SHORT RESEARCH AND DISCUSSION ARTICLE



Adaption and use of a quadcopter for targeted sampling of gaseous mercury in the atmosphere

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Abstract

We modified a popular and inexpensive quadcopter to collect gaseous mercury (Hg) on gold-coated quartz cartridges, and analyzed the traps using cold vapor atomic fluorescence spectrometry. Flight times averaged 16 min, limited by battery life, and yielded > 5 pg of Hg, well above the limit of detection (< 0.2 pg). We measured progressively higher concentrations upon both vertical and lateral approaches to a dish containing elemental Hg, demonstrating that the method can detect Hg emissions from a point source. Using the quadcopter, we measured atmospheric Hg near anthropogenic emission sources in the mid-south USA, including a municipal landfill, coal-fired power plant (CFPP), and a petroleum refinery. Average concentrations (± standard deviation) immediately downwind of the landfill were higher at ground level and 30 m compared to 60 and 120 m (5.3 ± 0.5 ng m⁻³, 5.4 ± 0.7 ng m⁻³, 4.2 ± 0.7 ng m⁻³, and 2.5 ± 0.3 ng m⁻³, respectively). Concentrations were also higher at an urban/ industrial area (Memphis) (3.3 ± 0.9 ng m⁻³) compared with a rural/background area (1.5 ± 0.2 ng m⁻³). Due to airspace flight restrictions near the CFPP and refinery, we were unable to access near-field (stack) plumes and did not observe differences between upwind and downwind locations. Overall, this study demonstrates that highly maneuverable multicopters can be used to probe Hg concentrations aloft, which may be particularly useful for evaluating Hg emissions from remote landscapes and transient sources that are inadequately characterized and leading to uncertainties in ecosystem budgets.

Keywords Atmospheric mercury · Landfill · Unmanned aerial vehicle · Multicopter · Coal-fired power plant · Petroleum refinery · Cold vapor atomic fluorescence spectrometry

Introduction

Mercury (Hg) is a persistent and toxic pollutant transported globally through the atmosphere (Schroeder and Munthe 1998; Gustin 2011). Airborne Hg stems from both natural and anthropogenic sources, and the latter, particularly the burning of fossil fuels, have led to an increase in Hg in the

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atmosphere (Pirrone et al. 2010; Krabbenhoft and Sunderland 2013). This increase is a worldwide environmental concern because airborne Hg deposits to terrestrial and aquatic systems where it can be transformed to methylmercury, a neurotoxin that accumulates in biological tissues and concentrates up food-chains to levels that can be toxic to wildlife and humans (Mason et al. 1995; Selin 2009). Thus, measuring Hg in the atmosphere is important to support models that help us understand Hg sources, deposition, cycling, and spatial and temporal trends in airborne Hg concentration. Furthermore, more comprehensive atmospheric monitoring is essential for evaluating the effectiveness of the recent Minamata Convention, a global regulatory mechanism to decrease environmental Hg loadings (Gustin et al. 2016).

Airborne Hg exists as gaseous elemental mercury (GEM = Hg^{0}), gaseous oxidized mercury (GOM; e.g., HgX₂, where X = Cl, Br, I), or particulate bound mercury (PBM), each with distinctive properties and environmental behavior (Seigneur et al. 2004). GEM is the predominant form and has a residence time estimated from months to years (Schroeder and Munthe

1998; Weiss-Penzias et al. 2003). GEM is slowly converted to soluble GOM through photochemical reactions and direct interaction with oxidants in the atmosphere (Holmes et al. 2010). GOM and PBM have shorter residence times than GEM and are readily removed through wet and dry deposition mechanisms (Lyman et al. 2007). Transport of PBM depends on the particle size and the meteorological conditions (Keeler et al. 1995). Natural emissions are primarily in the form of GEM, whereas anthropogenic emissions often include GEM, GOM, and PBM (Schroeder and Munthe 1998). In 2010, coal combustion accounted for the largest source ($\sim 70\%$) of Hg emissions in North America (United Nations Environment Programme 2013). A less-investigated source of Hg emissions are municipal landfills, which emit alkyl-Hg species and inorganic Hg during and after operation (Kim and Kim 2002; Lindberg et al. 2005).

