Impact of ultralow sulfur diesel (ULSD) waiver on air quality in Puerto

Rico in the aftermath of Hurricane Maria: A case study on the use of

lower-cost air quality monitors

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Abstract

In the aftermath of Hurricane Maria, the electricity grid in Puerto Rico was devastated, with over 90% of the island without electricity; as of December 2017, about 50% of the island lacked electricity, and power outages were common elsewhere. Backup generators are widely used, sometimes as the main source of electricity. The hurricane also damaged the island's existing air monitoring network and the University of Puerto Rico's observing facilities. We deployed four lower-cost air quality monitors (Real-time Affordable Multi-Pollutant or RAMP monitors) and a black carbon (BC) monitor in the San Juan Metro Area in November 2017. The first month of data collected with the RAMPs showed high sulfur dioxide (SO₂) and carbon monoxide (CO) concentrations of varying magnitudes each night. SO₂ and CO are strongly correlated (r² >0.9) at two sites ~5 km apart (University of Puerto Rico and an industrial area, Puerto Nuevo), suggesting a single source type. BC measured at the UPR site is also well correlated with CO and SO₂. While the RAMPs are not certified as a federal equivalent method, the RAMP SO₂ data suggests that the EPA's daily 1-hour maximum standard for SO₂ (75 ppb) was exceeded on almost 80% of the first 30 days of deployment (November-December 2017). In the wake of Hurricane Maria, Puerto Rico was granted a waiver from ultralow sulfur diesel (ULSD) requirements which, coupled with the continuing lack of grid power, appears to have significantly degraded the air quality in the region.

Keywords: sulfur dioxide, carbon monoxide, Hurricane Maria, low-cost sensors, air quality, backup generators

Introduction

Increases in fine particulate matter ($PM_{2.5}$) and sulfur dioxide (SO_2) result in premature mortality (*1-3*). SO_2 has other serious health impacts including severe migraines and heart rate variability (*4,5*). SO_2 is also important as a precursor to $PM_{2.5}$ downwind of emission sources. Over the past decade, US air quality has significantly improved with the introduction of cleaner fuels, including the replacement of high-sulfur and low-sulfur (<500 ppm-sulfur, LSD) diesel fuel with ultra-low sulfur diesel (<15 ppm-sulfur, ULSD), as fuel sulfur is directly linked to engine SO_2 and PM emissions (*6*). Diesel exhaust PM, a known carcinogen, is also strongly correlated with fuel sulfur content used in non-road diesel generators (*7*). In 2010, the US EPA set the NAAQS primary 1-hour standard for SO_2 in ambient air to 75 ppb (*8*).

Hurricane Maria, which hit Puerto Rico on September 20, 2017, devastated the electricity grid across the island. At one point, over 90% of Puerto Rico did not have electricity, and as of December 2017 about 50% of the island was without power. Even in areas with electricity, power outages were frequent. Hence, backup generators were widely used, putting significant pressure on the fuel supply chain. In response to this situation, the US EPA granted Puerto Rico a waiver from ULSD requirements in September 2017. The waiver was extended until November 15, 2017 and was in effect until existing stocks were depleted (9). This could have significant air quality impacts. Unfortunately, the hurricane also affected the local air quality monitoring network managed by the Puerto Rico Environmental Quality Board (EQB). For example, the San Juan Metro Area has five monitoring stations (Figure S1) that measure various criteria pollutants including SO₂ and PM_{2.5}. However, the instruments were damaged by the hurricane, and the continuing lack of electricity has meant a lack of official air quality data during this critical period. Recent reports have attributed thousands of additional deaths in Puerto Rico in 2017 after Hurricane Maria; for example, Kishore et al. (10) estimate 4,645 excess deaths between hurricane impact and December 31, 2017. Attribution of some of these excess mortalities and excess morbidity to hurricane

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response-related degradation in air quality will not be possible without measurements, which will be useful to guide future responses to similar disaster scenarios.

Low cost sensors can enable high-density urban air quality monitoring, fill in air quality data gaps especially in developing countries with limited resources, and be rapidly deployed to evaluate air quality during extreme events or after disasters. Several deployments of low-cost sensor packages are in progress, though published work thus far has focused on calibration of these sensors (*11-14*). The Real-time Affordable Multi-Pollutant (RAMP) monitor was developed at Carnegie Mellon University in collaboration with SenSevere (Pittsburgh, PA). The RAMP data can meet the EPA's quality criteria for "supplementary monitoring" for carbon monoxide (CO) and ozone (O₃), and "hot spot" standards for nitrogen dioxide (NO₂) (*13*). To the best of our knowledge, the use of lower-cost monitoring packages (~\$5,000/unit) has not yet been demonstrated in emergency situations.

