et al. 2004). Humans are not the only ones at risk; Hg also threatens fauna at the top of food chain. Birds, such as common loons, and mammals, such as otters, that eat the fish can also have high levels of Hg in their bodies.

Most of the Hg present in water bodies – and the fish within them – in New York State and the Northeast is deposited from the atmosphere (Bookman et al. 2008; NESCAUM 2008). Atmospheric emissions of Hg come mainly from combustion sources including electric utility, industrial, commercial, and institutional boilers and municipal waste and sewage sludge incinerators. The Hg in combusted fuels originates primarily from petroleum and coal. The USEPA Mercury Study Report to Congress (1997a) determined that the coal combustion in utility boilers constituted the largest source category for atmospheric Hg and also indicated there were, at the time, insufficient data and information available to estimate the amount of Hg emissions that result from the combustion of liquid fossil fuels.

Given recent measurements showing elevated Hg levels in freshwater fish, New York State and many other states have issued health advisories that recommend limiting the consumption of fish from state water bodies (NYS DOH 2010; USEPA 2010a). This is the best immediate approach for limiting exposure to Hg that is already present in the environment. Because it is believed that about 80-90% of atmospheric Hg deposition in New York State arises from out-of-state sources, including a major portion from sources outside the U.S. (NYSERDA 2002; 2005; Seigneur et al. 2003; 2004), broad regional as well as international efforts will be needed to reduce continuing Hg deposition to New York State water bodies. While this is a daunting challenge, studies have found that, depending on the characteristics of a given watershed, the availability of mercury for uptake by aquatic biota can decline rapidly within a year of deposition, with previously stored mercury in the watersheds being a relatively small source (Harris et al.

2007; Orihel et al. 2007; Orihel et al. 2008). Several studies have tracked decreases in fish tissue mercury levels correlated with decreases in regional and local mercury emission reductions (MassDEP 2006; Evers et al. 2007). For these water bodies, decreases in mercury air emissions can lead to rapid (years) decreases in mercury fish tissue levels.

While some improvement in Hg content in fish with decreasing emissions has been observed, these results may depend upon type of fish species and water shed characteristics, including land use patterns and changes, organic matter properties, acid/base (pH) levels, bacterial community, and water chemistry (Madison Declaration, 2007). Wide-spread long-term monitoring is expensive, limiting the ability to generalize broadly from results of specific fish tissue sampling studies (NYSERDA 2010). There is limited knowledge on how factors such as climate change and weather extremes (freeze/thaw, drying/saturation, etc.) may affect mercury levels, with modeling of physical attributes (e.g., watershed characteristics and climatic variables) providing only relatively modest predictive power of variance in fish tissue Hg concentrations in lakes and reservoirs (Shanley et al. 2005). For sites that have reported co-located sediment and fish tissue sampling results, no relationship between sediment Hg and fish tissue Hg has been found (Kamman et al. 2005). Sulfate reducing bacteria also play a role in methylating mercury, therefore reductions in emissions of sulfur oxides may influence the rate of Hg release or retention in soils and water bodies and ultimately fish tissue Hg concentrations (Drevnick et al. 2007).

To address Hg in the environment and its threat to human health, New York State 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 New York State 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 (NEIWPC 2007). Subsequently in 2009, New Jersey also received approval from the USEPA for a Hg TMDL in 122 impaired waters within the state that was set at a comparable level to the regional Hg TMDL previously established by New York State and the six New England states (NJ DEP 2009).

As noted above, the dominant source of Hg in surface waters of New York State and other states in the region is from atmospheric deposition, with contributions on the global, regional, and local scales (Bookman et al. 2008; NESCAUM 2008; NYSERDA 2002; 2005; Seigneur et al. 2003). To achieve the regional TMDL, New York State and the other states in the Northeast project that atmospheric deposition needs to be reduced up to 98% from 1998 levels (NEIWPC 2007).

In order to effectively target efforts that can reduce atmospheric deposition of mercury, air quality planners and modelers require accurate inventories of mercury air emission sources (Walcek et al. 2003). An inventory analysis of air emission sources in the Northeast identified residential fuel oil combustion as an important contributor to the Hg emissions in the region (NESCAUM 2005a). 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. The inventory estimates were based on emission factors from the USEPA's AP-42 Compilation of Air Pollutant Emission Factors, commonly referred to as AP-42 (USEPA 1998). This is a comprehensive list of emission factors developed by the USEPA to estimate the quantity of pollutants released into the atmosphere from a given activity. Emission factors from this compilation serve as a primary resource for emissions inventory development in the United States.

In contrast to estimates based on USEPA's AP-42 Hg emissions factor for oil combustion, more recent research on the Hg content of crude oil sponsored by the USEPA and Environment Canada suggests much lower emissions from petroleum fuels (Wilhelm et al. 2007; Environment Canada 2007). These analyses indicate a need to update the Hg emission factors for petroleum distillates.

The Hg emissions from oil combustion in New York State and the Northeast in general are difficult to estimate due to lack of data on concentrations of Hg compounds in liquid fuels. The concentration of Hg in crude oil is highly dependent on geologic location and can vary from 0.01 ppb to 10 ppm by weight (Wilhelm and Bloom 2000). An early estimate by the USEPA of Hg content in distillate oil was given as 120 ppb (USEPA 1997b). This level is much higher than later estimates finding levels below one ppb (Liang et al. 1996; Rising et al. 2004). This report addresses this data inconsistency through direct measurements of representative distillate fuels used in New York State and the Northeast.

While less than 1% of Hg emitted in 2002 was attributed to the combustion of natural gas from all combustion sources (NESCAUM 2005a), it is included in this study because it is a major residential fuel in several states in the Northeast. Therefore, the environmental importance of natural gas combustion cannot be ignored due to its proximity to population. In addition, Hg in natural gas is detrimental from an industrial standpoint. It can cause corrosion of aluminum structures and damage catalytic processes that have lead to expensive plant shut downs (Kinney 1975).

### **Background on Trace Elements and Other HAPs**

Trace elements pose significant public health risk due to inhalation toxicity or carcinogenicity of certain compounds containing these elements. The Clean Air Act Amendments of 1990 listed ten trace element compounds among its 188 hazardous air pollutants (HAPs). The Agency for Toxic Substances and Disease Registry (ATSDR) has developed 302 toxicological profiles including all the trace elements discussed in this report, with some of them updated recently. Much of the information regarding the health effects of trace elements is cited from the ATSDR, unless noted otherwise.

Lead is one of the oldest known environmental toxins (records date back to 4000 years ago), and because it was used in a broad variety of products, humans are still exposed to lead on a daily basis (Florea and Busselberg 2006). It has been studied and regulated extensively. Its health impacts include, but are not



limited to, neurotoxicity, developmental delays, hypertension, impaired hearing acuity, impaired hemoglobin synthesis, and male reproductive impairment (USEPA 2004). Children are more vulnerable to lead poisoning, and a bigger proportion of swallowed lead can enter the blood in children than in adults (ATSDR 2007a).

Inorganic arsenic has been recognized as a human poison since ancient times. Small oral doses may lead to stomachache, nausea, vomiting, and diarrhea, while large doses can result in death. Breathing high levels of arsenic in the air is likely to lead to a sore throat and irritated lungs (ATSDR 2007b).

Recent research suggests an association between nickel and vanadium concentrations in fine particulate matter and average daily mortality coefficients, with residual oil combustion being an important emissions source for these elements (Lippmann et al. 2006). A study in New York City suggested that increases in ambient levels of nickel and vanadium from residual heating oil and/or traffic may be associated with respiratory symptoms among very young children (Patel et al. 2009). ATSDR (2005a) reported that the most serious harmful health effects from exposure to nickel, such as chronic bronchitis and reduced lung function, have occurred in people who have breathed dust containing certain nickel compounds while working in nickel refineries. The levels of nickel in these workplaces, however, were much higher than usual levels in the environment. The most common harmful health effect on nickel in humans is an allergic reaction. ATSDR (2009) reported that breathing high levels of vanadium caused irritated lungs and eyes that can persist for days to weeks. Vanadium and vanadium compounds are hazardous, with the oxidized form of vanadium, vanadium pentoxide, more toxic than the elemental form (Moskalyk and Alfantazi 2003). A study on urban particles around Seville, Spain determined that vanadium, compared to the other metals, had the highest percentage (50.4%) in the soluble and exchangeable fraction, meaning that vanadium is the most available metal to the human body via respiration (Espinosa et al. 2002).

The major sources of lead emissions have historically been motor vehicles (such as cars and trucks) and industrial sources. As a result of the USEPA's regulatory efforts to remove lead from gasoline, levels of lead in the air decreased by 92% between 1980 and 2008 (USEPA 2010b). For New York State in 2002, lead emissions from non-road equipments and electricity generation comprised the top two biggest source sectors, with each contributing about 16 tons per year. The fossil fuel combustion and industrial processes are the third and fourth biggest source sectors, respectively, and each contributed about 12 tons per year. Coal combustion has been identified as the single largest emission source sector of most of the other trace elements except for lead. Emissions from oil combustion are generally small compared with coal, with the exception of the majority of nickel emissions coming from oil combustion (Friedman et al. 1993). While oil-fired power plants and residual oil used in industrial, commercial, and institutional (ICI) boilers and ocean-going vessels are thought to be the primary oil combustion sources for trace element emissions, more information is needed to assess the amount of trace elements emitted into the ambient air through the combustion of heating oil in New York State and the region.

Respiratory effects, such as inflammation of the lungs, chronic bronchitis, and chronic emphysema, are the primary effects noted from chronic (long-term) exposure to antimony in humans via inhalation (USEPA 2000). Acute (short-term) exposure to antimony can result in effects on the skin and eyes. Some antimony compounds have been used as a medicine to treat infection with parasites (ATSDR 1992). While the USEPA has not classified antimony for carcinogenicity, antimony trioxide is a possible carcinogen to humans (IARC 1998).

Unlike other trace elements discussed in this report, cobalt, manganese, selenium, and zinc have both beneficial and harmful effects on human health. They are essential nutrients for normal growth of plants and animals. Ingesting too much, however, can affect health. Some symptoms are cited here for reference. (1) Serious effects on the lungs have been found in people exposed to 0.005 mg/m<sup>3</sup> of cobalt while working with hard metal. The general public, however, is not likely to be exposed to that high level of cobalt dust (ATSDR 2004). (2) The inhalation of a large quantity of dust containing manganese may cause irritation of the lungs that could lead to pneumonia (ATSDR 2008). (3) Chronic inhalation exposure to selenium dioxide or elemental selenium as dust may have respiratory effects such as irritation of the nose, respiratory tract, and lungs, bronchial spasms, and coughing (ATSDR 2003). (4) If large doses of zinc (10-15 times higher than the Recommended Dietary Allowance) are taken by mouth even for a short time, stomach cramps, nausea, and vomiting may occur (ATSDR 2005b).

Of all the elements analyzed in this study, sulfur has the highest prevalence in No. 2 home heating oil. In the past, the average sulfur content of heating oil hovered around 0.25%, or 2500 ppm, although it has varied more in recent years (Batey and McDonald 2005). On average, at least 95% of the sulfur in the fuel converts to sulfur dioxide (SO<sub>2</sub>) upon combustion, so there is a linear relationship between the sulfur content of the fuel and SO<sub>2</sub> emissions (USEPA 1998). The combustion of No. 2 distillate oil in residential and commercial burners and furnaces is the second largest source sector of SO<sub>2</sub> emissions in the NESCAUM region<sup>2</sup> (electric power plants are the largest source sector) at over 120,000 tons per year, or 15% of the regional inventory (NESCAUM 2005b).

Acute exposure to high levels of SO<sub>2</sub> (e.g., 100 ppm) is an immediate danger to health and can be life-threatening; chronic exposure to persistent levels can cause respiratory symptoms and decreased lung function (ATSDR 1998). Upon oxidation (and often association with ammonium), gaseous SO<sub>2</sub> can convert to particle sulfate (NARSTO 2003). In the NESCAUM region, the overall mass of PM<sub>2.5</sub> (particulate matter with a diameter of less than 2.5 microns) is typically comprised of at least 40% sulfate and can be up to two-thirds of the total mass on the highest PM<sub>2.5</sub> days (NESCAUM 2006).

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<sup>2</sup> The NESCAUM region is comprised of the six New England States (Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, and Vermont) plus New Jersey and New York.