Studies of airborne Hg, particularly those that involve semi-continuous measurements, are typically performed at ground-level at fixed locations due to constraints of the instruments, such as electrical power and carrier gas tanks. Others have used portable instruments such as the Lumex, a Hg analyzer based on cold vapor atomic absorption spectrometry, although they tend to be used in areas with relatively high concentrations of Hg⁰, such as near artisanal and small-scale gold mining operations and in some work place environments (Cordy et al. 2011). A few studies have used mobile laboratories for spatially resolved data (Lan et al. 2015) or aircraft and helium airships for semi-continuous measurements aloft (Slemr et al. 2009; Lyman and Jaffe 2012; Deeds et al. 2013; Landis et al. 2014). Passive air samplers can also provide accurate measurements and improve the resolution and spatial range of data (McLagan et al. 2016). However, these samplers typically require extended deployment times (weeks to months) and are not suited for short-term targeted measurements aloft. Therefore, there remains an urgent need for simple and affordable methods that enable measurements of Hg in air at precise locations.

Probing chemical composition aloft is important for determining the sources, distribution, interactions, and fate of pollutants in the atmosphere. Unmanned aerial vehicles (UAVs) are increasingly being used for a variety of scientific studies, including investigations of pollutants in the lower troposphere (Chang et al. 2016). Whereas fixed wing UAVs have been used to sample the atmosphere over long distances (Corrigan et al. 2008), rotary-wing UAVs (multicopter drones) have several advantages that make them ideal for more localized studies, including maneuverability (vertical movement and hovering, negotiating confined spaces and limited takeoff terrain), low cost (as low as a few hundred U.S. dollars), lack of engine exhaust for electrically-powered UAVs (no contamination), capability to land on small spaces (e.g., ships and flat rooftops), and placement of more than rotors at the periphery equidistant around a central core (allowing sensors and sampling devices in the center of the craft) (Chang et al. 2016). Indeed, the adaptation of multicopters for air sampling may facilitate precise vertical and spatial contaminant profiling to ferret out point sources and gas leaks (Rossi et al. 2014). In another example, albeit a single rotor UAV, McGonigle et al. 2008 used a gas-powered helicopter with ultraviolet and infrared spectrometers and electrochemical sensors to measure volcanic carbon dioxide fluxes.

Sampling atmospheric Hg with a multicopter allows rapid deployment and may provide a means to better assess poorly characterized and/or intermittent sources of Hg emissions, such as remote landscapes and biomass burning (Friedli et al. 2009). In this study, we modified a common and inexpensive quadcopter for sampling gaseous Hg and evaluated its effectiveness to measure airborne Hg at specific heights and locations aloft. The aim was to optimize and evaluate the approach and to demonstrate application with field measurements near known emission sources. Because this short communication is the first paper on the use of multicopters for atmospheric Hg research, we include commentary on considerations and limitations when sampling gaseous Hg with multicopters. While we report field results, fully characterizing the Hg sources and their emission fluxes, either spatially or temporally, is beyond the scope of this work.

Materials and methods

Nomenclature

Because gold effectively captures all gaseous Hg species that are efficiently transported to its surface, including organic forms of Hg, measurements from gold traps that collect filtered air are referred to as "gaseous" or "vapor phase" Hg. A small percentage of Hg, usually as oxidized Hg species like HgCl₂, may adhere to the filter and tubing before the gold trap; however, this is the case for nearly all atmospheric Hg sampling equipment, and gaseous oxidized Hg is typically an order of magnitude lower than gaseous elemental Hg in ambient air (Schroeder and Munthe 1998). Herein, we refer to our measurements as gaseous Hg. Additionally, a drone is generally any unmanned aircraft that can be autonomous or remote controlled, while a multicopter is an unmanned helicopter with greater than two rotors.

Site descriptions

Concentrations of airborne Hg were determined from near a municipal landfill, a CFPP, and a petroleum refinery. Offsite locations near these facilities were chosen to avoid interfering with federal aviation laws regarding minimum proximity to commercial property and considering predominant wind directions at each site. To avoid interference with aircraft, sampling was restricted > 8 km from the nearest airport and to heights of < 120 m.

Three Rivers Landfill, located in Pontotoc, Mississippi, is an active municipal solid waste landfill that began operation in 1994. We sampled < 200 m downwind of the site on private land (34.299726 N; - 89.056689 W) on 10 January 2018. The landfill occupies about 0.1 km² of land, has a depth of about 33.5 m, and is about one-third full with an estimated capacity of ~13 million metric tons.