We present a case study of the valuable information provided by well-characterized, carefully controlled low-cost air quality monitors in an emergency situation where traditional reference monitors are not available. In response to the devastation caused by Hurricane Maria, we deployed four RAMPs in the San Juan Metro Area (SJMA) in the second half of November 2017. The advantage of the RAMPs is that they can be powered by solar panels and rapidly deployed. The RAMP data presented here show that the ULSD waiver policy in the aftermath of Hurricane Maria has significant air quality impacts on SJMA with high temporal and some spatial variability. While the measurements were made in SJMA, similar degradation in air quality can be expected elsewhere in Puerto Rico where backup generators are widely used and operated with non-ULSD fuel. The data can help inform future policy and community responses to hurricanes and other disasters if the ULSD regulation is waived due to situational pressures.

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Experimental methods

All four RAMPs measure CO, NO₂, and O₃. Two RAMPs measure SO₂ and two RAMPs measure nitric oxide (NO). Details of the RAMP sensor package are provided in (13). Relevant to the data presented here, the RAMP uses AlphaSense (UK) CO-B4 and SO2-B4 sensors for CO and SO₂ respectively and built-in temperature and relative humidity (RH) sensors as part of the CO₂ sensing module (CO2S-A, SST Sensing Ltd, UK). These are coupled to proprietary SenSevere electronics including wireless data transmission over a GSM network. The four RAMPs were collocated at the University of Puerto Rico's Rio Piedras campus (UPR) for about ten days for quality assurance. Figure S2 shows that the CO and SO₂ responses from the collocated RAMPs are highly correlated with each other. Thus, differences in measurements, when the RAMPs are relocated to other locations, reflect spatial differences in pollution and are not due to differences in sensor response. Subsequently, two RAMPs were deployed at two industrial areas (Cataño, RAMP 139 and Puerto Nuevo, RAMP 150) and RAMP 148 was installed at a residential location in Río Piedras (Figure S1), in addition to RAMP 156 at UPR. The expectation is that the usage of backup generators will be different at these locations due to different activity patterns between industrial and residential areas.

Ideally, the electrochemical gas sensors should be calibrated based on a local collocation with reference monitors. However, that has not been possible for several months after the hurricane due to the extensive infrastructure damage in Puerto Rico. Zimmerman et al. (*13*) show that simple calibration models using multiple linear regression (MLR) of the CO sensor response, temperature, and RH produced CO data that meets EPA guidelines for supplemental monitoring. Hagan et al. (*14*) show that linear calibration models perform well at SO₂ concentrations over 50 ppb. The advantage of using only these three parameters – analyte response, temperature, and RH – is that the calibrations are only affected by sensor characteristics and should transfer across regions irrespective of pollutant source mixes, unlike multipollutant machine learning models or higher order models like quadratic

regression that could be overfitted (*15*) and hence may not generalize as well. The calibrations used in this manuscript will be verified in the future based on local collocations in SJMA once the local EQB monitoring network has returned to normal operation.

The data presented here are based on calibration models built using collocations in Allegheny County, PA. First, the RAMPs were collocated with a Teledyne T300U CO monitor at the CMU campus in Pittsburgh, and MLR models were built on 28 days of this data (the training data set) evenly spread across the collocation period (*13*), with the remaining unseen collocation data used for performance testing. The Pearson r (coefficient of variation of mean absolute error, CvMAE) values were 0.69 (28%) for RAMPs 139 and 148 which were collocated at CMU between June 21-November 3, 2017; 0.86 (26%) for RAMP 150 (collocated July 25-October 23, 2017); and 0.85 (25%) for RAMP 156 (collocated July 24-November 3, 2017). The UPR collocation (Figure S2) shows that the precision for CO measurements is ± 100 ppb or $\pm 5\%$, whichever is larger.

