

**Size distribution of
atmospheric
particulate mercury**

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Size distribution of atmospheric particulate mercury in marine and coastal atmospheres

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Abstract

A study was conducted to determine the size distribution of particulate mercury (Hg^{P}) at a marine and coastal site, and compare the seasonality at both sites. Data was collected during summer 2009 and 2010, winter 2010, and spring 2010. Two cascade impactors were used to collect Hg^{P} in ten size fractions ranging from $> 10\mu\text{m}$ to $< 0.4\mu\text{m}$. During summer 2009, Hg^{P} was found mainly (50–60 %) in coarse fractions, 1.1 to $5.8\mu\text{m}$, composed of sea salt particles at both our coastal site (Thompson Farm) and marine site (Appledore Island). In winter, Hg^{P} at Thompson Farm was dominated (65 %) by fine particles, while in spring and summer 2010, at both sites, Hg^{P} was distributed across the coarse and fine fractions (40 % each). Using bulk filters to collect total Hg^{P} during each campaign, we show a diurnal cycle that matches that of gaseous elemental mercury. Finally, dry deposition rates of Hg^{P} were calculated to be $1.7\text{--}2.8\text{ ng m}^{-2}\text{ day}^{-1}$ in the summer, $4.6\text{ ng m}^{-2}\text{ day}^{-1}$ in the winter, and $2.5\text{ ng m}^{-2}\text{ day}^{-1}$ in the spring.

1 Introduction

Understanding mercury transport and chemical transformations in the atmosphere is a key component to establishing its global cycle. Schroeder and Munthe (1998) summarized the physical, chemical and toxicological properties of atmospheric mercury, as well as various atmospheric pathways including anthropogenic and natural sources, aerial transport and distribution, chemical and physical transformations, and wet and dry deposition to the Earth. More than a decade later, we know that mercury cycling in the atmosphere is far more complex than earlier expectations. Today, areas of active study include mercury distribution, seasonality, and complex chemical transformations on the regional-to-global scale.

Mercury in the atmosphere consists of three chemical forms including gaseous elemental mercury (Hg^0), reactive gaseous mercury ($\text{RGM} = \text{HgCl}_2 + \text{HgBr}_2 + \text{HgOBr} + \dots$),

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and particulate phase mercury (Hg^{P}). Hg^0 is the primary form of mercury emitted into the atmosphere from natural and anthropogenic sources. Hg^0 is oxidized to produce RGM by reaction with many oxidants which include ozone (O_3), hydroxyl radicals (OH), hypochlorous acid (HOCl), and halogen atoms. RGM can bind to particles to create Hg^{P} . Further, RGM can be reduced back to Hg^0 by SO_2 and sunlight (Lindberg and Stratton, 1998).

Very little is known about Hg^{P} in comparison to Hg^0 and RGM and even less is known about the size distribution of Hg^{P} in the atmosphere. A few studies have been performed confirming that the majority of Hg^{P} resides in smaller particles in the atmosphere, which can be transported long range (Wang et al., 2006). However, the majority of the size distribution data are for urban sites located in Asia. Tsai et al. (2003) reported that, for an urban site in Taiwan, an average of $\sim 70\%$ Hg^{P} in PM_{10} was found in $\text{PM}_{2.5}$. Wang et al. (2006) studied two locations in Beijing, an urban and suburban site, reporting that both sites had the largest Hg^{P} in $< 1\mu\text{m}$ size fraction when measuring samples from $> 7\mu\text{m}$ to $< 1\mu\text{m}$. Xiu et al. (2009) studied size-fractionated total Hg^{P} in urban, coastal Shanghai, China, at four size cut stages (18, 8.0, 3.7, 1.6 μm) and an after filter. Overall, there was more Hg^{P} in winter, with the largest amount in the $< 3.7\mu\text{m}$ range. Alvarez et al. (2004) analyzed various metals, including mercury, in 24 areas of Seville, Spain, an inland city along the River Guadalquivir. The maximum distribution of particles (accounting for $\sim 25\%$) was between 0.6 and 4.9 μm .

The benefit of our study location was the ability to collect and compare particulate data from both a marine and an inland, coastal site in the “tailpipe” of the United States. It was shown by Driscoll et al. (2007) that US emissions account for 40% to 65% of mercury deposition in the Northeast and that re-emission of US emissions also account for another 10% to 20%. Hg^{P} , measured in size fractions from $< 0.4\mu\text{m}$ to $> 10\mu\text{m}$, is expected to dominate the fractions correlating to sea salt aerosols (1–6 μm) formed from bursting bubbles and waves breaking, which can affect areas up to 25 km from the coastline (De Leeuw et al., 2000; Athanasopoulou et al. 2008), dust particles, and/or

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ultrafine and accumulation particles ($< 2 \mu\text{m}$) emitted directly from combustion sources and resulting from coagulation of small particles (Finlayson-Pitts and Pitts, 2000).

2 Campaign details

Thompson Farm and Appledore Island are part of the AIRMAP observing network (www.airmap.unh.edu). The benefit of conducting these campaigns at both a marine and an inland, coastal site is to ascertain differences and similarities in the phase partitioning and cycling in the two atmospheres. The marine site is located in the Gulf of Maine on Appledore Island (42.97°N , 70.62°W) about 12 km offshore from New Hampshire, Fig. 1. The inland site is located at Thompson Farm in coastal New Hampshire (43.11°N , 70.95°W) which is located about 25 km inland. A detailed description of the Thompson Farm site can be found in Sigler et al. (2009).

Six aerosol sampling campaigns were conducted at Thompson Farm and Appledore Island as part of a study on the cycling of mercury in the marine boundary layer. There were several objectives of the campaigns: (1) to quantify total and size-fractionated Hg^{P} ; (2) compare and contrast the marine and coastal site for distribution of Hg^{P} ; and (3) determine the importance of the size distribution of Hg^{P} in the marine boundary layer.