The Red Hills CFPP is a 440 MW facility located in Ackerman, MS; it reported a release of 186 kg of Hg in 2010 (USEPA United States Environmental Protection Agency 2010). The Red Hills facility uses lignite coal mined adjacent to the site. Upwind samples were collected \sim 5 km northwest near Jeff Busby State Park (33.412487 N, – 89.260724 W) and downwind samples \sim 1.5 km southwest off of Highway 9 (33.3725932 N, – 89.1983115 W) on 6 December 2016.

The Valero refinery, located in Memphis, TN, has a capacity of ~195,000 barrels per day and is a major supplier of jet fuel to the FedEx Corporation hub in Memphis. Upwind samples were collected ~3 km southwest near T.O. Fuller State Park (35.068225 N, -90.118496 N) and downwind ~250 m north at Martin Luther King Park (35.089112 N, -90.085740 W) on 10 December 2016.

Quadcopter modification for gaseous Hg sampling

We modified a popular and inexpensive quadcopter (Phantom 3 Professional, DJI Inc.) for sampling ambient air for gaseous Hg. The camera was removed and the quadcopter was outfitted with an air pump (AirLite, SKC Inc.) and a multiple (quad) tube holder with protective covers (Fig. 1). The holes in the covers were widened to fit a syringe filter ($0.2 \mu m$, PTFE). The exact particle size cutoff of the filter is not known because they were designed for a liquid rather than air, which has different fluid dynamics, but it is expected to be close to $0.2 \mu m$.

Prior to sampling, gold-coated quartz cartridges (Tekran Inc.) were heated in a stream of Hg-free argon (blanked) and sealed with Teflon plugs. Each gold trap has a serial number etched into its glass for identification and tracking and has heat-shrunk Teflon sleeves on each end that enable easy connection with instrument gas lines. The gold traps were connected to the quad tube holder with a small (~1-2-cm) portion of tygon tubing; the Teflon sleeve being inserted into the tygon tubing to the acrylic holder. The sampling equipment was secured to the quadcopter using zip ties. The air pump was turned on immediately before takeoff and was shut off immediately after landing. No portion of the air sampling apparatus was heated during sampling. The average flight time was about 15 min, limited by the battery life. Because the pump was manually turned on and off at ground-level, airborne Hg was collected during UAV transit to the desired sampling height; however, this was < 5% of the total sample collection time. Adding a pump that can be remotely turned on and off would allow sampling from only the desired height and location. For some multicopters, this may be possible by using the remote channels or circuitry of the gimbal for switching on and off the pump. Also, more-costly multicopter drones could provide longer sampling times and have additional carrying capacity. The pump flow rate was set to 300 ml min⁻¹, resulting in about 4–5 L air passing through the gold cartridges. The flow rate was checked using a calibrated rotameter. The gold traps were sealed with Teflon inserts, stored in a fridge at ~ 4 °C, and analyzed the next day by CVAFS, except for the landfill study where the traps were analyzed in the field (both analytical methods are described below).

For sampling near the CFPP and refinery, we used three gold traps and one sulfur dioxide (SO₂) colorimetric tube and collected samples at heights of ~50 m and ~75 m as indicated by the multicopter. With a total of thirteen gold traps available, we were limited to four sampling flights (two upwind and two downwind), with one gold trap as a field (trip) blank. For sampling near the landfill, we used four gold traps per flight.

Proof-of-concept and field sampling

To verify that the sampling method using the modified quadcopter can detect a point source of Hg emissions, we placed a 100 g pool of liquid Hg in an evaporating dish on the top of a 2.5 m ladder in an open field. For a lateral profile, we hovered the quadcopter outfitted with four gold traps at a height of 3 to 4 m and sampled at approximately 2, 5, and 10 m downwind from the source. We also sampled the ambient (upwind) air for comparison. For the vertical profile, we hovered at heights of approximately 2, 5, and 10 m over the mercury dish.

Determination of gaseous Hg by CVAFS and calculation of airborne Hg concentrations

Mercury collected on the gold traps was measured by CVAFS (cold vapor atomic fluorescence spectrometry) following U.S. Environmental Protection Agency Method IO-5 "Sampling and Analysis for Atmospheric Mercury" (USEPA United States Environmental Protection Agency 1999). This EPA-approved method was established to provide for uniform monitoring of atmospheric mercury levels. Two different instruments were used: a Tekran 2600 Hg analyzer for in-laboratory measurements, and a Brooks Rand TDM-II for field measurements. Both units utilize dual trap desorption modules. Briefly, the gold trap used for sampling was placed within the first heating coil of the instrument and heated in a stream of Hg-free argon.