An "average MLR" model was built using only the SO₂ response, temperature, and RH based on the collocation of sixteen RAMPs near a large point source of SO₂ in Liberty-Clairton, PA, alongside a Teledyne T100A UV-fluorescence SO₂ monitor. RAMP 150 was part of this collocation but not used to build the calibration model. The model performance for RAMP 150 during the Liberty-Clairton collocation showed a CvMAE of 44% and a fit ($r^2 = 0.82$) with a zero intercept and slope within uncertainty of unity (1.02±0.02), after an offset correction. Details are provided in the supplemental information. RAMP 156 was not included in the Liberty-Clairton collocation, but the UPR collocation (Figure S2) shows that the SO₂ responses of RAMPs 150 and 156 are strongly correlated with each other ($r^2 = 0.98$, slope 0.995±0.005), except RAMP 150 has a positive bias of 8 counts relative to RAMP 156. Therefore, the two RAMPs can be expected to perform similarly after the raw data from RAMP 156 are converted to "RAMP 150-equivalent" values.

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Each RAMP is connected to a low-cost PM monitor: #156 has a Met-One Neighborhood PM (NPM) monitor and the other three RAMPs have PurpleAir PM sensors. The NPM has a significant power draw because of the inlet heater that activates when RH exceeds 40%, and hence this sensor is installed at the UPR campus in Río Piedras where power is relatively stable. Both the NPM and the PurpleAir are optical particle sizers and nominally detect particles larger than 300 nm. Only the NPM data from the UPR site are shown here, as it has the longest record and the inlet heater should reduce humidity artifacts. However, the artifact may not be eliminated, and the particle mass reported may also reflect aerosol growth at higher humidity. This would cause the PM_{2.5} to be an overestimate when comparing to EPA standards that require RH between 30-40% (*16*). Further, the mass is reported as-is using the manufacturer's factory calibration. A Met-One BC-1050 monitor was also deployed at UPR and reports equivalent black carbon at 375 nm (eBC-375) and 880 nm (eBC-880), corrected for filter loading artifacts (*17*) using the manufacturer's software based on reference (*18*).

Results and Discussion

Figure 1(a) shows a time series of SO₂, CO, PM_{2.5}, and eBC data recorded at the UPR campus, which has the longest record so far. On several days, the CO and SO₂ concentrations reach 3-4 ppm and over 200 ppb, respectively. A distinct diurnal pattern is observed, with CO and SO₂ concentrations increasing in unison in the late afternoon, then peaking in the early morning hours of the next day. The eBC concentration shows a similar diurnal pattern, and to a lesser extent, so does $PM_{2.5}$. There appears to be a lag in SO₂ concentrations in the mornings as it does not fall in synchronicity with CO. However, this apparent lag could be an artifact of the MLR calibration model as it is not observed when using the QR calibration model (Figure S4 and related discussion there.) Overall, CO and SO₂ are strongly correlated ($r^2 > 0.9$, Figure S4), which indicates that they are emitted by the same combustion source. Figure 1(b) shows the diurnal profile of hourly SO₂ concentrations. SO₂ concentrations start rising around 6 PM, but concentrations are routinely the highest

between 4-8 AM local time; this could reflect a boundary layer effect trapping pollutants released over the previous evening. There is a broad distribution in the night-time peaks, which could be a result of different wind patterns and/or varying backup generator usage based on local power outages. As mentioned earlier, the current NAAQS 1-hour standard – defined as the "99th percentile of 1-hour daily maximum concentrations, averaged over 3 years" – for SO₂ is 75 ppb, which is near the 75th percentile of RAMP SO₂ data measured at UPR (Figure S5). This means that almost 20% of the first month of hourly SO₂ concentrations measured by the UPR RAMP exceeded the 1-hour standard.



Figure 1: (A) Time series of 15-minute concentrations of CO, SO₂, PM_{2.5}, and eBC measured at the UPR campus. (B) Diurnal profile of hourly SO₂ concentrations at UPR.