During the summer of 2009, an intensive two week campaign was conducted on Appledore Island from 20 July–4 August. Two cascade impactors were operated consecutively, each with a seven day time resolution. Bulk filter samples were also collected with three hour time resolution, and trace gases (hydrocarbons, halocarbons, alkyl nitrates, and selected sulfur gases) were collected in electropolished stainless steel canisters every hour. Analysis of the canisters was conducted in the trace gas laboratory at the University of New Hampshire. Automated Tekran speciated atmospheric mercury systems, with 5 min time resolution for Hg^0 and 3 h for Hg^{P} and RGM, were operated continuously at each site along with ozone and carbon monoxide with 1 min time resolution. Details of each campaign are listed in Table 1.

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Following the Appledore Island campaign, a second was conducted at Thompson Farm (7–18 August). The campaign consisted of two cascade impactors operated simultaneously for eleven days to determine the consistency in the Hg^{P} size distribution. At Thompson Farm, about 200 trace gases are measured year-round including oxygenated compounds measured with a proton transfer reaction mass spectrometer.

Finally, in the summer of 2009, a third campaign was run at Appledore Island (20 August–2 September). The campaign lasted a total of thirteen days. One impactor was run 12 h during the day (06:00 a.m.–06:00 p.m. local time) and the other run for 12 h every night. The campaign was conducted to investigate the difference between day and night phase partitioning and cycling of Hg^{P} .

Two more campaigns were conducted at Thompson Farm in the winter (21 January–10 February) and spring (5–25 April) 2010, times of peak concentration of mercury in the New England atmosphere (Mao et al., 2008; Sigler et al., 2009; Lombard et al., 2011). During both campaigns, the cascade impactors were run consecutively for ten days each having a campaign lasting a total of twenty days. Bulk filter samples were run with 24 h resolution. Concurrently, a continuous gas chromatograph was set up to measure trace gases. This complete dataset allowed for determination of the seasonality of the size distribution of Hg^{P} at the coastal site.

Finally, in the summer of 2010, two intensive campaigns were run simultaneously at both Thompson Farm and Appledore Island (26 July–9 August). The time resolution matched the first campaign at Appledore Island with two impactors at each site running consecutively for 7 days each and bulk filters at three hour time resolution. At Appledore Island, hourly canisters were collected; while at Thompson Farm, a continuous gas chromatograph analyzed trace gases. This final addition allowed for comparison of the two summer sets of size distribution of Hg^{P} , as well as direct comparison between the marine and coastal sites.

3 Methods

5 Sampling at Thompson Farm is 40 m above sea level at the top of a steel tower located just above the tree line. Sampling at Appledore Island is located 30 m above sea level at the top of a World War II lookout tower. Our group has been collecting Hg⁰ measurements at Thompson Farm since November 2003 and Appledore Island since July 2005 (Mao et al., 2008). During intensive field campaigns performed during summer 2009, winter 2010, spring 2010, and summer 2010, Hg^P was measured using three different methods: bulk filter Hg^P, size-fractionated Hg^P, and Hg^P with a Tekran model 1135. More detailed results on the comparison of the bulk filter samples and the Tekran model 1135 were published previously (Talbot et al., 2011).

10 The cascade impactors were Andersen Mark II Cascade Impactors with 10 filters, including a pre-filter and backup filter, capable of differentiating size distributions ranging from < 0.4 μm to > 10 μm (Table 2; discontinued, a similar model Series 20–800 eight stage non-viable impactor available from ThermoFisher Scientific Inc.). Millipore fluoropore filters of 90 mm diameter and 1 μm pore size were used for the impactor as well as the bulk sample filters. The filters were pre-cleaned in 12 h acid soaks of 30 % HNO₃ and 20 % HCl each. Blank filters went through the same handling process. For sampling the filters were placed in custom delrin holders and ambient air flowed through at ~ 120 standard liters per minute. The holders were washed with soapy deionized water and then soaked 12 h in 5 % HCl. Samples and blanks were stored in clean room bags. Filter extractions were conducted using 1.5 % BrCl and HCl for 24 h. They were then diluted to 0.5 % BrCl and HCl for analysis. Acid extracts were stored in Teflon bottles that were soaked 12 h in 50 % HNO₃, another 12 h in 30 % HCl, and finally soaked for 5 days in 5 % HCl. The average blank filter contained 25 pg of Hg, while the samples contained 10–100 times more Hg. Thus, the blank corrections were essentially in the background noise and contributed little to the overall uncertainty of the ambient measurements. It has been shown previously that filter methods have artifacts associated with the adsorption of RGM onto the particulates (Landis et al., 2002)

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or the loss of mercury when sampling times are greater than a few hours (Malcolm and Keeler, 2007). However, when tested in the laboratory, uptake by RGM was minimal and the loss of mercury is assumed to be the same for each impactor and each size fraction.

5 Analysis of these samples for Hg^0 was via cold vapor atomic fluorescence using a Tekran Series 2600 Liquid Analysis System using SnCl_2 as a reducing agent. Calibration standards were prepared from a 1000 ppm HgO in 3% HNO_3 Atomic Absorption solution purchased from Ricca Chemical Company. A certified reference material, ORMS-4 (Hg in water), purchased from the National Research Council Canada was
10 utilized as an external standard. The accuracy of the instrument using the external standard was < 10%. The analytical precision of repeated determinations of the ambient samples was better than 5%.