Across the region, sulfate is a major component of PM<sub>2.5</sub> during the winter months, when sales of No. 2 distillate fuel oil are at their highest (see the next section). Due to the wintertime meteorology, local sources of sulfate are increasingly important, because winter-time low inversion layers prevent vertical mixing, which inhibits dilution and dispersion of the accumulating pollution. For example, in New York City one third of the total winter-time PM<sub>2.5</sub> mass is urban (local) sulfate (i.e., not from long range transport) (NESCAUM 2006).

Exposure to PM<sub>2.5</sub> is associated with adverse human health effects. Research (including toxicological, clinical, and epidemiological studies) has found links to respiratory and cardiac impacts, from minor irritation to chronic disease. Key health effects studies have also identified a positive relationship between mortality and PM<sub>2.5</sub> (Abbey et al. 1999; Dockery et al. 1993; Lipfert et al. 2000; Pope et al., 1995). PM<sub>2.5</sub> itself is complex in nature, so it is difficult to pinpoint a single component (if one exists) to explain all the health effects observed. Nevertheless, source apportionment based studies tend to identify sulfate-associated sources as the top PM<sub>2.5</sub> source linked to daily mortality (Mar et al. 2006; Thurston et al. 2005). A Boston study determined that individuals with diabetes (which increases cardiovascular risk) are particularly vulnerable to sulfates; the researchers observed endothelium-dependent and -independent vascular reactivity when diabetics exposed to sulfate particle increases (O'Neill et al. 2005).

Recent reports indicate that lowering the sulfur content of home heating oil will significantly reduce the public health and environmental impacts of PM<sub>2.5</sub> at a favorable cost-benefit ratio (Batey and McDonald 2005; NESCAUM 2005b). There are also additional substantial benefits, including reduction of other air pollutants (80% in PM, 10% in NO<sub>x</sub>, 1-2% in CO<sub>2</sub>) and decreased boiler and furnace fouling rates, which translates to significant savings in service costs for the home heating oil customer.

Currently, essentially all highway and nonroad diesel fuel is required by the USEPA to meet the ultra-low-sulfur regulation (maximum content of 15 ppm) (Federal Register 2006). In July 2010, New York adopted a law requiring that all No. 2 heating oil sold in the state contain no more than 15 ppm sulfur as of July 1, 2012 and all No.4 heating oil sold in New York City contain no more than 1500 ppm sulfur as of October 1, 2012. Similar legislation or regulations have already passed in Connecticut and Maine and have been proposed in New Jersey and Pennsylvania (EIA 2010b).

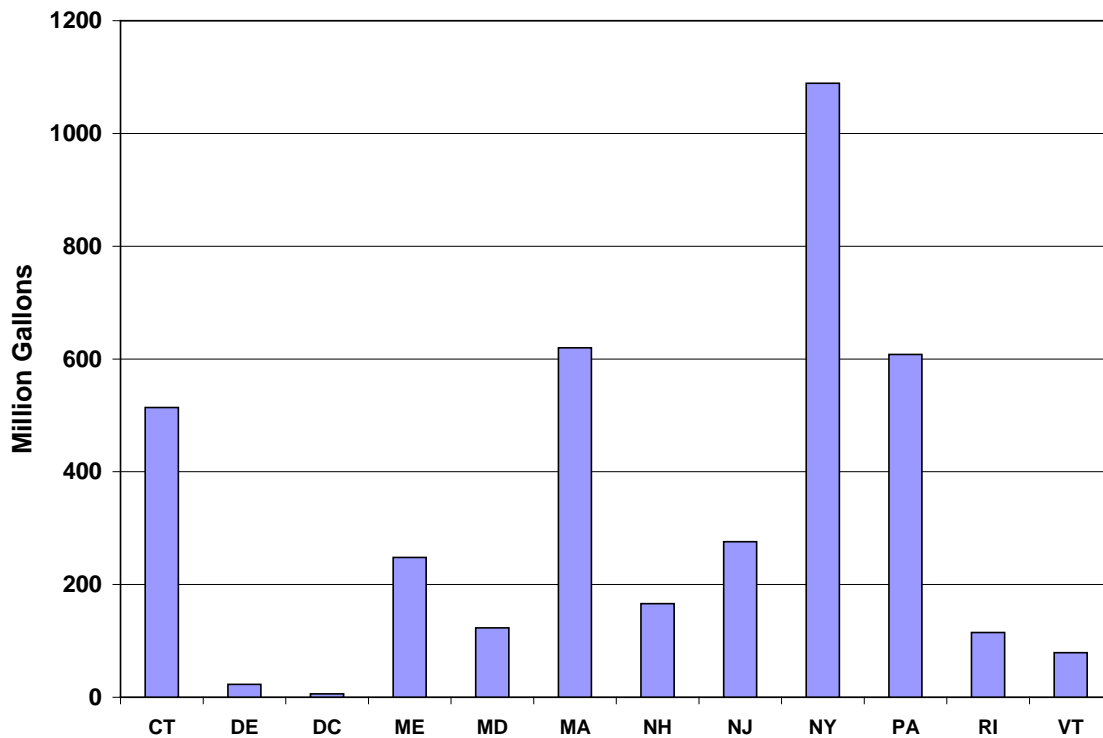
### **Residential Fuel Use in New York State and the Northeast**

In the United States, the majority of home heating oil is used in New York State and neighboring areas of the Northeast. About 82% of residential distillate oil sales in the U.S. in 2008 occurred in the region, and New York State has the highest percentage (23.5%) of sales among all states nationally (EIA 2009). Figure 1-1 gives the amount of fuel oil sales in the Northeast according to jurisdiction.

A prominent feature in the upper Northeast (New Jersey, New York, and New England) is that the share of distillate oil as a home heating fuel is much higher than the 2005 national average of 7% (EIA 2010c). In

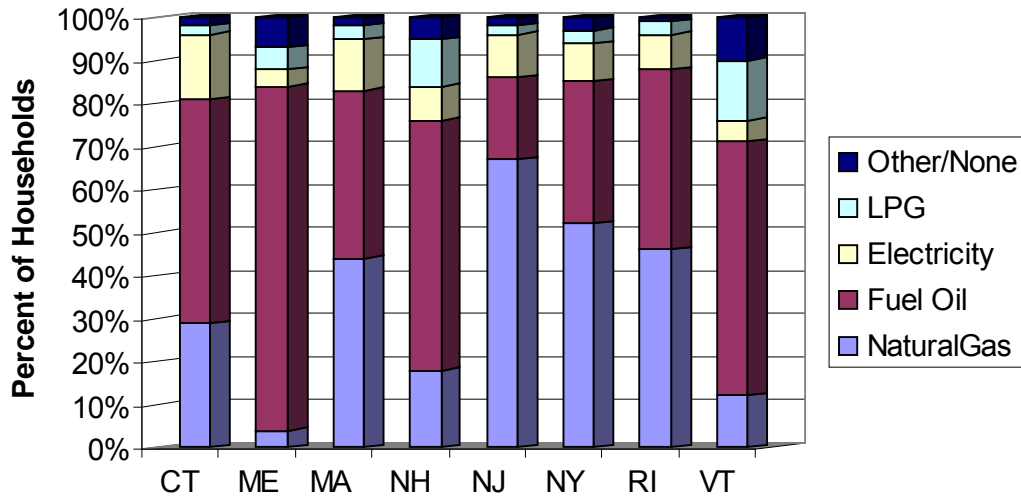
New York State, about 33% of households use fuel oil (EIA 2010d), with an estimated 2.2 million households using fuel oil for home heating in 2001 (NYSERDA 2007). Distillate oil is the primary home heating fuel in Connecticut, Maine, New Hampshire, and Vermont, with shares above 50% (Figure 1-2). The percentages of households that use fuel oil in Massachusetts and Rhode Island are around 40%, close to the share of natural gas.

Natural gas is a primary source of home heating in New York State and New Jersey, with percentage shares above the national average. In New York State, natural gas is used in 52% of homes. The share of households using natural gas as the home heating fuel is below the national average level in the other states, with relatively low use in Maine, Vermont, and New Hampshire (Figure 1-2).



Source: EIA 2009

**Figure 1-1. Residential Distillate Fuel Oil Sales in 2008 in the Northeast.**



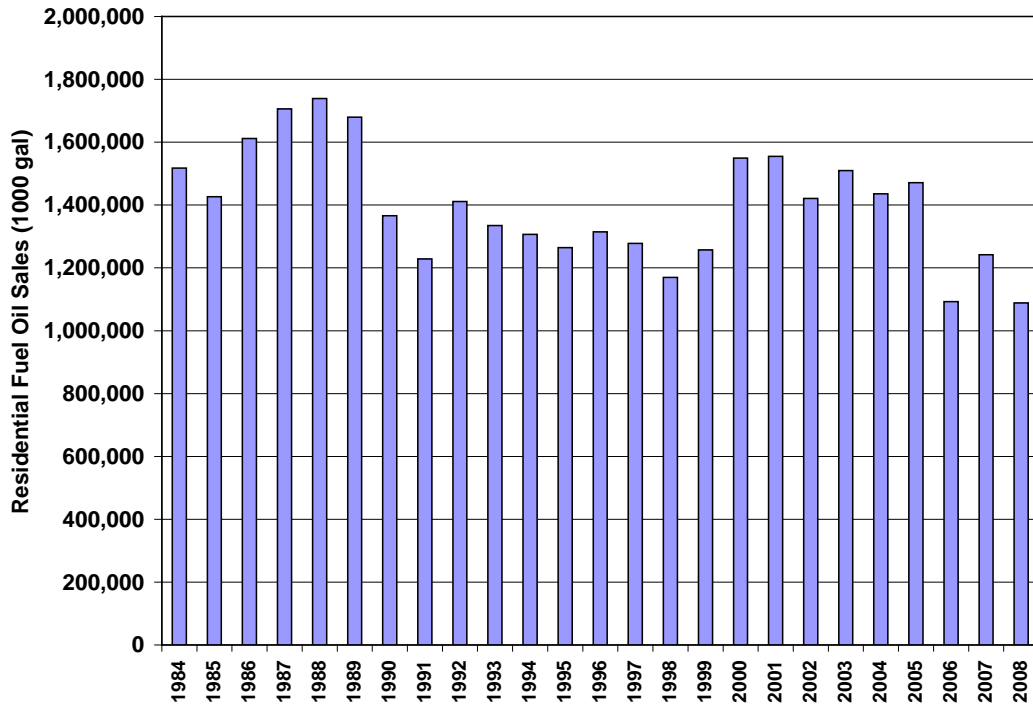
**Figure 1-2. Shares of Household Heating Fuels in the Upper Northeast States in 2000.**

With specific regard to New York State, a NYSERDA-sponsored study assessing the petroleum storage and delivery infrastructure in the New York City, Long Island, and Hudson River regions looked into the interplay of natural gas and residential heating oil (distillate) as they competed for market share (ICF Consulting 2006). Based on 2004 data, the most recent data available at the time of the report, residential oil appeared to be holding its market share in terms of total volume, but was losing market share to natural gas with population growth. Since 2004, however, residential heating oil sales volume has dropped dramatically (Figure 1-3). Heating oil sales have decreased by about 350 million gallons from 2004 to 2008 (a 24% decrease). The drop since the 1980s has been even larger, with a sales volume decrease of over one-third since a peak above 1.7 billion gallons in 1988 to a minimum of about 1.1 billion gallons in 2008, its lowest sales volume in at least 25 years. By contrast, residential natural gas consumption in New York State has increased by about 20% since 1984 (Figure 1-4).

Even though the residential sales volume was at a minimum in 2008, residential use of distillate oil in New York State was nearly as much as in the transportation sector, with both sectors accounting for over 75% of total sales that year. Table 1-1 provides the 2008 New York State volumes and percentages in sales of distillate and residual fuel oils by end use. Figure 1-5 shows the seasonality in all sales; the volumes are highest in the winter months when residential usage peaks.