PM_{2.5} concentrations appear relatively low at an hourly average $3.5\pm 2.3 \mu g/m^3$; the maximum is 12.7 $\mu g/m^3$ (Figure S5). This suggests there is not a significant new PM-related health risk to the residents of San Juan due to the generator usage. The fact that SO₂ concentrations are high at night when oxidant levels are low may limit local conversion to sulfate aerosol (19). Most diesel and gasoline exhaust particles from typical engines are smaller than 300 nm mobility diameter (*20,21*). A nucleation mode smaller than 30 nm has also been observed in diluted exhaust. This is likely related to fuel and lubricant sulfur content due to the use of LSD (<500 ppm-sulfur) instead of ULSD (<15 ppm-sulfur) leading to a significant increase in nucleation mode particles (*21,22*). Hence, the PM_{2.5} mass concentrations reported here may be underestimates. Although the US EPA does not regulate particle number, evidence suggests a causal relationship between ultrafine particles (UFP) and respiratory and cardiovascular effects (*23*). Thus, even if particle mass is low, the likely increase in UFP due to the use of non-ULSD fuel in backup generators may adversely affect human health in Puerto Rico.

Particulate emissions from backup generators are perhaps better reflected in the BC measurements. The average eBC-880 hourly concentration is $1.3\pm1.4 \ \mu g/m^3$, with a maximum of 8.9 $\mu g/m^3$. The eBC-375 is strongly correlated with eBC-880 (r² = 0.99, Figure 2), which suggests that light-absorbing organic carbon (e.g. from wood smoke) may not be a significant contributor to BC over San Juan. The eBC concentrations are also well correlated with CO and SO₂ (r² ~0.8, Figure 2). This indicates that the source of these high BC concentrations is likely combustion sources (like generators) burning high-sulfur fuel.



Figure 2: LEFT: The equivalent black carbon (eBC) reported at 375 nm, eBC-375, is strongly correlated with eBC-880. RIGHT: eBC is well correlated with CO.

Similar diurnal trends in SO₂ and CO are seen across the San Juan Metro Area (Figure S6), though the magnitudes vary. For example, the industrial Puerto Nuevo location experiences higher SO₂ concentrations than the UPR location. Between December 5-21, the SO₂ at Puerto Nuevo was 43 ± 45 ppb with a maximum of 272 ppb, while at UPR the SO₂ was 32 ± 30 ppb with a maximum of 190 ppb (the large standard deviations reflect the sharp diurnal profiles.) The CO data shows similar spatial variability; interestingly, the residential Rio Piedras location seems to experience higher CO on some days than the industrial Puerto Nuevo site. At Puerto Nuevo, the CO and SO₂ are strongly correlated and show the same SO₂/CO ratio as was seen at the UPR location (Figure S4). This suggests that while the pollutant source is the same, its influence is different in different parts of SJMA - as might be expected of backup generator use, as different parts of the region may lose power at different times.

To put the SO₂ concentrations into perspective, Figure 3 compares cumulative histograms of daily 1-hour maximum SO₂ concentrations recorded at the two EQB monitoring sites in Bayamon and Cataño (*24*), with the daily maximum 1-hour SO₂ values reported by the RAMPs at UPR and Puerto Nuevo (excluding days when the RAMP data had fewer than 24 hourly averages.) The daily maximum 1-hour SO₂ concentration at EQB #37 (Bayamon) and R Subramanian randomsubu@gmail.com

EQB #40 (Cataño) exceeded 75 ppb only two times between January 1, 2016 and June 30, 2017. However, the 75-ppb standard is exceeded on almost 80% of the study days over the first month of RAMP measurements.



Figure 3: Histograms of daily maximum 1-hour SO₂ reported by the two EQB sites in SJMA (Jan 1, 2016-June 30, 2017) and by the RAMPs deployed at UPR (Nov 22-Dec 21, 2017) and in Puerto Nuevo (Dec 6-21, 2017.)

Conclusions

These results - a set of independent measurements of CO, SO₂, PM_{2.5}, and BC - present compelling evidence that hurricane damage to the electricity grid and the ensuing ULSD waiver has had a significant impact on local air quality in the San Juan Metro Area, where ~2 million people live. Local SO₂ concentrations appear to have exceeded EPA standards on almost 80% of the days in the first month of sampling over November-December 2017 at the UPR and Puerto Nuevo locations. Generators are often close to living or otherwise occupied spaces; for example, hospitals in Puerto Rico were operating with diesel generators as the

primary source of power due to the unreliable nature of grid power (25). SO_2 and CO levels in such locations, filled with vulnerable populations, could be even higher than our observations and be accompanied by substantial negative health impacts.

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Supporting Information

The following files are available free of charge:

Additional figures and details of SO₂ calibration as described in the main text. (PDF)

Data Availability Statement

All raw data are publicly available on FigShare at

https://doi.org/10.6084/m9.figshare.5745360.v1

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