Fig. 1 Quadcopter outfitted with sampling equipment. Underneath view showing pump, acrylic quad tube holder, and three gold-coated cartridges (Hg traps) and a single SO_2 tube without protective tube covers (left), and aerial view showing the quadcopter, pump, tube covers, and syringe filters (right)



The desorbed Hg was collected onto a second gold trap, and it was subsequently heated, releasing the Hg directly into the atomic fluorescence detector system. The instrument was calibrated using a temperature-controlled Hg-vapor calibration source, a digital gas-tight syringe, and a loading rig to transfer a known amount of Hg to a gold-coated trap.

For our later work at the landfill site, we chose to bring the Hg analyzer into the field (Fig. 2). Field measurements are advantageous because analyzing traps in the laboratory limits the number of samples collected to the number of costly traps available and increases the likelihood of contamination during transport and storage. Moreover, it allows sampling and analysis using the same set of gold traps repetitively (in the same sampling configuration) to improve precision, generate more data (~40 min per sampling/analytical cycle), and provides an opportunity to adjust sampling (e.g., heights, locations) based on data obtained in the field. The instrument was setup on a portable table and supplied with high-purity argon via a lecture-bottle and with power using a 3500 W portable, gas-powered generator. The generator was placed approximately 30 m downwind of the analyzer and did not increase background values.

Gaseous Hg concentrations were calculated based on amounts of Hg determined using peak areas, the calibration equation, and the volume of air determined using the flow rate and sampling time. The limit of detection $(3\sigma \text{ criteria})$ for both instruments was < 0.2 pg of Hg, well below the > 5 pg typically collected in the field. Recoveries for external calibration checks were within 15% of expected values. All trip blanks were confirmed to be below the detection limit of the analyzers. Using two gold traps in series in the sampling apparatus, we found no evidence of breakthrough at the 0.3 L min⁻¹ flow rate used in this study. We also compared quadcopter data with continuous monitoring data (Tekran airborne speciation system). Background (ambient) Hg concentrations measured with the quadcopter were 1.7 ± 0.3 ng m³, similar to the 1.5 ± 0.2 ng m³ measured previously at the same location under similar conditions and time of year (Jiang et al. 2013). Taken together, this suggests that the quadcopter-sampling scheme does not alter the results and that the method yields reliable gaseous Hg concentration data.

Relative levels of sulfur dioxide

As a combustion plume tracer species, SO_2 was qualitatively compared between upwind and downwind sites using a Drager colorimetric tube. Because the flow rate used for the gold traps did not match that required by the SO_2 tube, concentrations read off the tubes are inaccurate and are not reported here. However, tubes showing more color change suggest higher levels of SO_2 , which might be expected if sampling occurred in a CFPP plume. Thus, we report the relative distance of color change in millimeters.

Results and discussion

Proof-of-concept for a point source

To demonstrate capability for detecting a Hg point source, we measured airborne Hg concentrations when sampling progressively closer to a pool of elemental Hg, in both lateral and vertical directions. Mercury has a relatively high vapor pressure (2.613×10^{-7} MPa at 25 °C) (Huber et al. 2006), and thus, our source



Fig. 2 Field analysis of quadcopter-deployed gold-coated Hg traps by CVAFS

would continually emit a detectable quantity of atoms to the atmosphere. Despite the downdraft generated by the quadcopter blades, we observed higher concentrations when sampling closer to the Hg source from both directions (Table 1). This capability is pertinent for measuring vertical profiles of gaseous Hg from contaminated soils or industrial sites, including municipal landfills. In a separate experiment to evaluate the effect of turbulence in the air column on sampling, we sampled air with and without the UAV rotors active near the point source dish of Hg. The former was obtained while hovering, the later by placing the quadcopter at the same hovering location using a long pole. We found no statistical difference (p = 0.96) between the groups, indicating that the turbulence in the air column has no measurable effect on sampling. Further, air velocity modeling for the quadcopter suggests that the air parcel above the active rotors being drawn down and sampled extends upward about 1 m (Yoon et al. 2017; Diaz and Yoon 2018). Thus, the bulk of the air parcel being sampled is relatively close to the true UAV position/height.

