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Exposure Assessment of Ambient Sulfur Dioxide Downwind of an Oil Refinery in Curaçao

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Abstract

Primary sources of atmospheric sulfur dioxide are anthropogenic activities associated with the burning of fossil fuels and industrial processes that may have associations with various morbidities and mortalities. As such, several regional and global regulatory agencies have recommended ambient air limits to reduce environmental exposures. The objectives of this study were to evaluate ambient levels of sulfur dioxide surrounding an oil refinery on the island of Curaçao. Levels which were then compared to literature values and recommended public health guidelines to determine potential public health risks. Concentrations of sulfur dioxide in Curacao were found to be among the highest globally with an increasing trend over time. While the epidemiological evidence does not conclusively suggest there is a health risk from these levels of exposure, SO_2 concentrations greatly exceed regulatory and guidance levels and suggest that further emissions control is warranted. Future recommendations include a more rigorous epidemiological study in Curaçao and expand the air monitoring efforts to include areas upwind of the refinery as well as additional petrochemical emissions.

Keywords

1. Introduction

Typical annual average concentrations of ambient sulfur dioxide, as of 2005, have ranged from 9 - 35 μg/m³ in North America, 8 - 36 μg/m³ in Europe, 40 - 70 μg/m³ in Latin America, 10 - 100 μg/m³ in Africa and 20 - 200 μg/m³ in Asia [1].

Atmospheric SO_2 is primarily the result of anthropogenic activities associated with the burning of fossil fuels and industrial processes (*i.e.*, oil refineries, coal burning, and biomass combustion) but can also be released naturally from volcanic activities, sea-salt emissions and sulfur gas oxidation [2] [3] [4]. Sulfur dioxide (SO_2) can be formed from the petroleum refining process and smelting industries, accounting for 15% - 25% of the estimated 140 - 350 million tons of sulfur compounds (*i.e.*, sulfur dioxide, sulfuric acids and sulfate) released into the atmosphere annually on a global basis [2] [3] [5].

The Wider Caribbean Region (WCR) includes a number of developing countries for which agriculture, oil and gas exploration in conjunction with processing, provide valuable sources of income. As the WCR is one of the most tourism-dependent regions of the world, factors that affect environmental health and sustainability will have inevitable impacts to the economies and quality of life in many already-needy countries. Approximately 100 oil refineries are located within the WCR, with one of largest and oldest refineries, Isla Refineriá, being located in Willemstad, Curaçao [6]. Communities downwind of Isla Refineriá and the major thoroughfare (Schottegatweg Ring) circling the refinery and the bay have self reported from questionnaires higher than average frequencies of headaches, nausea, chronic lung ailments, asthma and cancer [7]. These self-reported questionnaire results have not been validated. A legacy of human health and environmental issues is the basis of a historical debate and conflict between the public and the local government of Curaçao. However, to our knowledge there has never been an exposure assessment conducted to evaluate ambient atmospheric levels of refinery emissions and their associated public health risks in Curaçao. Sanhueza *et al.* [8] determined that all areas downwind (≥ 5 km) of the Isla Refineriá in Curaçao were subject to sulfate contamination exceeding levels which have been previously associated with morbidity (≥ 8 - 12 $\mu g/m^3$). In addition, the 2007 yearly average SO_2 levels (152 $\mu g/m^3$) measured downwind of the refinery were double the air quality standards for Curaçao (80 $\mu g/m^3$) and exceeded acceptable international guidelines (40 - 60 $\mu g/m^3$) by almost 2.5 times [9] [10]. In 2009, a court order required the refinery to reduce the excessive SO_2 emissions and particulates starting from January 1, 2010.

Sulfur dioxide has been associated with various morbidities demonstrated by controlled exposure experiments conducted in the early 1950's [11] [12]. Epidemiological studies have reported that some sulfur dioxide exposures may be associated with respiratory irritation, bronchoconstriction and have the potential for causing respiratory and pulmonary changes and cardiovascular abnormalities in both healthy and asthmatic individuals [12] [13] [14] [15] [16]. The controlled experiments in the 1950s examined the effects of SO_2 inhalation using controlled exposure experiments on healthy individuals. These studies revealed considerable inter-individual variability among healthy individuals however bronchoconstriction responses in most were induced at levels approaching 5 ppm (10,480 - 13,100 $\mu g/m^3$).

The short term effects from sulfur dioxide exposure at much lower and more plausible episodic concentrations between 0.20 and 1 ppm (524 - 2620 μg/m^3) were also evaluated using controlled chamber experiments in normal, atopic and asthmatic volunteers [16] [17]. Normal and atopic volunteers showed little response at these levels, whereas some atopic volunteers and most of the asthmatics developed bronchoconstriction and respiratory symptoms. Even at elevated ventilation during exercise, there has been limited evidence of SO$_2$ induced respiratory effects in normal, healthy subjects following short-term exposures of ≤ 1ppm (2620 μg/m^3) [12] [15] [16] [17]. Bronchoconstriction and compromised lung function tend to occur at lower concentrations (≤0.4 ppm or 1048 μg/m^3) in asthmatic and some atopic individuals, with some reports of symptoms occurring as low as 0.10 ppm (262 μg/m^3) when combined with exercise or another irritant (*i.e.*, ozone) [14] [15] [16] [18] [19] [20]. The respiratory responses in healthy, atopic or asthmatic subjects can also be increased by exercise and oral ventilation [15] [16] [20] [21] [22]. Several epidemiological studies have also reported some associations between some SO$_2$ exposures and mortality. However, there are many inconsistencies between studies and the measures of association are often not strong enough to suggest mortality risks.