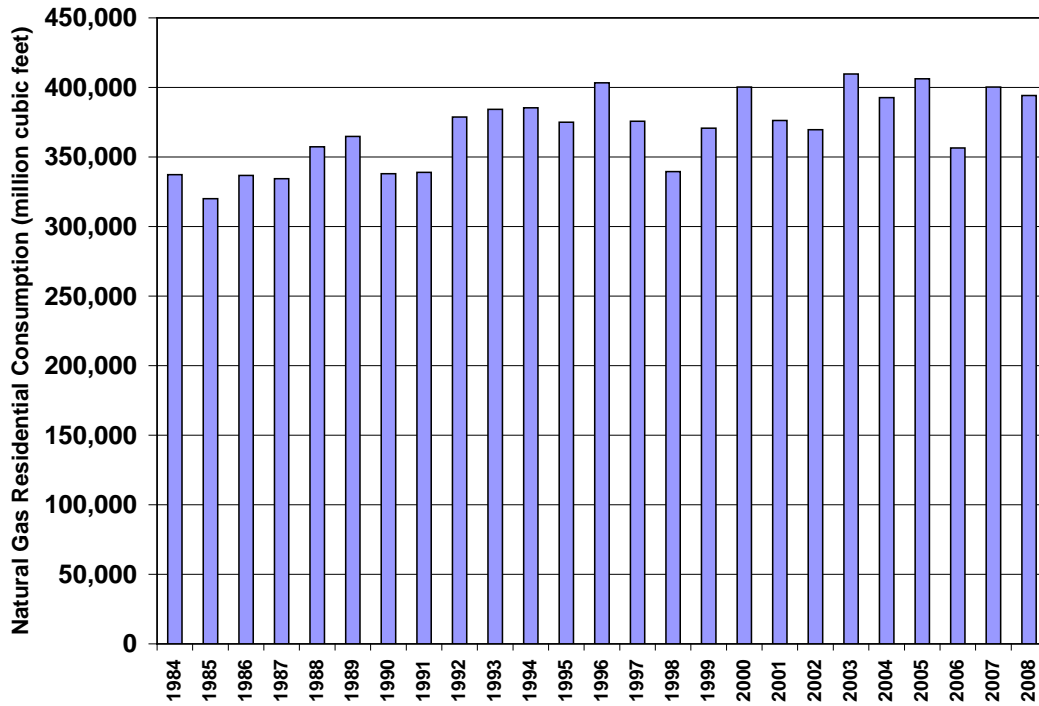
The county-level distribution of fuel oil consumption in New York State is shown in Figure 1-6. The latest available data is for 2008, and comes from the U.S. Census Bureau's American Community Survey (ACS). The ACS provides the number of households who primarily use fuel oil for heating (note that the ACS is

conducted only in counties with populations greater than 20,000). The average household distillate fuel oil consumption was estimated by dividing the 2008 residential sales volume by the total number of households primarily using fuel oil. The geographic distribution plotted in the figure was estimated by applying this factor to the number of households per county. As expected, the six most populous counties are estimated to have the highest consumption.



Source: EIA 2009

**Figure 1-3. Annual Residential Fuel Oil Sales in New York State, 1984-2008.**



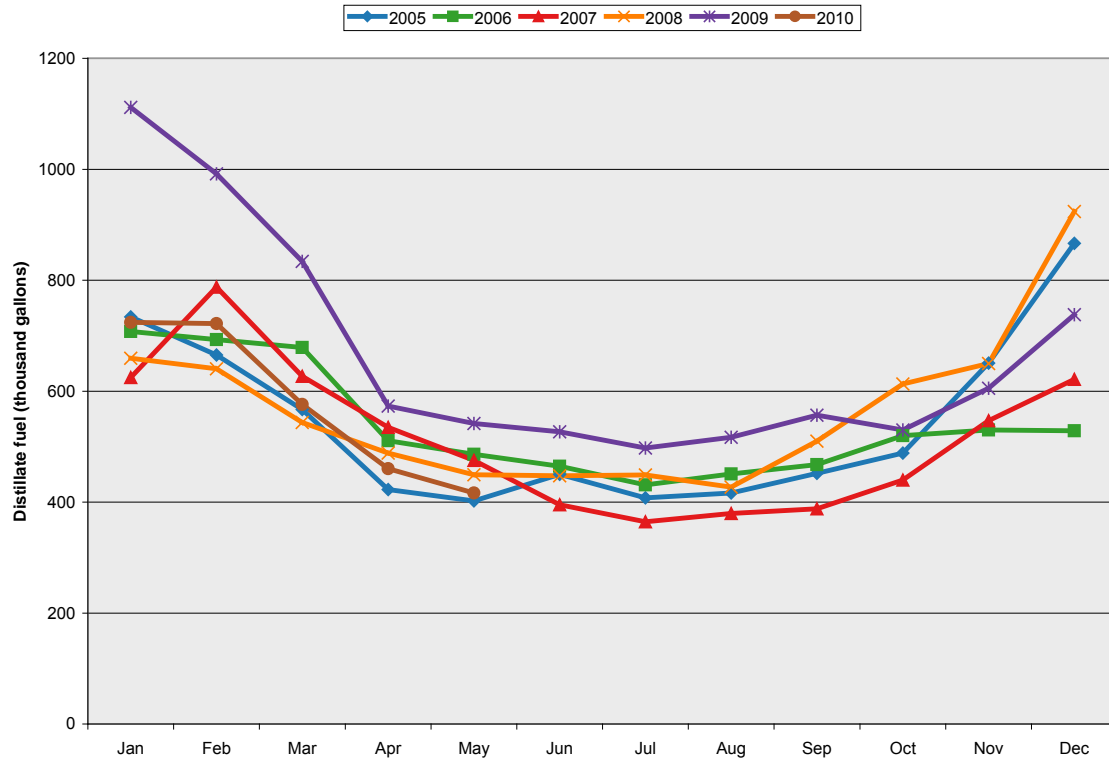
Source: EIA 2010e

Figure 1-4. Annual Residential Natural Gas Consumption in New York State, 1984-2008.

Table 1-1. 2008 Distillate and Residual Fuel Oil Sales in New York State Based on End Use

Sector	Distillate Fuel Oil		Residual Fuel Oil	
	Thousand Gallons	Percentage (%)	Thousand Gallons	Percentage (%)
Residential	1,088,618	37.0		
Commercial	526,526	17.9	273,185	34.5
Industrial	48,999	1.7	43,983	5.6
Farm	41,076	1.4		
Electric Power	16,793	0.6	103,837	13.1
Oil Company	877	0.0	467	0.1
Transportation	1,172,617	39.8	369,650	46.7
Military	3,929	0.1	0	0.0
Off-Highway	45,684	1.6		
Other	0	0.0	27	0.0
<b>TOTAL</b>	<b>2,945,119</b>	<b>100.0</b>	<b>791,149</b>	<b>100.0</b>

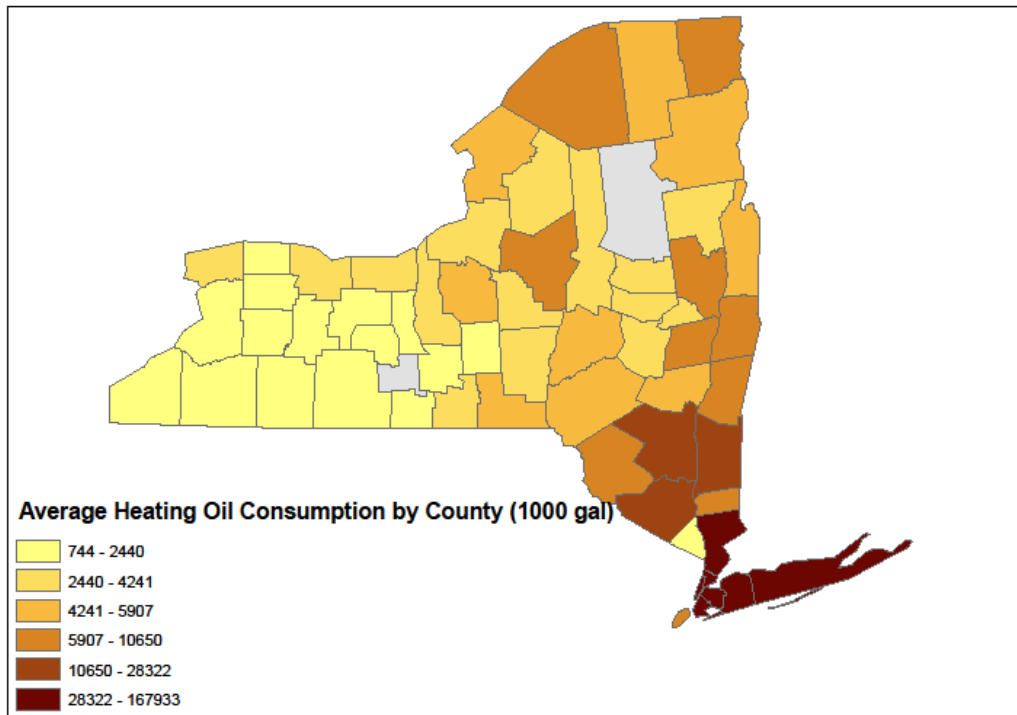
Source: EIA 2009



Source: EIA 2010f

**Figure 1-5. Monthly New York Distillate Oil Retail Deliveries.**





Sources: EIA 2009; U.S. Census Bureau 2009 (gray-shaded counties have populations below 20,000 and were not covered in the Census Bureau's American Community Survey).

**Figure 1-6. Estimated 2008 Residential Distillate Fuel Oil Consumption by New York State County (Thousand Gallons).**

### **Mercury and Trace Elements in Crude Oil**

Crude oil refers to the unrefined petroleum taken from the ground. The trace amounts of Hg and other elements in crude oil are of interest not only because of the toxicity of these compounds but also because of harmful effects they can have on refining equipment and the impact on the market value of the fuel (Wilhelm and Kirchgessner 2003; Hardaway et al. 2004). Mercury and elements from crude oil can be released to the environment through combustion of the refined products or through oil spills. The amount of Hg and other trace elements in crude oil varies considerably and is dependant on its geologic location (Wilhelm et al. 2000).

### ***Mercury***

Levels of total Hg in crude oil have been reported as low as 0.1  $\mu\text{g}/\text{kg}$  (Kelly et al. 2003) and as high as 10,000  $\mu\text{g}/\text{kg}$  (Wilhelm and Bloom 2000). It can be found in crude oil in several different chemical forms. These forms differ in their chemical and physical properties and include elemental Hg, dissolved organic Hg, inorganic Hg salts, complexed Hg, suspended Hg compounds, and suspended adsorbed Hg (USEPA 2001).

Elemental Hg is soluble in hydrocarbon liquids to only a few parts per million (ppm) but can adsorb onto metallic surfaces or suspended solids in the liquid, resulting in the suspended adsorbed form. In contrast, organic Hg compounds are highly soluble in liquid oil while having similar adsorptive properties to elemental Hg. Due to differences in solubilities and boiling points, organic Hg compounds can be separated from each other and from elemental Hg by distillation.

Inorganic Hg salts are soluble in liquid oil and can also be found in the suspended form or attached to suspended particles. Suspended Hg compounds are compounds insoluble in water and oil and thus are present as a suspended particle. The most common examples in this category are mercuric sulfide (HgS) and mercuric selenide (HgSe). Finally, complexed Hg refers to Hg bound to other constituents, such as an organic sulfide, thiol, or thiophene. These complexes are only postulated to exist in crude oil and condensates but have not been identified with certainty. Their existence is inferred from chromatographic experiments and operational speciation experiments (Wilhelm and Bloom 2000).

Wilhelm et al. (2007) provides a recent analysis of Hg levels in domestic and imported crude oils processed in the United States in 2004. Based on 170 different oil streams, the researchers estimated a total mean of 7.3 µg/kg total Hg in crude oil. The individual measurements showed a range of <0.5 µg/kg to 600 µg/kg. Crude oils originating in the United States were found to contain, on average, 4.3 µg/kg total Hg with the highest concentrations found in crudes produced in California. Of the imported crude oil, the highest concentrations of total Hg were found in Asian crudes, with an average concentration of 220 µg/kg. This average was dominated by reported concentrations of crude oil imported from Thailand (593 µg/kg) and Vietnam (66.5 µg/kg). Aside from domestic production, the largest contributor to the United States' supply of crude oil is from the Middle East. The estimated average concentration in oil streams from Saudi Arabia, Iraq, and Kuwait was 0.8 µg/kg (Wilhelm et al. 2007).

Environment Canada sponsored a survey of Hg content of crude oil processed in Canada between November 2003 and March 2006 (Environment Canada 2007). The study looked at 32 different crude oil streams, comprising 70% of Canada's total 2002 market volume. The study reported an average total Hg concentration of  $2.6 \pm 0.5$  µg/kg in all crude oil processed in Canada. The total Hg content of crude oil produced in Canada was found to be lower on average than found in imported crudes. The range of Hg concentrations from domestic and imported fuels was found to be 0.1-50 µg/kg.

While Wilhelm et al. (2007) and Environment Canada (2007) provide the most recent estimates of total Hg levels in crude oil, several previous studies have characterized these concentrations in crude oil from several points of origin. In the early 1970s, Shah et al. (1970) reported average concentrations of Hg ranging between 20 to 7500 µg/kg. Since then, analytical methods have improved dramatically and allowed for more accurate and sensitive methods for detecting Hg. Table 1-2 below summarizes reported Hg levels in crude oils from a variety of sources and analyzed by different detection methods.