4 Campaign results and discussion

15 In summer 2009, Hg^P was found in coarse particles > 1.1 μm at Appledore Island (Fig. 2a). The coarse aerosols are attributed primarily to sea salt particles. Sea salt aerosols can have diameters in a range of sizes from 0.2 μm (fine) to more than 2000 μm (coarse) (Athanasopoulou et al., 2008). The majority of sea salt aerosols are in the 1–10 μm range. Sodium and chloride, making up 85% of elements in sea salt aerosols, have peak diameters around 4 μm (Wall et al., 1988; Athanasopoulou et al.,
20 2008; Finlayson-Pitts and Pitts, 2000). In the data set shown in Fig. 2a, about 60% of the summer data is from sea salt, in the range of 1.1–5.8 μm . Hg^P results are reported as mixing ratios in parts per quadrillion by volume (ppqv), such that 1 ng m^{-3} is 112 ppqv Hg . The first week had about half of the total Hg^P than during the second week. It is noted that the first week was stormy and rained the majority of the
25 time, while the second week was sunny and clear. Rain events scrub mercury from the atmosphere (Mao et al., 2012), thus lowering the amount sampled by the impactor.

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The sensitivity of the two impactors was tested at Thompson Farm, where both were run simultaneously. The results are shown in Fig. 2b. There is a 16% difference in the two impactors' total mercury, likely due to variability in the atmosphere. The overall size distribution trends are similar, giving confidence in our size distributions. Both Thompson Farm and Appledore Island showed similar total particulate mercury over the course of the campaigns during the summer, with both sites showing the majority of particles in the sea salt size range, which can exist up to 25 km inland (De Leeuw et al., 2000; Athanasopoulou et al., 2008).

During the initial campaign at Appledore Island, it appeared that there was a trend in daytime versus nighttime Hg^{P} as indicated by data from the automated system. Therefore, another size distribution analysis was planned to quantify this effect. As shown in Fig. 3, large size fractions of Hg^{P} dominate during daytime, showing more than twice as much total Hg^{P} during daylight hours compared to nighttime (cycles from 10:00 UTC to 22:00 UTC). This could be attributed to more RGM production during sunny days and subsequently depositing RGM to the surface of particles to yield more Hg^{P} during the day (Sigler et al., 2009).

In winter at Thompson Farm, about 65% of the Hg^{P} was found in fine particles $< 1.1 \mu\text{m}$ (Fig. 4). These fine particles are attributed to fine crustal dust, sulfate aerosols, organic matter, and soot particles commonly found at continental locations. Fine particles are high in winter and spring, consistent with increases in combustion sources related to wintertime heating and long-range transport (Jaffe et al., 2005; Weiss-Penzias et al., 2007; Xiu et al., 2009; Wang et al., 2006). The dominance of the fine particles may also be attributed to the fact that smaller particles are much less scavenged in the winter than the summer (Lombard et al., 2011). On average, there is more wet deposition in summer than in winter as shown in Lombard et al. (2011). More rain in the warm season scavenges more particles and leads to less Hg^{P} . The total Hg^{P} observed during the winter is more than twice the total amount seen in summer and spring, confirming reports from Tsai et al. (2003) and Wang et al. (2006) who showed higher total Hg^{P} in winter, confirming a decline in mercury during the warm season due

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to the strength of the removal processes (Mao et al., 2008). In addition, westerly flow in winter combined with colder temperatures may advect more Hg^{P} of continental origin, largely in fine particle size fractions, to the area than in summertime (Mao et al., 2008).

Generally, the peak concentration of mercury in the atmosphere in New England is in the springtime (Mao et al., 2008; Sigler et al., 2009; Lombard et al. 2011). It is believed that this occurrence is attributed to surface re-emission of mercury during snow melt (Vanarsdale et al., 2005). However, the 2010 winter was warm, and snow was melting much earlier than April, which is probably why the winter campaign impactor contained more total Hg^{P} than the spring impactor. The spring results showed a mixture of fine and coarse particles implying a transition from winter to summer cycling (Fig. 5).

The summer 2010 results are similar to those of the spring, showing both fine and coarse particles dominating Hg^{P} at both sites. Thompson Farm (Fig. 6a) had more of an influence from fine particles during the first week which may be attributed to the source of air. During the first week, the air masses came from north and west, while the second week was impacted by air from the south and had marine origins. It is interesting to note that Appledore Island (Fig. 6b) had more Hg^{P} than Thompson Farm, especially in the sea salt region of the size distribution possibly due to the involvement of halogen chemistry in Hg cycling in the marine boundary layer such that more RGM is produced which then leads to more Hg^{P} (Holmes et al., 2009; Mao et al., 2008; Hedgecock and Pirrone, 2001; Sigler et al., 2009). The distribution of fine and coarse particles at each location could reflect the influence of marine air on coastal air and vice versa. An earlier study showed that Appledore Island is influenced by continental air about 14% of the time, while Thompson Farm is influenced by marine air about 30% of the time in summer (Chen et al., 2007). Table 3 summarizes the major findings of the campaign.

In comparing the Appledore Island impactors operated during both summers, it is clear that the marine site is heavily impacted by sea salt particles and that finer particles influenced the marine air more during the summer of 2010 which may be a result of many factors including source of the air masses, wind speed, and less rain, allowing

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fine particles to travel farther. The amount of total Hg^{P} integrated over all size fractions was very similar for both summers, with the exception mentioned previously, which implies that the difference in size distribution in the two summers did not affect the total Hg^{P} . This phenomenon is possibly because the marine site is dominated by larger particles which affect the total Hg^{P} more than the fine particles.

Thompson Farm, during the two summers, also showed more fine particles in the summer of 2010 and more influence by marine air in summer 2009. Again, the total amount of Hg^{P} is similar during both summers; however, there seems to be more variability in total Hg^{P} at this site. Hg^{P} is more particle size dependent at Thompson Farm than at Appledore Island, possibly because when larger sea salt particles reach the site, they greatly influence the total Hg^{P} .

The first summer campaign showed very different patterns between the marine and coastal sites, while the second summer campaign, conducted simultaneously at both sites, showed very similar trends in size distribution. Backward trajectories can help explain this occurrence. The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model was used (<http://www.arl.noaa.gov>). The trajectories were run for 24 h using the EDAS-40-km archive grid. Dates in mid-campaign show that during the first summer, Appledore Island was influenced by air coming from the south at the end of July, while Thompson Farm was influenced by air from the north in mid-August (Fig. 7a, b). This explains why the two campaigns exhibited different size distributions. However, during summer 2010, backward trajectories show that both sites were influenced by the same air parcels that originated from the southwest in early August (Fig. 7c, d) leading to similar size distributions. The difference in the patterns is thus attributed to the time difference between the campaigns, and it is likely that had the summer 2009 campaigns been conducted simultaneously, the size distribution of Hg^{P} would be similar.