Vertical profile at a municipal landfill

Mercury is in a variety of products that end up in municipal landfills, including fluorescent lights, batteries, electrical components, and thermometers. Mercury emissions from landfills have been poorly investigated despite their high source potential (Kim and Kim 2002). Gaseous Hg concentrations in landfill gas have been measured at $\mu g m^{-3}$ levels, while methylated species occur at ng m^{-3} levels (Lindberg et al. 2005). One of the most important advantages of sampling with multicopters is its capability to conduct vertical profiles. Here, we measured gaseous Hg concentrations immediately downwind of an active municipal landfill at ground-level, 30, 60, and 120 m. Average Hg concentrations (\pm standard deviation) were 5.3 \pm 0.5 ng m⁻³, 5.4 \pm 0.7 ng m^{-3} , $4.2 \pm 0.2 \text{ ng m}^{-3}$, $2.5 \pm 0.2 \text{ ng m}^{-3}$, respectively. This demonstrates that the technique is indeed capable of measuring a vertical gradient above a source known for environmental Hg emissions to the atmosphere. Moreover, the downwind concentrations at ground-level and 30 m above the ground are about four to five times higher than both the rural Ackerman site $(1.3 \pm 0.2 \text{ ng m}^3)$ and the background of the region (Jiang et al. 2013), which is consistent with levels reported elsewhere for downwind of the working face of municipal landfills (Lindberg et al. 2005). Others have reported even higher Hg concentrations (up to 420 ng m⁻³) in municipal landfill gas (Kim and Kim 2002; Tao et al. 2017).

Differences in ambient Hg concentrations between an urban (Memphis, TN) and rural (Ackermann, MS) areas

Whereas atmospheric Hg at both urban and rural areas vary considerably on different temporal scales and with wind patterns, urban concentrations tend to be higher and are often directly Table 1 Summary of point-source proof-of-concept study

Purpose	Source	Wind direction and speed (km hr ⁻¹)	Position	Gaseous Hg (ng m^{-3}) ($n = 4$)
Vertical profile	100 g pool of elemental Hg in an evaporating dish on top of a 2.5 m ladder	NE, calm to 4	Ambient 2 m above source 5 m above source 10 m above	1.2 ± 0.3 40.4 ± 4.1 5.4 ± 0.3 4.5 ± 0.9
Lateral profile, collected at ~4 m (1.5 m higher than source)		ESE, 6–8	Ambient / Upwind 2 m downwind 5 m downwind 10 m downwind	1.7 ± 0.3 40.7 ± 1.7 15.8 ± 1.9 5.9 ± 1.4

impacted by local anthropogenic sources (Liu et al. 2010). Here, we compare data between the urban (Memphis) site when the wind was coming from a direction over the city, with a rural background (Ackermann) site. The rural (upwind) site is relatively free of anthropogenic sources compared to the urban site, which has chemical and manufacturing plants, as well as traffic emissions. The ambient urban/industrial concentrations are at least double that of rural concentrations $(3.3 \pm 0.9 \text{ ng m}^3 \text{ versus})$ 1.3 ± 0.2 ng m³), consistent with other studies of urban-rural differences (e.g., Liu et al. 2010). The concentrations in Memphis are slightly higher than those measured in Detroit $(2.5 \pm 1.4 \text{ ng m}^{-3})$ (Liu et al. 2010), similar to those reported in Seoul, South Korea $(3.7 \pm 0.8 \text{ ng m}^{-3})$ (Kim et al. 2013), but lower than Nanjing, China $(7.9 \pm 7.0 \text{ ng m}^{-3})$ (Zhu et al. 2012). Mercury concentrations in Oxford, MS, nearly equidistant between Memphis and Ackerman, tend to be highest when air masses stem from the Memphis direction (Jiang et al. 2013). A more detailed examination of urban-rural differences is beyond the scope of this methodology study; instead, the reader is referred Jiang et al. (2013) for detailed information on patterns of atmospheric Hg in northern Mississippi or Liu et al. (2010) for urban-rural differences in Hg speciation.