**Table 1-2. Total Mercury in Crude Oil of Different Origins**

Reference	Source	N	Mean (ug/kg)	Range (ug/kg)	Method
Shah <i>et al.</i> 1970	US, California	NA	7551	81-29688	Instrumental Neutron Activation Analysis
Shah <i>et al.</i> 1970	Libya	NA	739	62.4-2078	Instrumental Neutron Activation Analysis
Shah <i>et al.</i> 1970	US, Louisiana	NA	22.5	NA	Instrumental Neutron Activation Analysis
Shah <i>et al.</i> 1970	US, Wyoming	NA	76.8	NA	Instrumental Neutron Activation Analysis
Filby <i>et al.</i> 1994	United States, Heavy Crude	6	<47	NA	ICP-MS
Filby <i>et al.</i> 1994	United States, Light Crude	6	<27	NA	ICP-MS
Musa <i>et al.</i> 1995	Libya	7	3.1	0.1-12.2	Neutron Activation Analysis
Magaw <i>et al.</i> 1999	Middle East	2	<10	NA	Cold Vapor Atomic Absorption
Magaw <i>et al.</i> 1999	Africa	4	<10	NA	Cold Vapor Atomic Absorption
Magaw <i>et al.</i> 1999	North America	11	146	ND-1560	Cold Vapor Atomic Absorption
Magaw <i>et al.</i> 1999	Asia	4	<10	NA	Cold Vapor Atomic Absorption
Magaw <i>et al.</i> 1999	South America	4	<10	NA	Cold Vapor Atomic Absorption
Magaw <i>et al.</i> 1999	North Sea	1	<10	NA	Cold Vapor Atomic Absorption
Bloom 2000	NA	76	1505	NA	Cold Vapor Atomic Fluorescence Spectrometry
Bloom 2000	NA	39	3009	NA	Cold Vapor Atomic Fluorescence Spectrometry
Bloom 2000	NA	37	1.2	NA	Cold Vapor Atomic Fluorescence Spectrometry
Liang <i>et al.</i> 2000	NA	11	4.4	1.6-7.2	Thermal Decomposition and Atomic Fluorescence Spectroscopy
Kelly <i>et al.</i> 2003	US, Texas	9	0.139	0.127-0.151	Isotope Dilution Cold-Vapor ICP-MS
Kelly <i>et al.</i> 2003	US, Texas	18	0.129	0.119-0.140	Isotope Dilution Cold-Vapor ICP-MS
Kelly <i>et al.</i> 2003	US, Texas	6	0.053	0.044-0.061	Isotope Dilution Cold-Vapor ICP-MS
Kelly <i>et al.</i> 2003	US, Texas	11	0.042	0.039-0.046	Isotope Dilution Cold-Vapor ICP-MS
Wilhelm <i>et al.</i> 2007	Africa, 7 Countries	21	2.7	0.3-13.3	Combustion and Digestion Atomic Fluorescence
Wilhelm <i>et al.</i> 2007	Asia, 3 Countries	4	220.1	0.8-593.1	Combustion and Digestion Atomic Fluorescence
Wilhelm <i>et al.</i> 2007	Canada	32	2.1	NA	Combustion and Digestion Atomic Fluorescence
Wilhelm <i>et al.</i> 2007	Europe, 3 Countries	9	8.7	3.1-19.5	Combustion and Digestion Atomic Fluorescence
Wilhelm <i>et al.</i> 2007	Mexico	9	1.3	NA	Combustion and Digestion Atomic Fluorescence
Wilhelm <i>et al.</i> 2007	Middle East, 3 Countries	24	0.8	0.7-0.9	Combustion and Digestion Atomic Fluorescence
Wilhelm <i>et al.</i> 2007	South America, 5 Countries	28	5.3	1.1-16.1	Combustion and Digestion Atomic Fluorescence
Wilhelm <i>et al.</i> 2007	United States, 10 States	42	4.3	1.4-11.3	Combustion and Digestion Atomic Fluorescence
Environment Canada, 2007	Canada	109	2.6	0.1-50	Cold Vapor Atomic Absorption and Fluorescence

**Trace Elements**

Crude oils generally contain trace concentrations of elements in the part per billion (ppb) to part per million (ppm) range. Similarly to Hg, the content of the other trace elements in crude oil is a characteristic of the location where the oil is produced and can be released to the atmosphere through combustion processes.

Of the other trace elements, nickel and vanadium are the most abundant metallic elements in crude oil (Shah *et al.* 1970; Filby *et al.* 1994). They are generally found in the ppm range. Arsenic, cobalt, manganese, lead, selenium, and antimony are generally found in crude oil in the ppb range. Table 1-3 below summarizes the levels of As, Pb, Mn, Ni, Zn, Co, V, Se, and Sb reported in the literature.

**Table 1-3. Trace Elements in Crude Oil**

Reference	Source	As	Pb	Mn	Ni (ppm)	Zn	Co	V (ppm)	Se	Sb
Shah <i>et al.</i> 1970	U.S. California	379			194	27985	3344		679	
Shah <i>et al.</i> 1970	Libya	191			77	49234	92		517	
Shah <i>et al.</i> 1970	U.S. Louisiana	46			345	3571	29		26	
Shah <i>et al.</i> 1970	U.S. Wyoming	111			113	6820	90		321	
Raghavan <i>et al.</i> 1979	India							6-8		
Ugarković and Premierl 1987	Moslavina				4.5-11			0.02- 2.5		
Olajire and Oderinde 1993	Nigeria	< 0.2	10- 1400	2800- 6200	5.0-11	< 10		14-99		
Stacy 1994	Venezuela	284	150	210	117	692	178	1100		303
Filby <i>et al.</i> 1994	U.S. Heavy Crude	20			92	94	162	355	276	15
Filby <i>et al.</i> 1994	U.S. Light Crude	12			10	170	61	2.8	120	28
Musa <i>et al.</i> 1995	Libya			133	3.3	353	7	1.9	6	317
Al-Swaidan 1996	Saudi Arabia, Heavy Crude		810		9.4			138		
Al-Swaidan 1996	Saudi Arabia, Medium Crude		440		6.9			8.8		
Al-Swaidan 1996	Saudi Arabia, Light Crude		300		3.1			11.3		
Magaw <i>et al.</i> 1999	Several Countries	60	32		20		270	63	160	11

Note: Concentrations shown in table are in µg/kg (ppb) unless indicated otherwise (Ni, V).

### Mercury and Trace Elements in Refined Petroleum Products

#### Mercury

Petroleum products resulting from the refining of crude oils commonly contain Hg compounds in various chemical forms. Since the early 1980s, several estimates of Hg in No. 2 distillate oil have been published, describing a wide range of concentrations. The USEPA (1981) estimated the concentration of Hg in No. 2 oil as 400 ppb (µg/kg), and USEPA (1997b) estimated it as <120 ppb. Several studies have been released reporting levels well below these estimates. Liang *et al.* (1996) and Rising *et al.* (2004) reported values below one ppb (0.59 ppb and <0.2 ppb, respectively). Bloom (2000) found Hg concentrations of 1.32 ppb (µg/kg) in all light distillates. In addition, total Hg levels in diesel fuel have been reported as high as 3.0 µg/kg to as low as 0.034 µg/kg while the levels in gasoline have been found at 0.04 – 3.2 µg/kg (Liang *et al.* 1996; Kelly *et al.* 2003; Conaway *et al.* 2005). Table 1-4 below summarizes published estimates of Hg in No. 2 fuel oil and other refined petroleum products.

**Table 1-4. Mercury in Refined Petroleum Products.**

Reference	Fuel Type	N	Mean (µg/kg)	Method
EPA 1997b	No.2 Distillate Oil		< 120	
Liang <i>et al.</i> 1996	Heating oil	1	0.59	CVAFS
Bloom 2000	Light Distillates	14	1.32	CVAFS
Rising <i>et al.</i> 2004	Gas Turbine Fuel (No. 2)	13	< 0.2	ICP-MS
EPA 1997b	Residual Fuel Oil		4	
Bloom 2000	Utility Fuel Oil	21	0.67	CVAFS
Kelly <i>et al.</i> 2003	Residual Fuel Oil	5	3.46	IDCV-ICP-MS
Liang <i>et al.</i> 1996	Diesel (U.S.)	1	0.4	CVAFS
Liang <i>et al.</i> 1996	Diesel	1	2.97	CVAFS
Hoyer <i>et al.</i> 2004	Diesel	1	0.0050	
Kelly <i>et al.</i> 2003	Diesel	6	0.034	IDCV-ICP-MS
Conaway <i>et al.</i> 2005	Diesel	19	0.15	CVAFS
Won <i>et al.</i> 2007	Diesel		0.219	
Liang <i>et al.</i> 1996	Gasoline (U.S.)	5	0.22-1.43	CVAFS
Liang <i>et al.</i> 1996	Gasoline (Monaco)	2	0.72-0.96	CVAFS
Liang <i>et al.</i> 1996	Gasoline (Slovenia)	1	1.20	CVAFS
Liang <i>et al.</i> 1996	Gasoline (Algeria)	1	3.20	CVAFS
Hoyer <i>et al.</i> 2004	Gasoline	3	0.071-0.259	
Conaway <i>et al.</i> 2005	Gasoline	20	0.5	CVAFS
Won <i>et al.</i> 2007	Gasoline		0.781	
Liang <i>et al.</i> 1996	Kerosene	1	0.04	CVAFS
Oslén <i>et al.</i> 1997	Naphtha	4	15	ICP-MS
Tao <i>et al.</i> 1998	Naphtha	3	40	ICP-MS

### **Trace Elements**

While several studies have examined levels of trace elements in crude oil, information is sparse on the levels of these compounds in refined products, and is tabulated in Table 1-5. Rising *et al.* (2004) collected No. 2 distillate oil samples from gas turbine installations in 10 U.S. states and analyzed the samples by ICP-MS. They reported mean concentrations of 15.0 ppb for lead, 28.9 ppb for nickel, and 5.5 ppb for manganese. Levels of arsenic and cadmium were reported at below the detection limit, 0.9 and 0.1 ppb, respectively. Heathcote *et al.* (2000) examined the levels of nine elements in motor-vehicle fuels using ICP-MS. The analysis found concentrations in No. 2 diesel of 0.3 to 5.3 ppb for lead, below the detection limit of 2.0 ppb for nickel, 0.7 to 6.5 ppb for vanadium, below the detection limit of 2.0 ppb for manganese, and 5.1 to 12.7 ppb for zinc. Olajire and Oderinde (1993) found that the trace element concentrations in heavy distillate were close to the levels in crude oil (Table 1-3). The reason for high Ni and V concentrations in the light gas oil measured by Ugarković and Premerl (1987) is unknown.

**Table 1-5. Trace Elements in Refined Petroleum Products.**

Reference	Fuel type	As	Pb	Mn	Ni	Zn	Co	V	Se	Sb
Ugarković and Premerl 1987 (Moslavina)	Light gas oil				2.0 (ppm)			0.15 (ppm)		
Ugarković and Premerl 1987 (Moslavina)	Heavy gas oil				1.8 (ppm)			0.3 (ppm)		
Olajire and Oderinde 1993 (Nigeria)	Heavy distillate	< 0.2	10-1120	2.4-3.8 (ppm)	5.5-11 (ppm)	< 10		14-99 (ppm)		
Heathcote <i>et al.</i> 2000 (U.S.)	Diesel		0.3-5.3	< 2.0	< 2.0	5.1-12.7		0.7-6.5	1.4	
Rising <i>et al.</i> 2004	No. 2 fuel oil	< 0.9	15.0	5.5	28.9				< 5	

Note: Concentrations shown in table are in  $\mu\text{g}/\text{kg}$  (ppb) unless indicated otherwise.

### Mercury and Trace Elements in Natural Gas

#### *Mercury*

In natural gas, the elemental form of Hg is predominant. The organic form is rarely detected while trace amounts of dimethylmercury have been reported (USEPA 2001). Mercury concentrations in natural gas vary geologically from 0 to  $> 300 \mu\text{g}/\text{N m}^3$ , where ‘N’ means normal conditions corresponding to standard pressure and temperature. Table 1-6 lists the average Hg content measured in natural gas in different regions in the world. Some of the highest concentrations occur in Southeast Asia, e.g., Indonesia and the Gulf of Thailand. Some high Hg level gas fields are also found in Europe.