The summer 2010 campaign also allowed for direct comparison of bulk filter data at Thompson Farm and Appledore Island. Details about the previous seasonal data can be found in Talbot et al. (2011). The bulk filters tracked each other nicely with similar

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5 mixing ratios and general trends in elevated and reduced mixing ratios, as shown in Fig. 8. There are a couple discrepancies between the two sites; specifically, Thompson Farm has spikes in data which may be attributed to small differences in local events. On early 2 August, the large peak occurred during the filter sample following a smoke/fire smell in the area. Smoke smells also occurred at Appledore Island on 1 August and 8 August due to fire on an adjacent island, ~ 1 km away with relatively weaker impact. The 6 August event at Thompson Farm occurred after a period of extreme fog.

10 Furthermore, peaks in Hg^{P} coincide with enhancements in hydrocarbons in the atmosphere at both sites (Figs. 9 and 10). Tracer compounds include isoprene, a biogenic or continental emission tracer, and tetrachloroethylene, an urban emission tracer, CO , O_3 , ethyne, and monoterpenes. Hg^{P} peaks on Appledore Island were correlated with enhancements in carbon monoxide as well as biogenic species such as isoprene, α -terpene, and β -terpene suggesting a continental influence confirmed by wind patterns from the west which bring in air masses of continental origin.

15 Bulk filter results also confirm a discrepancy with the Tekran; the Tekran is less responsive to the enhancements in Hg^{P} that were associated with those in hydrocarbons (Talbot et al., 2011). This difference may be due to a positive artifact at Thompson Farm as evidence indicates the large peaks in filter Hg^{P} may be due to a RGM artifact (Fig. 11a). The figure shows the bulk filter Hg^{P} in black, the Tekran Hg^{P} in green, and the bulk filter Hg^{P} minus the Tekran RGM in red. The green and red points correlate better than the black and red points, showing that RGM may contribute to a positive artifact on the filters at Thompson Farm. Landis et al. (2002) reported a significant RGM artifact on filters where KCl-coated denuders were not used and RGM exceeded 15 pg m^{-3} , conditions that rarely happen at either of our sites. However, the filters and Tekran tracked each other better at Appledore Island (Fig. 11b) which may be attributed to the removal of the $\text{PM}_{2.5}$ elutriator on the Tekran inlet, which removes the majority of the particulate mercury at Appledore Island. RGM does not appear to significantly contribute to bulk filter measurements of Hg^{P} , which agrees with studies done by Malcolm and Keeler (2007) and Talbot et al. (2011) who showed that RGM does not always

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contribute artifacts. RGM at Appledore Island during this summer is at much higher concentrations than at Thompson Farm, while Hg^{P} is at similar concentrations at each site. RGM may be contributing at Appledore Island to some extent, but high levels of RGM do not seem to indicate more interference.

5 The seasonality of the bulk filter data at Thompson Farm shows that spring has relatively constant levels of Hg^{P} , while winter and summer show more variability with increased levels and more pollution events (Talbot et al., 2011). In addition, the bulk filters showed a diurnal cycle that matches that of elemental mercury (Fig. 12), as reported by Mao et al. (2008) for summer. Xiu et al. (2009) recorded similar results
10 showing a diurnal pattern with a peak in the early morning hours closely related to the diurnal pattern of Hg^{0} . Both the marine and coastal sites show similar times of depletion, with a pattern most likely due to the nocturnal inversion layer and night-time removal pathways. There was a peak in Hg^{P} just before and after the depletion suggesting enhancement in Hg^{P} due to generation by nighttime chemical reactions and daytime photochemical reactions. The latter is corroborated by the pattern correlated to enhanced RGM during the daytime from mixing and photochemically induced reactions, such that enhanced RGM leads to enhanced Hg^{P} (Tsai et al., 2003). More data is needed to confirm the diurnal pattern seen here.

15 The data was used to calculate Hg^{P} dry deposition rates. Rates were calculated to be 20 $1.7 \text{ ng m}^{-2} \text{ day}^{-1}$ in summer, $4.6 \text{ ng m}^{-2} \text{ day}^{-1}$ in winter, and $2.5 \text{ ng m}^{-2} \text{ day}^{-1}$ in spring at Thompson Farm and $2.8 \text{ ng m}^{-2} \text{ day}^{-1}$ in summer at Appledore Island. The flux is the product of the atmospheric concentration and the average deposition velocity of Hg^{P} , 0.5 cm s^{-1} (Landis and Keeler, 2002). There is more deposition at Appledore Island during the summer than at Thompson Farm, due to the large portion of Hg^{P} in sea salt sized particles. Thompson Farm results show the seasonality of the deposition, with the most dry deposition occurring during the winter; it has been shown that the most extensive Hg^{P} deposition occurs during the winter months (Wang et al., 2006). Averaging the seasons, Thompson Farm shows an annual deposition rate of $1.1 \mu\text{g m}^{-2} \text{ yr}^{-1}$ similar to Reinfelder et al. (2004) who reported Hg^{P} deposition rates at several locations

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in New Jersey ranging from $0.8\text{--}2.5\ \mu\text{g m}^{-2}\text{ yr}^{-1}$ and Landis and Keeler (2002) who reported an Hg^{P} deposition flux of $1.2\ \mu\text{g m}^{-2}\text{ yr}^{-1}$ in the Lake Michigan basin. Thompson Farm seasonal results, however, show that yearly data must be taken into account and annually averages cannot be factored using just one season of data.