Ambient Hg concentrations near a CFPP and refinery

Measurement precision for the sampling flights averaged 12% (range 4.3 to 28%). Because there was no significant difference between them, data from the 50 and 75 m sampling heights were combined. Although the colorimetric tubes suggest (qualitatively) higher levels of SO₂ downwind of the CFPP, we found no significant difference for gaseous Hg between downwind and upwind locations (Table 2). Gaseous Hg concentrations

Table 2Summary of gaseousmercury concentrations measuredin this study

Source/location	Wind direction and speed range (km hr^{-1})	Relative position	Height (m)	Average gaseous Hg (ng m ⁻³)	SO ₂ colorimetric change (mm)
Three Rivers Landfill/Pontoto- c, MS	SSE, 4–10	Downwind	Ground 30	$5.3 \pm 0.5 \ (n = 4)$ $5.4 \pm 0.7 \ (n = 8)$	Not used
			60 120	$4.3 \pm 0.7 (n = 4)$ $2.5 \pm 0.3 (n = 4)$	
Red Hills CFPP/Ackerman, MS	NNW, 10–16	Upwind/ background	50 75	$1.3 \pm 0.1 \ (n = 3)$ $1.4 \pm 0.1 \ (n = 3)$	No change
		Downwind	50	$1.6 \pm 0.4 \ (n = 3)$	7
			75	$1.6 \pm 0.1 \ (n = 3)$	8
Valero Refinery/Memp- his, TN	SE, 8–12	Upwind/ background	Ground 50	$\begin{array}{l} 4.4 \pm 0.5 \; (n=3) \\ 3.4 \pm 0.9 \; (n=3) \end{array}$	24
		Downwind	50 75	$\begin{array}{l} 2.8 \pm 0.9 \; (n=3) \\ 3.4 \pm 0.7 \; (n=3) \end{array}$	23

near the refinery were also similar between downwind and upwind sites. However, given restrictions in airspace around power plants, we sampled over a kilometer from the stacks. Thus, it is likely that emissions from the power plant were either missed or already greatly diluted. Indeed, the measured concentrations seem to reflect ambient background rather than plume enhanced concentrations, the latter has been shown to increase GEM by as much as 6 ng m⁻³ (Deeds et al. 2013).

Sampling considerations, limitations, and future work

Air sampling using multicopters has a number of advantages, including low cost, portability, and the capability to target precise locations aloft that permits vertical profiling. To simplify sampling, we used three quadcopter batteries and a charger that plugs into a vehicle's cigarette lighter, allowing us to charge the batteries between flights or during travel between sampling locations. Adding an additional multicopter drone(s) would greatly increase both the number of samples and the number of locations sampled. While gold traps can be sealed and shipped overnight for analysis, we have shown that using an instrument in the field is feasible and both increases throughput and informs on sampling plans in near real time. An additional benefit of increased sample throughput is the ability to collect sufficient spatially resolved data to effectively scan an area and create a heat map of airborne Hg.

Other considerations include sampling flight times, which will vary between multicopter types and manufacturers and will depend on the weight of the sampling equipment. Adding a pump that can be remotely turned on and off would allow sampling from only the desired height and location. Weather is also a factor. High winds can prevent flying, and high humidity and airborne particulates may negatively affect the efficiency of Hg collection. Our quadcopter was able to sample without any difficulty with 26 to 32 km hr⁻¹ sustained winds, but operating it above ~40 km hr⁻¹ is not advised.

To identify power plant plumes, instruments with fast response and real-time telemetry are required; use of a SO₂ colorimetric tube is insufficient. Employment of electrochemical SO₂ sensors would improve plume detection as demonstrated in volcanic plume studies (McGonigle et al. 2008). While measurements of Hg species in near-field power plant plumes are of interest to study changes in Hg speciation and near-source impacts, how multicopters handle changes in buoyancy within the near-field plume and whether filters clogging will affect pump rates and Hg collection remains to be determined. Similarly, sampling in areas with smoke from biomass burning may prove problematic as the filters will clog with particulates and cause the pump to stall out. Given airspace restrictions around power plants, a collaboration with a CFPP company or the Electric Power Research Institute is needed if multicopters are to be used for sampling near-field plume measurements.

Others have shown that Hg^0 is the dominant form of Hg in downwind plumes of CFPPs (Edgerton et al. 2006); however, there is also significant in-plume (near-field) reduction of Hg species ($Hg^{II} \rightarrow Hg^0$), the degree of which is influenced by the coal's composition and characteristics (Landis et al. 2014). Because of the importance of determining Hg species, future multicopter work should also explore methods to sample Hg species, not just total gaseous Hg. For example, tubes containing Tenax or CarbotrapTM adsorbers can be used to collect volatile organic forms of Hg (e.g., dimethyl-Hg) (Lindberg et al. 2005), although they should be checked to determine the extent they capture GEM as well. Glass fiber filters can also be incorporated and used for PBM measurements.