Because Hg can cause corrosion of aluminum structures and damage catalytic processes that have led to expensive plant shut downs (Kinney 1975), many gas processing plants employ Hg removal processes consisting of adsorbents specific to Hg. The Hg removal processes are particularly important if the feeds contain high levels of Hg, if aluminum heat exchangers are used, or if downstream customers have Hg specifications. Mercury removal is required on almost all liquefied natural gas plants as the low temperatures they operate under usually condenses Hg (USEPA 2001). Abu El Ela *et al.* (2006) described Hg levels in natural gas before and after installation of Hg removal equipment at an Egyptian gas plant. They reported Hg concentrations in natural gas ranging between 17 and  $71 \mu\text{g}/\text{N m}^3$  before removal and between 0.53 and  $0.92 \mu\text{g}/\text{N m}^3$  after removal.

**Table 1-6. Total Mercury in Natural Gas and Gas Condensate**

Reference	Location	Natural Gas µg/N m <sup>3</sup>	Gas Condensate µg/kg
Attari and Chao 1993	U.S.	<0.2	
Bingham 1990; Gijsselman 1991	Netherlands	0-300	
Muchlis 1981; Situmorang and Muchlis 1986	Indonesian	180-300	
Hennico <i>et al.</i> 1991	Middle East	<50	
Hennico <i>et al.</i> 1991	South Africa	100	
Hennico <i>et al.</i> 1991	Far East	50-300	
Ryzhov <i>et al.</i> 2003	Russia	1.2-47	
Abu El Ela <i>et al.</i> 2006	Egypt	17-71	
Abu El Ela <i>et al.</i> 2006	Egypt (outlet)	0.53-0.92	
Abu El Ela <i>et al.</i> 2006	South America	50-120	50-100
Abu El Ela <i>et al.</i> 2006	Gulf of Thailand	100-400	400-1200
Abu El Ela <i>et al.</i> 2006	North Africa	50-80	20-50
Shafawi <i>et al.</i> 1999	Unknown		10-74
Tao <i>et al.</i> 1998	Unknown		18.1-256
Zettlitzer <i>et al.</i> 1997	North German		4000-9000
Sarrazin <i>et al.</i> 1993	Unknown		10-3000
Wilhelm 2001	U.S. oil refineries		<10
Won <i>et al.</i> 2007	Vehicle LPG		1.82

For natural gas condensate, the average Hg contents also vary in different regions in the world as listed in Table 1-6. Several authors provided more detailed information. Shafawi *et al.* (1999) examined Hg levels in five commercially available natural gas condensates using atomic fluorescence spectrometry. They reported Hg levels of 7-50 µg/l (10-74 µg/kg) in the gas condensates from a variety of organic, inorganic, and elemental forms. Tao *et al.* (1998) looked at Hg speciation in natural gas condensate using GC-ICP-MS and identified five species of Hg in gas condensates – elemental Hg, mercury chloride, dimethylmercury, methylethylmercury, and diethylmercury.

#### ***Other Hazardous Trace Elements***

Arsenic was studied more intensively than other trace elements partly due to its extreme toxic effects on humans and wildlife and partly due to it being a catalyst poison like Hg and sulfur. It exists in natural gas predominantly in the form of trialkylarsines, including trimethylarsine (As(CH<sub>3</sub>)<sub>3</sub>, the major component), dimethylethylarsine, methyl-diethylarsine, and triethylarsine (Bouyssiére *et al.* 2001; Trahan 2008). As Hg, arsenic content in natural gas varies geographically. Delgado-Morales *et al.* (1994) reported that natural gas from a field in southeastern New Mexico contained arsenic at concentrations of 200 to 2500 µg/m<sup>3</sup> in the form of trialkylarsines. Irgolic *et al.* (1991) examined arsenic compounds in natural gas using hydride generation and GC-MS detection. They found a wide range of concentrations from several wells at multiple gas fields, reporting a range of 10 to 63000 µg/m<sup>3</sup> total arsenic. They also noted that this estimate may be low due to the use of aluminum canisters when collecting the gas samples. The same investigators also determined natural

gas concentrations from four gas wells using GC-MS. They found that total arsenic concentrations ranged from 21 to 217  $\mu\text{g}/\text{m}^3$  across the four wells. It was found that 55% to 80% of the arsenic was in the form of trimethylarsine and an additional 5% to 10% were from other forms of trialkylarsines. Attari and Chao (1993) reported total arsenic concentrations of less than five  $\mu\text{g}/\text{m}^3$  in the United States. We note that arsenic removal facilities have been applied at gas wells with high arsenic concentrations. Newpoint Gas (2007) reported an ability to reduce arsenic concentrations from 1200  $\mu\text{g}/\text{m}^3$  to < 10  $\mu\text{g}/\text{m}^3$ .

Limited information on trace element levels other than arsenic in natural gas was found. Häsänen et al. (1986) reported that trace elements were not released in significant amounts in the combustion of natural gas. They examined emissions of  $\text{SO}_2$ ,  $\text{NO}_x$ , Pb, Cd, Hg, Be, V, Ni, Cr, Mn, Zn, As, Co, Mo, U, Th, and  $^{210}\text{Po}$  from combustion of peat, coal, heavy fuel oil, and natural gas. They concluded that the only significant emission from combustion of natural gas was  $\text{NO}_x$ . Schmidt (1998) examined lead precipitates in natural gas, noting that the first estimates of lead in natural gas were made in 1975 where average concentrations of 1  $\mu\text{g}/\text{m}^3$  were reported in gases from fields in northwest Germany. Therefore, it was postulated that the trace element's concentrations in sales natural gas was relatively low.

### **Mercury and Trace Elements in Liquid Petroleum Gas (LPG)**

There is very limited public information on Hg and other trace elements in liquid petroleum gas (LPG – a gas condensate comprised of propane and/or butane). Wilhelm (2001) estimated that the Hg content in LPG used on-site at refineries is less than 10 ppb. Won et al. (2007) reported a Hg content of 1.23  $\mu\text{g}/\text{l}$  (~3 ppb) in vehicle LPG.

### **Current Emission Factors for Mercury and Trace Elements**

According to the USEPA (1997b), the emission factor for No. 2 distillate oil is 0.86  $\text{lb}/10^6$  gallon, which roughly corresponds to Hg content of 120  $\mu\text{g}/\text{kg}$  (ppb), which assumes 100% of the Hg is emitted to air from oil combustion. However, the Hg content used in the calculation of this emission factor is not likely representative of most No. 2 fuels. The more recent studies identified in this report have measured levels typically much lower than this, with estimates of the Hg content in No. 2 oil at around 1 ppb. Other estimates of Hg emission factors in fuel oil can be found in Table 1-7.

The Hg content for each emission factor is listed for comparison with Table 1-4. As is evident, the Hg contents implicit in the USEPA emission factors are much higher than the more recent studies. The emission factors for No. 6 residual oil and the corresponding Hg content found in different studies are also listed for reference.

The Hg emission factor for natural gas combustion is 2.6E-04 ( $\text{lb}/10^6$  scf) in AP-42 (USEPA 1998). The corresponding Hg content is 4.40 ( $\mu\text{g}/\text{N m}^3$ ).<sup>3</sup> This value is likely to be close to the Hg content of most

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<sup>3</sup> To convert from the emission factor (EF) in  $\text{lb}/10^6$  scf to mercury content (MC) in  $\mu\text{g}/\text{N m}^3$  for natural gas, 1 lb = 454 grams (g), and 1 scf = 0.026853  $\text{N m}^3$  are used. The standard temperature and pressure corresponding to normal cubic meters ( $\text{N m}^3$ ) are 0°C (273.15 K) and 101.325 kPa (1 atm), while they are 60°F and 1 atm for standard cubic feet (scf).  $\text{MC} = \text{EF} * 454 (\text{g}/\text{lb})/0.026853 (\text{N m}^3/\text{scf}) * 1.0\text{E}6 \mu\text{g}/\text{g}$ .



natural gas consumed in the United States. As described previously, due to the low Hg concentrations in natural gas produced domestically in the United States and the removal of Hg at the natural gas processing plant, the Hg content in sales natural gas in the United States is likely to be around one ppb.

**Table 1-7. Reported Mercury Emission Factors for Distillate and Residual Oils**

Reference	#2 Distillate Oil		#6 Residual Oil	
	Emission factor lb/10 <sup>6</sup> gallon	Hg content ppb	Emission Factor lb/10 <sup>6</sup> gallon	Hg content ppb
USEPA Hg Report to Congress 1997a	0.96	136	0.93	118
USEPA L&E Report 1997b	0.86	120	0.033	4.2
USEPA AP-42 1998	0.42	60	0.113	14
NHDES 2003	0.013	1.4	0.025	3.2

*Note:* To convert from lb/10<sup>6</sup> gal to ppb, the density of #2 distillate oil is assumed to be 7.05 lb/gal, and the density of #6 residual oil is assumed to be 7.9 lb/gal.

Table 1-8 lists emission factors for trace elements from distillate fuel oil and natural gas combustions as contained in AP-42 (USEPA 1998). For distillate oil, the trace element contents assumed in the emission factors are much higher than the recently reported estimates as listed in Table 1-5. On the other hand, the emission factors from natural gas combustion seem reasonable from the limited information collected for this report. The emission factors from residual oil combustion are also listed in Table 1-8 for comparison. As expected, the emission factors for trace elements for residual oil are higher than distillate oil due to the low volatility of these elements. As such, the emission factors for Sb, Co and V, available only for residual fuel oil in AP-42, can be regarded as the upper limits for distillate oil.

**Table 1-8. Emission Factors of Trace Elements for Distillate and Residual Fuel Oils and Natural Gas.**

Trace Element	#2 Distillate Oil		#6 Residual Oil		Natural Gas	
	Emission factor lb/10 <sup>6</sup> gal	Emission factor lb/MMBtu	Emission factor lb/10 <sup>6</sup> gal	Emission factor lb/MMBtu	Emission factor lb/10 <sup>6</sup> scf	Emission factor lb/MMBtu
V	n/a	n/a	31.8	2.12E-04	2.3E-03	2.2E-06
Mn	0.83	6.E-06	3	2.E-05	3.8E-04	3.7E-07
Co	n/a	n/a	6.02	4.02E-05	8.4E-05	8.2E-08
Ni	0.42	3.E-06	84.5	5.64E-04	2.1E-03	2.0E-06
Zn	0.56	4.E-06	29.1	1.94E-04	2.9E-02	2.8E-05
As	0.56	4.E-06	1.32	8.82E-06	2.0E-04	1.9E-07
Se	2.08	1.5E-05	0.683	4.56E-06	<2.4E-05	<2.3E-08
Sb	n/a	n/a	5.25	3.51E-05	n/a	n/a
Hg	0.42	3.E-06	0.113	7.55E-07	2.6E-04	2.5E-07
Pb	1.25	9.E-06	1.51	1.01E-05	5.0E-04	4.9E-07

Source: AP-42, USEPA 1998.

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## SECTION 2

### **Fuel Oil Analytical Methods**

Analysis of fuel oils was performed by a certified and accredited testing laboratory (Intertek Caleb Brett) under contract to NESCAUM. The testing was done in two phases. The initial phase (Phase I) covered three months and focused on determining the levels of mercury (Hg), lead (Pb), nickel (Ni), vanadium (V), zinc (Zn), cobalt (Co), arsenic (As), selenium (Se), sulfur (S) and manganese (Mn) in primarily No. 2 home heating oil as well as a small set of ultra-low-sulfur and nonroad diesel samples. The structure of the second phase (Phase II) was based on results obtained from Phase I and extended for about a year after Phase I.

A subset of the home heating samples was analyzed for Hg by cold vapor atomic absorption as an independent measurement. In addition, sulfur content of the fuels was tested using X-ray fluorescence if the distributors were not already performing those tests.

Additional details on the methods, procedures, and locations of the two sampling phases are described in the following sections.

### ***Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Analytical Methods for Mercury and Other Trace Elements***

Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry that is highly sensitive and capable of detecting and quantifying a range of metals and several non-metals at concentrations in the parts per billion range and below (Ammann 2007). A nebulizer sample droplet is introduced into a charged plasma created at high temperature (~10,000 C) within the instrument. The sample droplet and any solids within it vaporize at the high temperatures within the plasma, and break down into atoms. The plasma temperature is also sufficiently high enough to ionize an atom after vaporization into a singly charged ion with the loss of its most loosely bound electron. The positively charged ion is then passed through a mass spectrometer (typically a mass quadrupole) where trace element ions can be discriminated according to their mass and then electronically detected, with the detection signal proportional to the concentration of the atomic species in the sample droplet.