5 Conclusions

A study was conducted to evaluate the size distribution and seasonality of atmospheric particulate mercury in marine and coastal atmospheres. It was determined that: (1) the aerosol size distribution and amount of total Hg^{P} is influenced by location, weather and source of air; (2) our coastal and marine sites are often affected by the same source of air; (3) the bulk filters show much higher concentrations of Hg^{P} than the automated system. Further, a diurnal cycle of Hg^{P} is shown that matches that of Hg^{0} . Dry deposition of Hg^{P} is calculated for each season, showing that winter has the highest removal rates.

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Table 1. Sampling details for Hg^P.

Season	Dates	Location	Sample type – time resolution
Summer 2009	20 Jul–4 Aug	Appledore Island	Bulk filters – 3 h Impactor – 7 days
	7 Aug–18 Aug	Thompson Farm	Impactor – 11 days
	20 Aug–2 Sep	Appledore Island	Impactor – 13 days
Winter 2010	21 Jan–10 Feb	Thompson Farm	Bulk filters – 24 h Impactor – 10 days
Spring 2010	5 Apr–25 Apr	Thompson Farm	Bulk filter – 24 h Impactor – 10 days
Summer 2010	26 Jul–9 Aug	Appledore Island	Bulk filter – 3 h Impactor – 7 days
	26 Jul–9 Aug	Thompson Farm	Bulk filter – 3 h Impactor – 7 days

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Table 2. Andersen Mark II cascade impactor size distribution.

Pre-separator	> 10 μm
Stage 0	9.0–10.0 μm
Stage 1	5.8–9.0 μm
Stage 2	4.7–5.8 μm
Stage 3	3.3–4.7 μm
Stage 4	2.1–3.3 μm
Stage 5	1.1–2.1 μm
Stage 6	0.7–1.1 μm
Stage 7	0.4–0.7 μm
Backup filter	< 0.4 μm

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Table 3. Major findings on the size distribution of Hg^P.

	Thompson Farm	Appledore Island
Summer 2009	–Hg ^P composed of sea salt size/coarse particles (~ 4 μm, 50 %) and fine dust particles (23 %)	–Hg ^P in coarse fraction, composed of sea salt size particles (50–60 %) –Daytime produces about two times more Hg ^P than nighttime –First campaign had many rain events
Winter 2010	–Hg ^P dominated by fine dust particles < 1 μm (65 %)	
Spring 2010	–Most amount of Hg ^P (1.68 ppqv) mixture of fine (40 %) and coarse particles (38 %)	
Summer 2010	–Hg ^P in both fine (28 %) and coarse fractions (47 %) –Least amount of Hg ^P (0.45 ppqv)	–Hg ^P in both fine (30 %) and coarse fractions (50 %) –Appledore Island had two times more total Hg ^P



Fig. 1. Locations for the campaign: coastal site located at Thompson Farm in New Hampshire (43.11° N, 70.95° W); marine site located in the Gulf of Maine on Appledore Island (42.97° N, 70.62° W).

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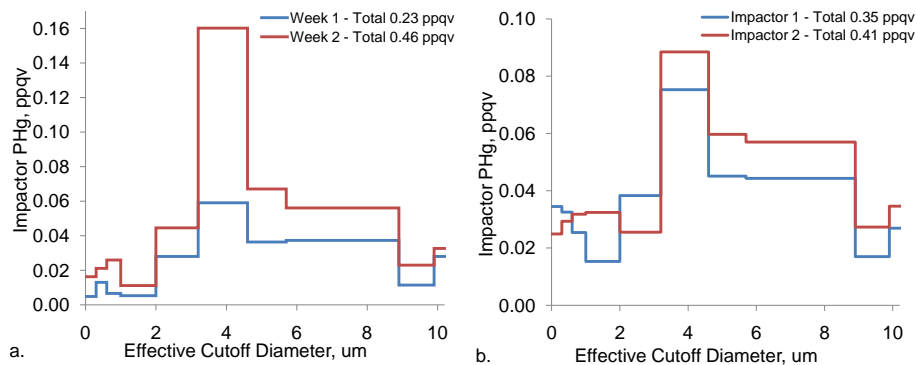


Fig. 2. Size distribution of Hg^P at Appledore Island **(a)** and Thompson Farm **(b)** for summer 2009 showing similar total Hg^P at both sites with enhanced levels of coarse size fractions.

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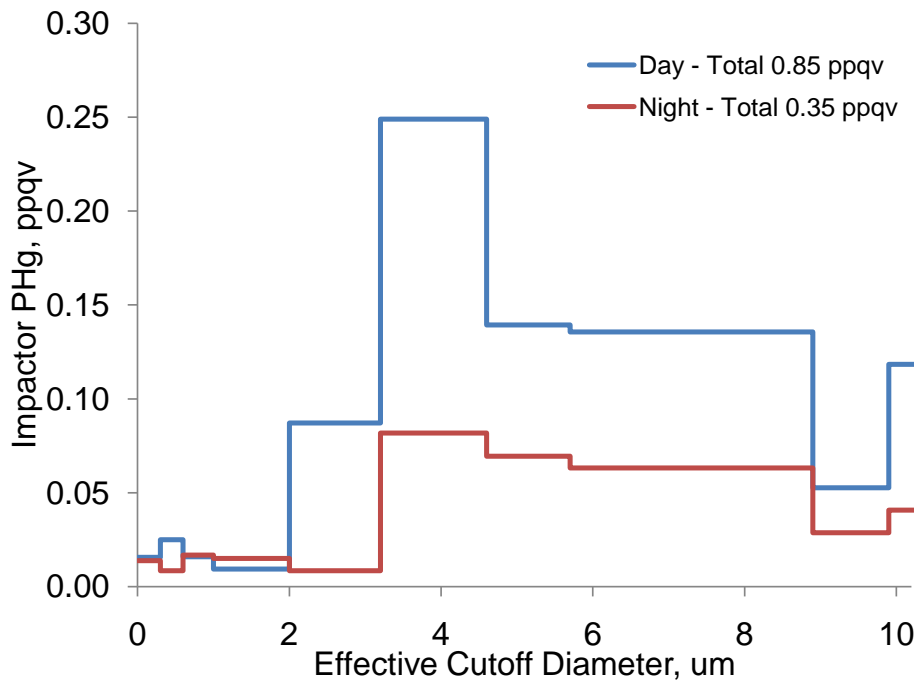


Fig. 3. Diurnal distribution of Hg^{P} at Appledore Island in summer 2009. There is more than twice as much Hg^{P} during the day, most likely due to enhanced sea salt generation.