Conclusions

UAVs are increasingly playing a role in atmospheric and remote sensing studies. This study, for the first time, demonstrated that pilotable multicopter drones can also be adapted to probe Hg concentrations aloft. The technique is robust and has the sensitivity and precision to measure ambient Hg concentrations and the maneuverability to investigate and characterize specific emission sources. Moreover, because the sampling technique is portable, it may be particularly useful for evaluating Hg emissions from landscapes and transient sources, such as biomass burning, which are poorly characterized and lead to uncertainties in ecosystem budgets. However, airspace and flight restrictions need to be carefully considered before using multicopters for air sampling. The paper includes issues that could benefit from improvements in the future.

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References

- Chang CC, Wang JL, Chang CY, Liang MC, Lin MR (2016) Development of a multicopter-carried whole air sampling apparatus and its applications in environmental studies. Chemosphere 144: 484–492
- Cordy P, Veiga MM, Salih I et al (2011) Mercury contamination from artisanal gold mining in Antioquia, Colombia: the worlds highest per capita mercury pollution. Sci Total Environ 410:154–160
- Corrigan CE, Roberts GC, Ramana MV, Kim D, Ramanathan V (2008) Capturing vertical profiles of aerosols and black carbon over the Indian Ocean using autonomous unmanned aerial vehicles. Atmos Chem Phys Discuss 7(4):737–747
- Deeds DA, Banic CM, Lu J, Daggupaty SJ (2013) Mercury speciation in a coal-fired power plant plume: an aircraft-based study of emissions from the 3640 MW Nanticoke Generating Station, Ontario, Canada. Geophys Res Atmos 118:1–17
- Diaz PV, Yoon S (2018) High-fidelity computational aerodynamics of multi-rotor unmanned aerial vehicles. AIAA SciTech Forum, Areospace Sciences Meeting, Kissimmee
- Edgerton ES, Hartsell BE, Jansen JJ (2006) Mercury speciation in coalfired power plant plumes observed at three surface sites in the southeastern U.S. Environ Sci Technol 40:4563–4570
- Friedli HR, Arellano AF, Cinnirella S, Pirrone N (2009) Initial estimates of mercury emissions to the atmosphere from global biomass burning. Environ Sci Technol 43:3507–3513
- Gustin MS (2011) Exchange of mercury between the atmosphere and terrestrial ecosystems. Environmental chemistry and toxicology of mercury. John Wiley and Sons, New York, pp 423–451
- Gustin MS, Evers DC, Bank MS et al (2016) Importance of integration and implementation of emerging and future mercury research into the Minamata Convention. Environ Sci Technol 50(6):2767–2770
- Holmes CD, Jacob DJ, Corbitt ES, Mao J, Yang X, Talbot R, Slemr F (2010) Global atmospheric model for mercury including oxidation by bromine atoms. Atmos Chem Phys 10(24):12037–12057
- Huber ML, Laesecke A, Friend DG (2006) The vapor pressure of mercury. National Institute of Science and Technology NISTIR 6643, Brahmapur, p 17
- Jiang Y, Cizdziel JV, Lu D (2013) Temporal patterns of atmospheric mercury species in northern Mississippi during 2011–2012: influence of sudden population swings. Chemosphere 93(9):1694–1700