**ICP-MS method for No. 2 home heating oil and diesels.** The analytical method for No. 2 home heating oil and the diesel grades was ITM\_1051, Intertek Caleb Brett's standard method for ICP-MS analysis by dilution in an organic matrix. Under the ITM\_1051 method, the samples are diluted with semi-conductor grade xylenes at a minimum dilution of 1:10 for analyzing by ICP-MS. Sample introduction is by self-aspirating perfluoroalkoxy (PFA) nebulizer. Calibration standards are also prepared in xylenes from organometallic standards. Calibration ranges vary by element and expected result, but are usually in the 0-25 ppb range using a four-point curve, including a calibration blank. Minimum linearity for acceptance is  $r^2 \geq 0.995$ . A check standard is run before and after every sample set with  $\pm 20\%$  the accepted value required. A sample blank is prepared with the samples and is run with the samples. The sample blank value

must be less than the minimum detection limit (MDL) for the data to be used. A minimum of one sample per ten is 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 (H<sub>2</sub>) reaction cell is used to eliminate interferences for problematic elements.

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

The minimum detection limits for the trace elements investigated by the ICP-MS technique for No. 2 heating oil and the diesel grades are shown in Table 2-1.

**Table 2-1. ICP-MS Minimum Detection Limits for Trace Elements in No. 2 Heating Oil and Diesels**

Element	ppb
As	1
Co	6
Hg	2
Mn	5
Ni	3
Pb	4
Sb	10
Se	5
V	4
Zn	6

**ICP-MS method for No. 6 fuel oil.** Because No. 6 fuel oil is relatively heavy, it is more difficult to run a trace element analysis by simple dilution as with No. 2 home heating oil and the diesel grades. To prepare a sample appropriate for analysis required a preliminary digestion step before analysis by ICP-MS, which is Intertek Caleb Brett's method ITM\_1052. The ITM\_1052 method covers eight different digestion techniques depending on analytical need. If samples require charring with sulfuric acid first, this is done in a closed vessel so that volatiles are not lost. The addition of sulfuric acid can interfere with the Zn results, which can be largely avoided by employing a helium collision cell.

After digestion, the samples are run by ICP-MS. Calibration is by four-point curve using standards prepared from commercially available multi-element aqueous standards. Minimum linearity for acceptance is  $r^2 \geq 0.995$ . An independent check standard is run before and after every sample set with  $\pm 20\%$  the accepted value required. A sample blank is prepared with the samples and is run with the samples. The sample blank value must be less than the MDL for the data to be used. Minimum of one sample per ten is run in duplicate with the RSD of the duplicate samples required to be less than 20% for any result higher than the MDL. A minimum of one sample in ten has a spiked sample prepared with a measured recover of 70-130% required to validate the analysis. A H2 reaction cell is used to eliminate interferences for problematic elements.

The minimum detection limits for the trace elements investigated by the ICP-MS technique for No. 6 fuel oil are given in Table 2-2. Note that the MDLs for No. 6 fuel oil are higher than that of No. 2 heating oil and the diesel grades.

**Table 2-2. ICP-MS Minimum Detection Limits for Trace Elements in No. 6 Fuel Oil**

Element	ppb
As	20
Co	10
Hg	25
Mn	10
Ni	25
Pb	10
Sb	30
Se	100
V	10
Zn	125

***Cold Vapor Atomic Absorption Analytical Method for Mercury***

Cold Vapor Atomic Absorption (CVAA) is a more sensitive method for detecting Hg than the ICP-MS method, with a Hg detection limit of 1 ppb for all fuel oil types tested in this study. CVAA is an optical technique that measures the absorption of atomic elemental Hg entrained in a gas flow within the instrument. The fuel oil samples were treated according to a combustion-amalgamation process given by Universal Oil Products (UOP) Method UOP 938.

***X-ray Fluorescence Analytical Methods for Sulfur***

Sulfur concentrations in conventional No. 2 home heating oil and off-road diesel were obtained by energy-dispersive X-ray fluorescence spectrometry according to ASTM Method D4294 (ASTM International

2003). This method is typically applied to a concentration range of 0.0150 to 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 (ASTM International 2005).

### Fuel Oil Sampling

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.

Oil samples were shipped to the Intertek Caleb Brett laboratory in Deer Park, TX for analysis. Sample chain of custody was maintained so that metals analyses and sulfur results could be tracked to each sample. Sample treatment and analysis followed the Intertek Caleb Brett in-house standard operating procedures.

Sample collection sites included terminals in Albany, the Bronx, and Long Island, NY; and Revere and Quincy, MA. Samples were collected by Intertek Caleb Brett field staff who had received training in industry standard operating procedures prior to sample collection. A total of 137 fuel samples were collected for analysis, 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 sulfur diesel, 11 ultra-low-sulfur diesel, 8 biodiesel, and 16 residual oil samples. The terminals sampled by Intertek Caleb Brett for No. 2 home heating oil are given in Table 2-3 and the locations for No. 6 fuel oil and diesels are given in Table 2-4.

**Table 2-3. Sampling Locations for No. 2 Home Heating Oil**

Location	Distributor	Terminal
<b>No. 2</b>		
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

**Table 2-4. Sampling Locations for No. 6 Fuel Oil and Diesel**

<b>Location</b>	<b>Distributor</b>	<b>Terminal</b>
<b>No. 6</b>		
New York, NY	Sprague	Sprague – Stuyvesant-Bronx
Boston, MA	Global	Global – Chelsea
<b>Biodiesel</b>		
New Jersey	Sprague	Sprague – Elizabeth, NJ
<b>Ultra-Low Diesel</b>		
New York, NY	Sprague	Sprague – Stuyvesant-Bronx
<b>Nonroad Diesel</b>		
New York, NY	Sprague	Sprague – Stuyvesant-Bronx



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## SECTION 3

### Results for Trace Element Content in Distillates and Residual Oil

#### *Sample Reproducibility*

In order to validate the analysis results, quality assurance and quality control (QA/QC) checks must be followed. As described in Section 2, Intertek Caleb Brett followed procedures to test and verify the performance of its laboratory instrumentation. In addition, duplicate samples were collected to verify the collection and storage procedures. A total of 36 duplicate samples (34 distillate oil, one ultra-low-sulfur diesel, and one residual fuel oil) were drawn from the same storage tank but collected, shipped, and analyzed separately from the original samples. Table 3-1 shows the comparison of the trace element concentrations of the duplicate samples (distillate and diesel) with the corresponding original sample.

**Table 3-1. Sulfur and Trace Element Analysis Comparison for 35 Distillate/Diesel Duplicate Samples**

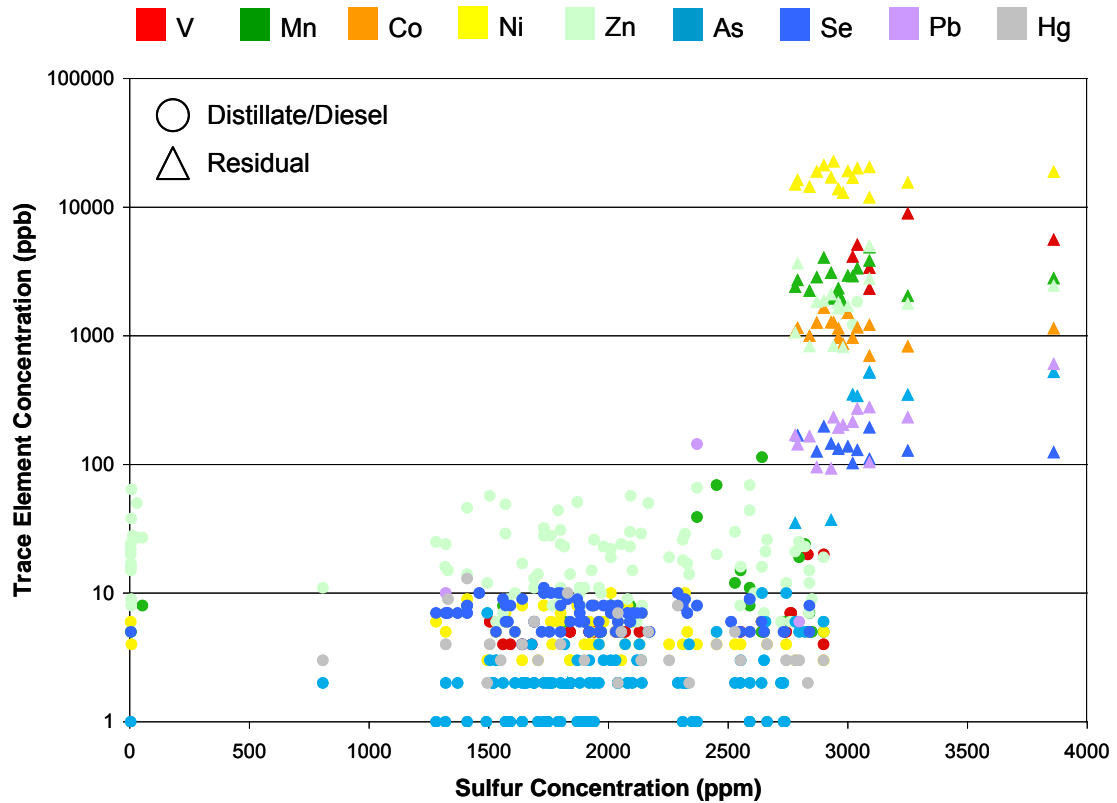
	S	V	Mn	Co	Ni	Zn	As	Se	Pb	Hg
<b>Average Percent Difference</b>	1.1%	0.0%	6.2%	0.0%	8.0%	30.7%	18.7%	10.1%	0.0%	11.0%
<b>Median Percent Difference</b>	0.5%	0.0%	0.0%	0.0%	0.0%	12.2%	0.0%	0.0%	0.0%	0.0%
<b>Pairs with Same Conc.</b>	8	35	31	35	27	11	25	23	35	31
<b>Pairs with Measurable Conc.</b>	35	7	5	0	15	19	26	19	0	1

*Note:* No paired samples were tested for antimony (Sb).

Unlike the residual fuel oil samples, many of the trace element concentrations in the distillate oil and diesel samples were below the method detection limit (MDL). The MDL for each trace element by ICP-MS was provided in Table 2-1 and Table 2-2. In all samples used in this duplicate comparison, the trace metal concentration of cobalt and lead were below the MDL, and for this reason, all 35 sample pairs were determined to have the same trace element concentration. Therefore, the percent difference between the cobalt/lead concentration for each duplicate and original sample is 0%. On the other end, all 35 pairs of samples had detectable amounts of sulfur; while only eight of the pairs had the same exact sulfur concentration, the average percent difference is only 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.

#### *Assessment of Trace Element Relationships with Sulfur Content*

For this project, samples of varying sulfur content (from ultra-low-sulfur diesel to residual fuel oil) were purposely collected and analyzed. The intent behind this approach was to be able to assess if there are any relationships between the sulfur content of refined petroleum products and the trace element concentrations. Figure 3-1 displays the trace element concentration (only those with detectable concentrations) versus the sulfur content of the sample. The distillate oil and diesel samples are represented by circles, and the residual fuel oil samples are represented by triangles.



**Figure 3-1. Trace Element Concentration versus Sulfur Content in Fuel Samples.**

Figure 3-1 shows that there is no strong relationship between the concentration of any trace element and the sulfur content of the fuel sample. Instead, the figure best illustrates the differences between the residual fuel oil and the distillate oil/diesel samples. In general, the trace element concentrations in residual fuel oil are at least an order of magnitude higher than in distillate heating oil and diesel. Mercury is the exception, as it was below the ICP-MS minimum detection level (MDL) in all the residual fuel oil samples. Although the Hg content was not detectable in most samples, the ICP-MS MDL for Hg in residual fuel oil was higher (25 ppb vs. 2 ppb) than in distillate oil (see Table 2-1 and Table 2-2), and none of the residual oil samples had detectable Hg levels by ICP-MS. Based on the refining method (where residual fuel oil is the remaining crude oil after the other fuel types are distilled off), it is reasonable to expect that the concentrations for these trace elements would be higher in residual fuel oils than in distillate oils. Mercury, being more volatile, could possibly distill out of the residual fuel oil, while the other trace elements tend to remain behind.

## **DETERMINATION OF EMISSION FACTORS**

### *Trace Element Concentrations by Fuel Type*

Table 3-2 and Table 3-3 summarize the analytical results, according to fuel type. The elements in Table 3-2 were those most frequently found in the samples, whereas the concentrations of the elements included in

Table 3-3 were more likely to be below the MDL. Table 3-3 also includes the Hg concentrations, as measured by the more sensitive CVAA technique.