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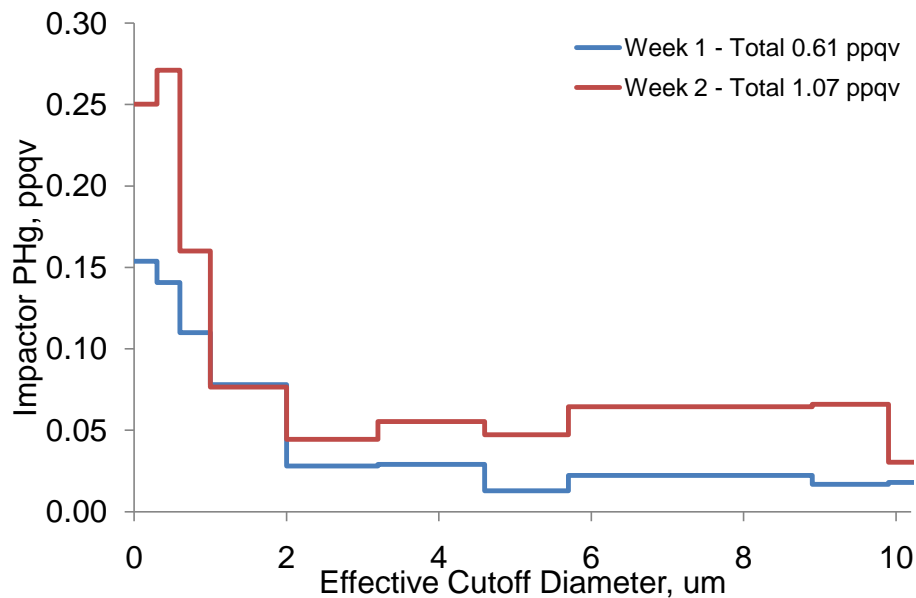


Fig. 4. Size distribution of Hg^P at Thompson Farm during winter 2010 showing the majority of Hg^P in the fine particle range.

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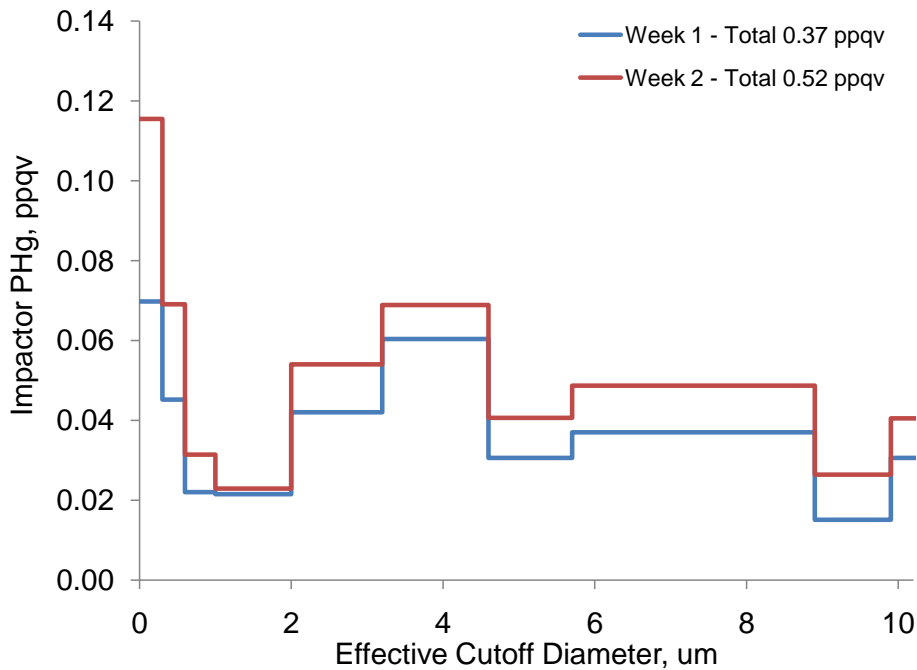


Fig. 5. Size distribution of Hg^{P} at Thompson Farm in spring 2010 which shows a distribution of fine and coarse size fractions.

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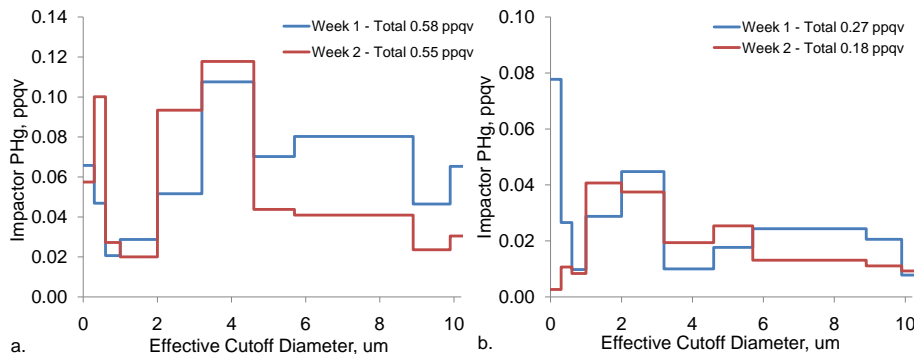


Fig. 6. Size distribution of Hg^P at Appledore Island **(a)** and Thompson Farm **(b)** during summer 2010 showing similar distributions of Hg^P at both sites with Appledore Island exhibiting twice as much total Hg^P.