- Keeler G, Glinsorn G, Pirrone N (1995) Particulate mercury in the atmosphere: its significance, transport, transformation and sources. Water Air Soil Pollut 80(1–4):159–168
- Kim KH, Kim MY (2002) Mercury emissions as landfill gas from a large-scale abandoned landfill site in Seoul. Atmos Environ 36:4919–4928
- Kim KH, Yoon HO, Brown RJ, Jeon EC, Sohn JR, Jung K (2013) Simultaneous monitoring of total gaseous mercury at four urban monitoring stations in Seoul, Korea. Atmos Res 132–133:199–208
- Krabbenhoft DP, Sunderland EM (2013) Global change and mercury. Science 341:1457–1458
- Lan X, Talbot R, Laine P, Torres A, Lefer B, Flynn J (2015) Atmospheric mercury in the Barnett Shale Area, Texas: implications for emissions from oil and gas processing. Environ Sci Technol 49(17):10692–10700
- Landis MS, Ryan JV, Schure AF, Laudal D (2014) Behavior of mercury emissions from a commercial coal-fired power plant: the relationship between stack speciation and near-field plume measurements. Environ Sci Technol 48:13540–13548
- Lindberg SE, Southworth G, Prestbo EM, Wallschläger D, Bogle MA, Price J (2005) Gaseous methyl- and inorganic mercury in landfill gas from landfills in Florida, Minnesota, Delaware, and California. Atmos Environ 39(2):249–258
- Liu B, Keller GJ, Dvonch JT, Barres JA, Lynam MM, Marsik FJ, Morgan JT (2010) Temporal variability of mercury speciation in urban air. Atmos Environ 44:2013–2023
- Lyman SN, Jaffe DA (2012) Formation and fate of oxidized mercury in the upper troposphere and lower stratosphere. Nat Geosci 5:114–117
- Lyman SN, Gustin MS, Prestbo EM, Marsik FJ (2007) Estimation of dry deposition of atmospheric mercury in Nevada by direct and indirect methods. Environ Sci Technol 41(6):1970–1976
- Mason RP, Reinfelder JR, Morel FMM (1995) Bioaccumulation of mercury and methylmercury. Water Air Soil Pollut 80:915–921
- McGonigle AJS, Aiuppa A, Giudice G, et al (2008) Unmanned aerial vehicle measurements of volcanic carbon dioxide fluxes. Geophys Res Lett 35(6)
- McLagan D, Mitchell C, Huang H, Lei Y, Cole A, Steffen A, Hung H, Wania F (2016) A high-precision passive air sampler for gaseous mercury. Environ Sci Technol Lett 3:24–29
- Pirrone N, Cinnirella S, Feng X, Finkelman RB, Friedli HR, Leaner J, Mason R, Mukherjee AB, Stracher GB, Streets DG, Telmer K (2010) Global mercury emissions to the atmosphere from anthropogenic and natural sources. Atmos Chem Phys 10(13):5951–5964
- Rossi M, Brunelli, D, Adami A, Lorenzelli L, Menna F, Remondino F (2014) Gas-drone: portable gas sensing system on UAVs for gas leakage localization. Sensors 1431–1434
- Schroeder WH, Munthe J (1998) Atmospheric mercury—an overview. Atmos Environ 32(5):809–822
- Seigneur C, Vijayaraghavan K, Lohman K, Karamchandani P, Scott C (2004) Global source attribution for mercury deposition in the United States. Environ Sci Technol 38(2):555–569
- Selin NE (2009) Global biogeochemical cycling of mercury: a review. Annu Rev Environ Resour 34:43–63
- Slemr F, Ebinghaus R, Brenninkmeijer CAM, Hermann M, Kock HH, Martinsson BG, Schuck T, Sprung D, van Velthoven P, Zahn A, Ziereis H (2009) Gaseous mercury distribution in the upper troposphere and lower stratosphere observed onboard the CARIBIC passenger aircraft. Atmos Chem Phys 9(6):1957–1969
- Tao Z, Liu Y, Zhou M, Chai X (2017) Exchange pattern of gaseous elemental mercury in landfill: mercury deposition under vegetation coverage and interactive effects of multiple meteorological conditions. Environ Sci Pollut Res 24:26586–26593
- United Nations Environment Programme (2013) Technical background report for the global mercury assessment 2013. AMAP, Oslo
- USEPA United States Environmental Protection Agency (1999) Compendium method IO-5, sampling and analysis for vapor and

particle phase in ambient air utilizing cold vapor atomic fluorescence spectrometry (CVAFS). EPA/625/R-96/010a

- USEPA United States Environmental Protection Agency (2010) Toxic release inventory. http://www.epa.gov/tri/s
- Weiss-Penzias P, Jaffe DA, McClintick A, Prestbo EM, Landis MS (2003) Gaseous elemental mercury in the marine boundary layer: evidence for rapid removal in anthropogenic pollution. Environ Sci Technol 37(17):3755–3763
- Yoon S, Diaz PV, Boyd Jr DD, Chan WM, Theodore CR (2017) Computational aerodynamic modeling of small quadcopter vehicles. American Helicopter Society (AHS) 73rd Annual Forum, Fort Worth, Texas
- Zhu J, Wang T, Talbot RW, Huang X (2012) Characteristics of atmospheric total gaseous mercury (TGM) observed in urban Nanjing, China. Atmos Chem Phys 12(24):12103–12118