**Table 3-2. Analytical Results of Trace Elements by ICP-MS**

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

*Notes:* Units are given in ppb except for S, which is in ppm. Parentheticals in the table represent the number of samples with that measurement or that were used to create the value. 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.

\* Averages calculated by substituting half MDL values for samples with undetectable levels.

In these tables, the quantity in parenthesis represents the number of samples with that measurement or, in the case of determining averages, the number of samples used in the calculation. The tables show that a significant number of home heating/diesel, ultra-low-sulfur diesel, and biodiesel samples have trace element (excluding sulfur) concentrations below the MDL. For example, less than 50% of the distillate oil samples had detectable amounts (>3 ppb) of nickel by ICP-MS. Also, no distillate samples recorded cobalt or antimony levels above instrument detection limits, whereas they were measured in residual oil at relatively high concentrations. Averages marked by an asterisk (\*) were calculated using half of the MDL as substitutes for samples with unquantifiable concentrations.

**Table 3-3. Analytical Results of Trace Elements by ICP-MS and Hg by CVAA**

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

*Notes:* Units are given in ppb. Parentheticals in the table represent the number of samples with that measurement or that were used to create the value. 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.

\*Averages calculated by substituting half MDL values for samples with undetectable levels.

As was illustrated in Figure 3-1, Table 3-2 and Table 3-3 show that the trace element content for all species, except Hg, are higher in residual fuel oils than in distillate oil and diesel fuels. In comparing the two analytical approaches for Hg measurements, Hg was detected in just over 25% of the distillate oil samples by ICP-MS, whereas it was measured in over 80% of the samples using the CVAA technique. By substituting half of the MDL for samples without measurable levels, the average concentration of 2 ppb agrees for both methods. As mentioned, none of the residual oil samples had detectable Hg levels by ICP-MS. Of the three residual oil samples measured by CVAA, an average of 1.3 ppb was calculated.

***Comparison of Emission Factors***

Table 3-4 provides the emission factors of trace elements for distillate and residual fuel oils based upon the average concentrations measured in this work.

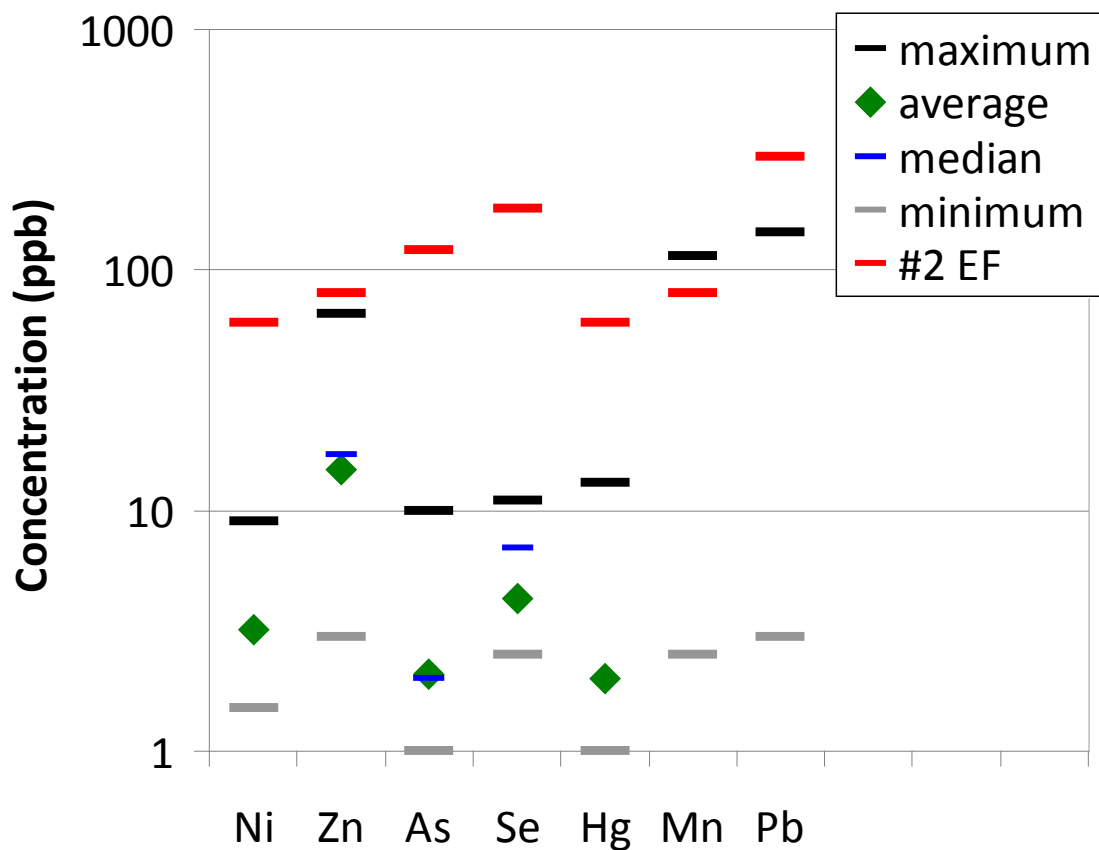
**Table 3-4. Emission Factors of Trace Elements for Distillate and Residual Fuel Oils**

Trace Element	#2 Distillate Oil		#6 Residual Oil	
	Emission Factor lb/10 <sup>6</sup> gal	Concentration ppb	Emission Factor lb/10 <sup>6</sup> gal	Concentration ppb
As	0.0147	2.1	1.36	172
Pb			1.49	188
Mn			22.5	2851
Ni	0.0224	3.2	134	16,988
Zn	0.104	14.8	15.5	1,963
Co			8.79	1113
V			23.4	2,967
Hg	0.014	2.0	0.016	2
Se	0.0303	4.3	0.945	119

Figure 3-2 and Figure 3-3 compare the trace element concentrations determined in this work with the concentrations based upon the emission factors provided in AP-42 for distillate heating oil and residual fuel oil, respectively (see also Table 3-6). The black bar represents the maximum measured value and the gray bar represents the minimum value (most often half of the MDL). The green diamond and blue bar represent the average and median values based on the samples measured in this study. The red bars indicate the trace element concentrations according to the AP-42 emission factors.

For home heating oil, Figure 3-2 illustrates that the trace elemental content based on the information provided in AP-42 exceeds the average measured concentration by almost an order of magnitude or more. With the slight exception of Mn, the AP-42 concentrations are all greater than the maximum recorded levels. Because the maximum emission from the combustion of fuel cannot exceed the trace element concentration in the fuel, using the AP-42 emission factors would clearly overestimate the trace element emissions from these in-use distillate oil samples. Even using the average measurement concentrations would represent an upper bound of emissions, because it assumes that all the trace elements are completely emitted during combustion.

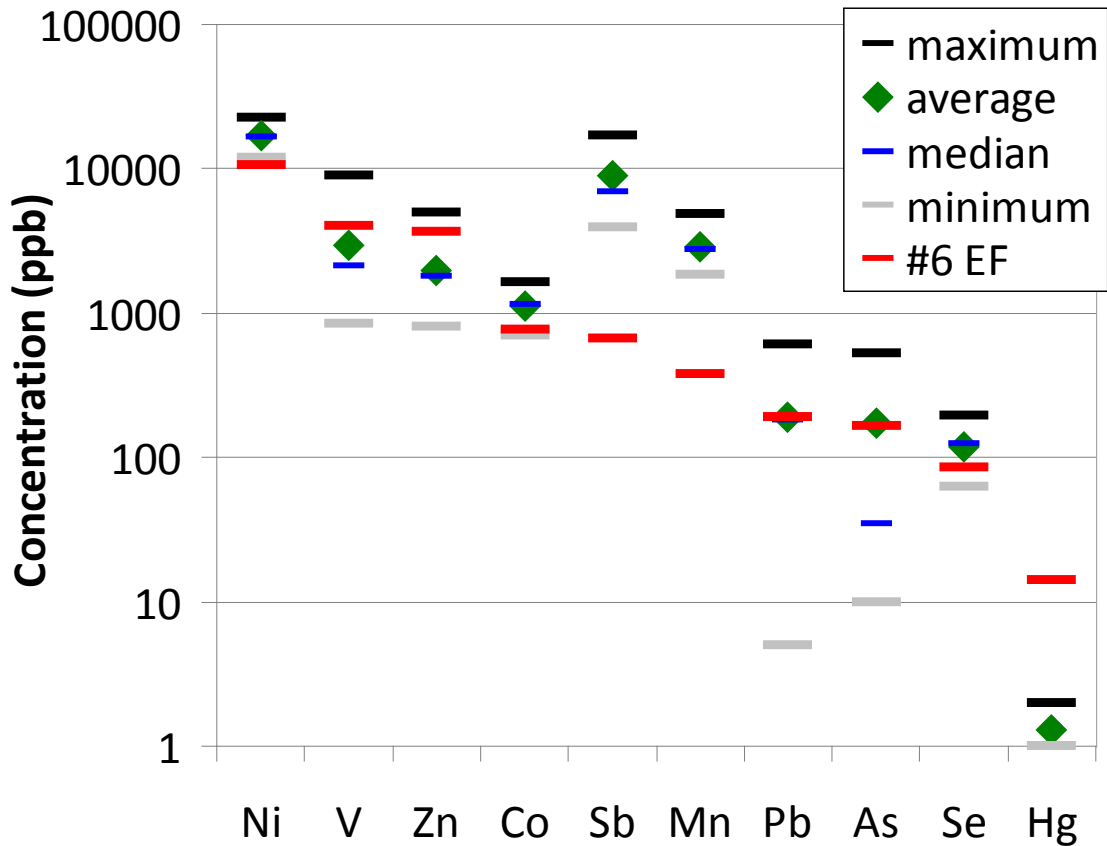
Figure 3-3 illustrates better agreement between the measured concentrations and those derived from AP-42 emission factors for trace elements in residual fuel oils. For most elements, the AP-42 derived concentrations fall within the range of measured concentrations. The measured average concentration for Pb and As aligns favorably with the emission factor estimate. Still, for Ni, Sb, and Mn, the AP-42 concentration is lower for the measured range. As is the case with distillate oils, the AP-42 concentration for Hg is significantly higher than the concentrations measured in the residual oil samples. Based on this work, the average concentration of Hg for both No. 2 and No. 6 fuel oils is 2 ppb. According to AP-42, the inferred Hg concentrations are 60 ppb and 14 ppb, respectively; therefore, using the AP-42 factors would overestimate the Hg emissions by factors of 30 and 7 for the combustion of these fuels.



**Figure 3-2. Comparison of Measured Elemental Concentrations and Concentrations from AP-42 Emission Factors: Distillate Oil.**

Analysis of biodiesel 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-sulfur diesel with trace elemental composition at or below that determined for home heating oil. The sulfur level in biodiesel, however, appears on average to be higher (27.3 ppm) than ultra-low-sulfur diesel (5.6 ppm), although the small number of samples (eight) may not be representative. A study on sulfur levels in biodiesel derived from a wide range of feedstocks (vegetable oils, grease, and animal fats) indicated that sulfur levels in at least some biodiesel feedstocks are relatively high compared to ultra-low-sulfur diesel ( $\leq 15$  ppm), depending on growing conditions or processing. As such, biodiesel in and of itself may not necessarily meet ultra-low-sulfur diesel requirements (Thompson and He 2006; He and Van Gerpen 2008). Biodiesel certification as a low sulfur fuel is possible, with the biodiesel industry having developed a voluntary fuel accreditation program called BQ-9000 that includes certification testing for 15 ppm (as well as 500 ppm) sulfur content in pure (100%) biodiesel (National Biodiesel Board 2008). Accreditation under the BQ-9000 program requires that the fuel must meet the biodiesel certification levels established by the industry

standard method ASTM D6751 (ASTM International 2010a). In addition, the October 2008 revisions to the ASTM International specifications for diesel fuels (ASTM D975-08a) and fuel oils used for home heating and boiler applications (ASTM D396-08b) include the same requirements for blends up to 5% biodiesel (ASTM International 2009; ASTM International 2010b). These bioblends must meet the same regulations as their non-blended counterparts.