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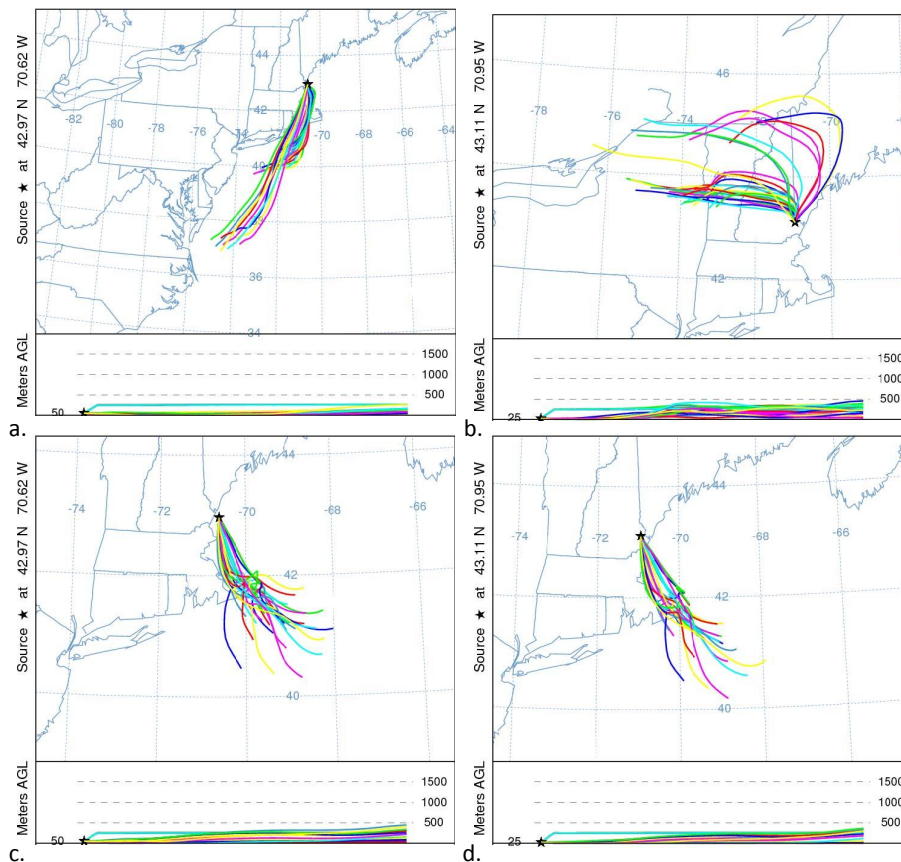


Fig. 7. HYSPLIT backward trajectories for Appledore Island (a 26 July 2009 and c 2 August 2010) and Thompson Farm (b 11 August 2009 and d 2 August 2010) showing different air parcels affecting the sites during 2009 and similar air parcels during 2010.

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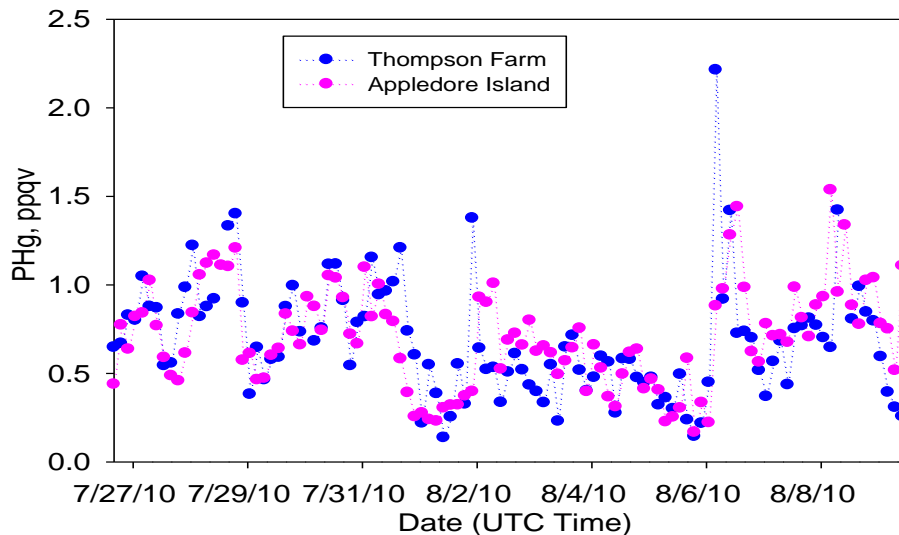


Fig. 8. Bulk filter data from Summer 2010 at Thompson Farm (blue) and Appledore Island (pink) showing both sites track each other nicely as a result of similar sources of air masses as shown in Fig. 6. There are some discrepancies between the two locations; Thompson Farm has two outlying points which may be attributed to local interferences that affected Thompson Farm but not Appledore Island, such as fires and fog.

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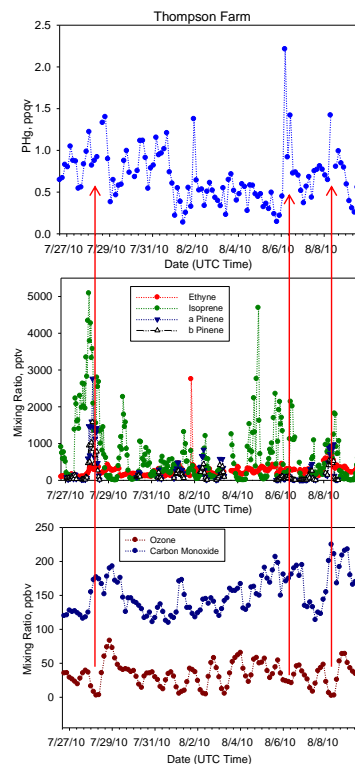


Fig. 9. Hydrocarbon data correlates with Hg^{P} peaks shown for Thompson Farm. Top panel: bulk filter data for Thompson Farm during summer 2010. Middle panel: hydrocarbon data from GC showing ethyne (red), isoprene (green), α -pinene (blue), and β -pinene (black). Bottom panel: ozone (red) and carbon monoxide (blue) data from Thompson Farm. Based on CO and C_2H_2 , this is a relatively clean time period. Results show that peaks in hydrocarbon data and carbon monoxide indicate an increase in Hg^{P} to the region. It also shows that Hg^{P} has many sources, as shown by the elevation in some substances does not always indicate an elevation in Hg^{P} .