**Figure 3-3. Comparison of Measured Trace Element Concentrations and Concentrations from AP-42 Emission Factors: Residual Oil.**

**Revision of 2002 New York State Mercury Emissions Inventory**

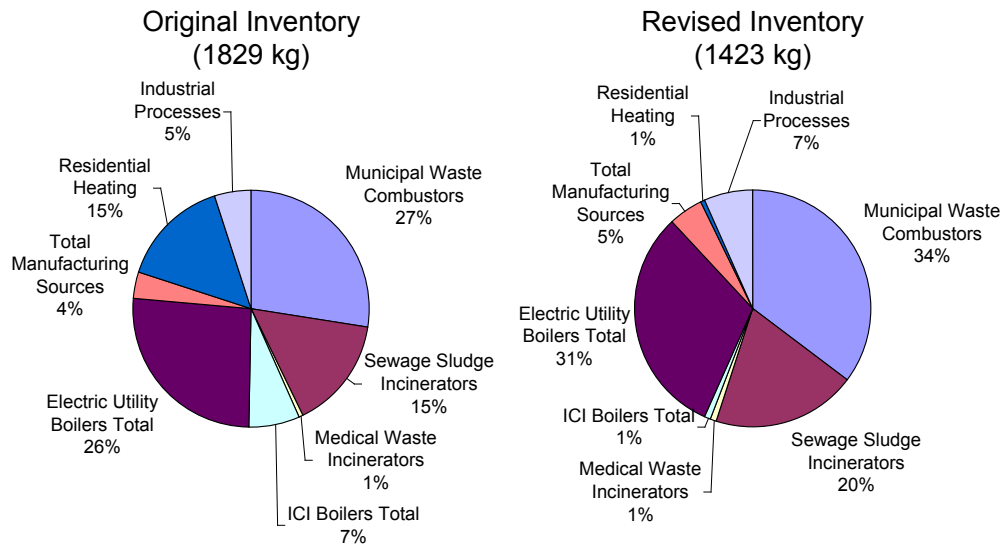
In order to illustrate the impact that the results from this work have on emissions inventory data, we revisited the 2002 Hg inventory for New York State. NESCAUM previously updated a baseline 1996 anthropogenic Hg emissions inventory for the northeast states (Connecticut, Maine, Massachusetts, New Hampshire, New Jersey, New York, Rhode Island, and Vermont) to the year 2002 (NESCAUM 2005). In the 2002 inventory, the AP-42 emission factors were employed to estimate the emissions from the oil



combustion source categories, including industrial/commercial/institutional (ICI) oil-fired boilers, electric utility oil-fired boilers, and residential heating from distillate heating oil.

The original 2002 inventory for New York State can be revised by adjusting the Hg emissions by factors of 30 or 7, depending upon the fuel type, based on the results of fuel sampling described in this report. For the adjustments, it was assumed that all of the fuel used by electric utility boilers is residual, that all of the fuel used in residential heating is distillate, and that the fuel combusted by ICI oil-fired boilers (note that EIA classifies apartment buildings as commercial) is 75% distillate and 25% residual. Figure 3-4 displays the percent each general source category represents of the entire 2002 New York State inventory before and after the revisions.

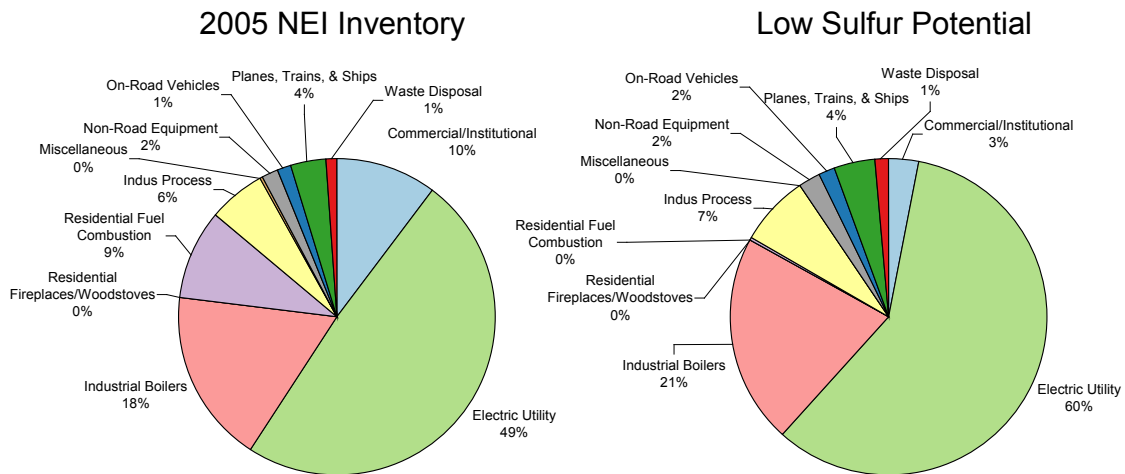
When adjusting the 2002 New York State inventory estimates using the emission factors determined in this work, the contributions of residential heating and ICI boilers to the overall state-wide Hg emissions drop from 15% and 7%, respectively, to only 1%. These adjustments make the contributions from the other source categories relatively more significant; for example, the emissions from sewage sludge incineration represent 20% of the entire inventory rather than 15% after the revisions. Municipal waste combustors continue to contribute the largest share of Hg air emissions in New York State, increasing from 27% to 34% of total state-wide emissions when the fuel oil combustion contributions are adjusted to reflect the observed lower Hg content in fuel oil. Note that although the emission estimate of oil-fired electric utility boilers was adjusted, the majority of Hg emissions from electric utility boilers in New York State are from coal-fired boilers, so the total contribution from all electric utility boilers actually becomes more significant after the revisions.



**Figure 3-4. General Source Category Contributions to the 2002 New York State Anthropogenic Mercury Emissions Inventory.**

### Estimated Reductions in New York State Sulfur Dioxide Emissions Based on Ultra-Low-Sulfur-Fuel

As discussed in Section 1, New York State recently passed legislation establishing an ultra-low-sulfur (15 ppm) fuel standard for No. 2 home heating oil by July 2012. By examining the New York's new requirement relative to a recent state SO<sub>2</sub> emissions inventory, the projected impact of the new law can be quantified. According to the USEPA's 2005 National Emissions Inventory (NEI), a total of 34,814 short tons of SO<sub>2</sub> (~9% of the total state inventory) were attributed to residential fossil fuel combustion in New York State in 2005 (USEPA 2009). In 2005, 1,471,188 thousand gallons of distillate fuel oil were sold for residential use. If the sulfur level in this fuel was 15 ppm, a maximum of 150 short tons SO<sub>2</sub> would have been released by residential combustion of distillate fuel. This calculation indicates that New York's new law would result in a 99% SO<sub>2</sub> emissions reduction from the residential sector such that this sector's share of the total state-wide SO<sub>2</sub> emissions inventory would drop to less than 1%. The reduction is illustrated in Figure 3-5, which compares the original 2005 NEI SO<sub>2</sub> emissions inventory for New York State with a hypothetical adjusted inventory incorporating a lower sulfur fuel content level. Note that in the adjusted inventory, the SO<sub>2</sub> emissions from the commercial/institutional category were also recalculated based on the volume sales (distillate and residual fuel oils) for that sector according to the EIA. A sulfur content of 15 ppm and 3,020 ppm (the average level based on the data in this study) were assumed for distillate oil and residual oil, respectively. For other categories burning fuel oil (i.e., industrial boilers and electric utility), it is difficult to separate the fuel oil SO<sub>2</sub> emissions in these categories from the coal combustion emissions; therefore, the SO<sub>2</sub> emissions from all other categories remained unchanged from the original inventory.



**Figure 3-5. General Source Category Contributions to the 2005 New York State Sulfur Dioxide Emissions Inventory.**

It is important to keep in mind that the residential distillate fuel oil reductions will be largest during the heating season (winter months). As mentioned in Section 1, sulfate is a significant component of PM<sub>2.5</sub>

during the wintertime, with a large local contribution under stagnant meteorological conditions. In addition, because residential oil combustion emissions occur in close proximity to where people live, reductions in sulfur emissions result in targeted reductions in public exposure to these pollutants.

**Comparison with Speciate Emission Profiles**

As mentioned above, the measured trace element concentrations in the fuel samples should represent the upper limit of the emissions, assuming that all trace elements are emitted to the air during combustion. It is interesting to compare the fuel-based emission factors determined in this work with current source profiles, largely obtained by in-stack measurements. SPECIATE is a USEPA database of speciated emissions profiles of air pollution sources (Hsu and Divita 2009). Recently, Reff et al. (2009) used the source profiles in SPECIATE to create a national emissions inventory of fine particulate matter (PM<sub>2.5</sub>) for the year 2001. We were provided with the emissions estimates for New York for 2001 from both distillate oil combustion and residual oil combustion. Using the total amounts of distillate oil and residual fuel oil consumed by New York State in 2001 as provided by the Energy Information Administration (EIA), trace element emissions were estimated using the emission factors determined in this work. Table 3-5 compares the total 2001 New York State emissions estimates for trace elements from combustion of distillate and residual fuel oils from the calculations in this work with the SPECIATE-based calculations.

**Table 3-5. Trace Element Emissions Estimates from Distillate and Residual Oil Combustion in New York State, 2001**

	#2 Distillate		#6 Residual	
	NESCAUM ton/yr	SPECIATE ton/yr	NESCAUM ton/yr	SPECIATE ton/yr
As	0.0251		0.86	
Pb			0.942	
Mn			14.2	0.0873
Ni	0.0383		84.7	1.14
Zn	0.0178	4.26	9.8	0.174
Co			5.56	
V			14.8	1.93
Hg	0.0239		0.0101	
Se	0.0518		0.597	

With the exception of zinc emissions from distillate oil, all of the trace element estimates based on the SPECIATE profiles are less than the values determined from the measurements made in this work. It is reasonable that the SPECIATE estimates are lower, because those estimates are based on stack measurements and it is possible that trace elements are not completely emitted during combustion, or completely captured in the stack measurements. Given that zinc was the only trace element studied in this work that was also listed in the SPECIATE source profile for distillate oil, it is difficult to interpret whether zinc is an outlier in the source profile or if the entire profile may need to be examined.

Of special note is that the SPECIATE estimates give relatively more emissions of V than Ni from residual fuel oil combustion, whereas the estimates from this work indicate Ni content is greater than V content by a factor of five. It has been seen that the ratio of V to Ni in crude oil varies over a wide range (0.17 – 6.67), which may be correlated with the maturity of the crude oil (i.e., age of the reservoir rock) such that the V/Ni ratio decreases with increasing geologic time (Musa et al. 1995). Interestingly, all of the residual oil samples measured in this work, which presumably derive from diverse production fields, had higher Ni content than V content.

### Summary

This work provides an up-to-date estimate of trace elemental composition of distillate fuels used in the state of New York and surrounding areas. 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 emissions from residual oil and reveals its relative contribution to be even greater than previously estimated when compared to emissions from home heating oil.

Table 3-6 summarizes and compares mercury and other trace element emission factors from AP-42 and the fuel sampling results for New York State and the Northeast described in this report. With this state and region-specific information, the fuel sampling results can be employed by air quality program managers in their work to develop improved inventories of emissions. Because these inventories form the basis for decisions, either by direct analysis or use in air quality modeling exercises, they 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.

**Table 3-6. Comparison of Emission Factors (EF) and Concentrations of Trace Elements for Distillate and Residual Fuel Oils**

Trace Element	#2 Distillate Oil				#6 Residual Oil			
	NESCAUM		AP-42		NESCAUM		AP-42	
	EF lb/10 <sup>6</sup> gal	Conc. ppb	EF lb/10 <sup>6</sup> gal	Conc. ppb	EF lb/10 <sup>6</sup> gal	Conc. ppb	EF lb/10 <sup>6</sup> gal	Conc. ppb
V			n/a	n/a	23.4	2,967	31.8	4,025
Mn			0.83	120	22.5	2851	3	380
Co			n/a	n/a	8.79	1113	6.02	762
Ni	0.0224	3.2	0.42	60	134	16,988	84.5	10,696
Zn	0.104	14.8	0.56	80	15.5	1,963	29.1	3,684
As	0.0147	2.1	0.56	80	1.36	172	1.32	167
Se	0.0303	4.3	2.08	295	0.945	119	0.683	86
Sb			n/a	n/a	70.1	8,873	5.25	665
Hg	0.014	2.0	0.42	60	0.016	2	0.113	14
Pb			1.25	179	1.49	188	1.51	191

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**DETERMINATION OF SULFUR AND TOXIC METALS CONTENT OF  
DISTILLATES AND RESIDUAL OIL IN THE STATE OF NEW YORK**

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**FINAL REPORT 10-31**

**STATE OF NEW YORK  
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