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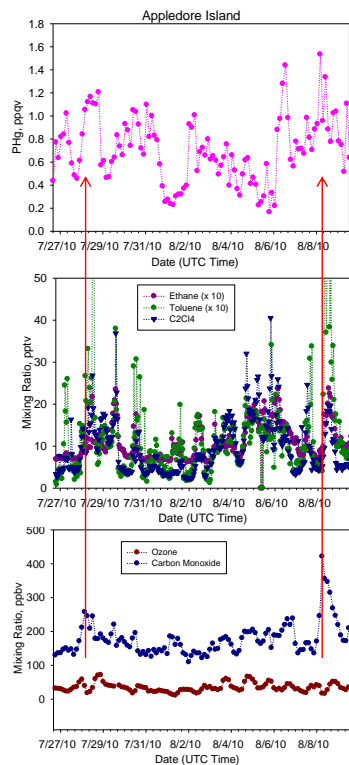



Fig. 10. Hydrocarbon data correlates with Hg^{P} peaks shown for Appledore Island. Top panel: bulk filter data for Appledore Island during summer 2010. Middle panel: hydrocarbon data from hourly canister samples showing ethane (purple), toluene (green), and tetrachloroethane (blue). Ethane values are graphed as a factor of 100 and toluene is a factor of 10. Bottom panel: ozone (red) and carbon monoxide (blue) data from Appledore Island. The same is shown for Appledore Island, where peaks in different substances indicate elevation in Hg^{P} .

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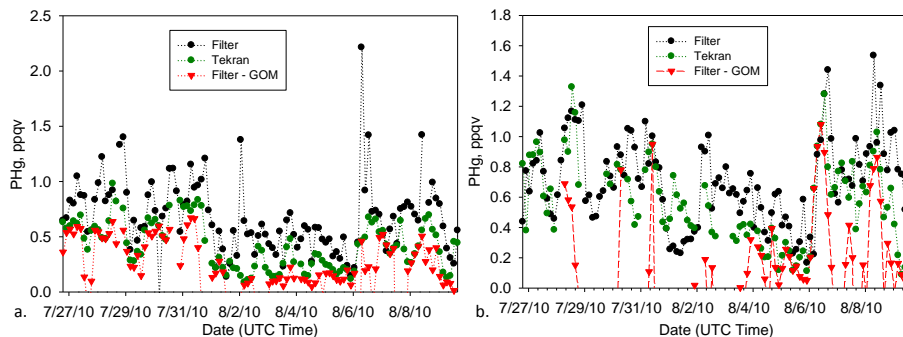


Fig. 11. Comparison of Tekran data (green) and bulk filter data (black) with filter-RGM data (red) from Thompson Farm **(a)** and Appledore Island **(b)**. It appears that Thompson Farm may occasionally be affected by a RGM artifact as shown by the red data, while Appledore Island filters track the Tekran much better which may be a result of removal of the impactor on the Tekran at Appledore Island. It is still unclear if RGM affects Hg^{P} measurements using filters.

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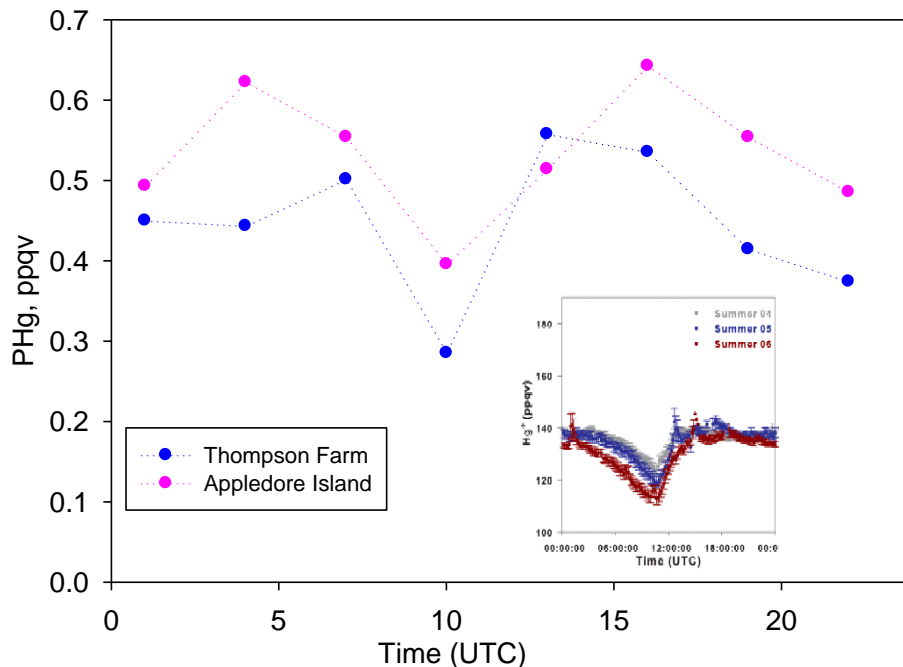


Fig. 12. Diurnal cycle of Hg^{P} at Thompson Farm (blue) and Appledore Island (pink) with inlay of Hg^{0} diurnal cycle at Thompson Farm (Mao et al., 2008). Both sites show a minimum at night and maximum points just before and just after the minimum possibly due to nighttime chemical reactions and photochemical generation.

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