The objective of this study was to conduct an exposure assessment for ambient levels of SO$_2$ downwind of an oil refinery (Isla Refineriá) in Curaçao. This was accomplished by analyzing hourly, daily, and monthly SO$_2$ measurements over a four year period (2010-2014) to determine if any temporal trends exist and to compare levels with public health guidelines in order to assess potential public health risks in Curaçao.

2. Methods

2.1. Site Selection

Approximately 40 miles off the coast of Venezuela lies the island of Curaçao in the southern Caribbean. Curaçao is located in the Southern Caribbean Dry Zone, which is characterized by a semi-arid to arid climate, with a distinguishable dry and rainy season, and sustained easterlies. The island is approximately 59 kilometers in length, 4 - 11 kilometers wide and a total land mass area of ~443 km^2. The population of ~152,000 consists of greater than 50 nationalities with Dutch and Papiamento as the official languages. The majority of the population (>130,000) resides in Willemstad which is home to the Isla Refineriá.

2.2. Air Quality and Meteorological Parameters

Two air monitoring stations, Beth Chaim and Kas Chikitu, commissioned by the government of Curaçao have been collecting validated and continuous measurements of air quality parameters (SO$_2$, PM$_{10}$, TSP, H$_2$S) since mid-2010. The Beth Chaim station is located at the western edge, downwind of the Schottegat industrial area of the refinery and only measures SO$_2$ and TSP. Kas Chikitu is located approximately 2 - 3 km downwind in the Marchena/Wishi residential

area and is primarily used to monitor the residential load of SO_2, hydrogen sulfide (H_2S) and PM_{10}. Available hourly and daily measurements of SO_2 were downloaded from June 1, 2010 through December 31, 2014 for analysis from the Kas Chikitu station. Twenty-four hour SO_2 daily means were downloaded from the Beth Haim station (n = 1605) and the Kas Chikitu station (n = 1622). Monitoring stations operate in accordance with the ISO/IEC 17025 accreditation (certificate number L 426) of GGD Amsterdam using ultraviolet fluorescence (Thermo 43i-TLE and Thermo 450i Gas Analyzer) methodology to measure SO_2. Daily meteorological data (*i.e.,* temperature, precipitation, humidity, wind speed) in Curacao was downloaded from the Tutiempo Network from January 1, 2010 through December 31, 2014.

2.3. Data Analysis

All SO_2 data is expressed in $\mu g/m^3$. All data analysis was performed using Statistica Version 6.1 (Stat Soft, Inc., Tulsa, OK). If data did not meet the assumptions of normality, nonparametric hypothesis tests were performed. If a potential explanatory variable was categorical (e.g., year), the nonparametric Kruskal-Wallis ANOVA was run using α = 0.05. If the Kruskal-Wallis ANOVA was found to be significant multiple comparisons revealed significant differences between categorical factors. Concentrations of SO_2 were compared daily and annually and correlations were also evaluated against environmental factors (*i.e.,* temperature, precipitation, humidity and wind speed).

3. Results and Discussion

3.1. Ambient Concentrations of Sulfur Dioxide

Daily SO_2 mean concentrations were downloaded from two local air stations in Curaçao, Beth Haim (n = 1605) and Kas Chikitu (n = 1622). The 24-hour daily mean concentrations ranged from 0.2 to 449 $\mu g/m^3$ and 6.8 to 139 $\mu g/m^3$ at the Beth Haim and Kas Chikitu stations, respectively (**Figure 1**). Mean annual concentrations at the Beth Haim station ranged from 38.9 $\mu g/m^3$ in 2010 to 170.4 $\mu g/m^3$ in 2014 (**Figure 2**). Similar, statistically significant temporal trends were observed at the Beth Haim station with a moderately strong increasing trend (R^2 = 0.86) over time. Mean annual SO2 concentrations at the Kas Chikitu station ranged from 35.6 $\mu g/m^3$ in 2010 to 55.5 $\mu g/m^3$ in 2014, also illustrating a moderately strong increasing trend (R^2 = 0.86) over time (**Figure 2**). Increasing trends in PM_{10} concentrations downwind of the refinery were also reported (Pulster, unpublished data).

3.2. Global Comparison of SO_2

Annual concentrations measured at the Beth Haim station increased 338% since 2010 and 36% since 2011. Similarly, annual concentrations increased at the Kas Chikitu station 36% since 2010 and 17% since 2011. Conversely, global trends for SO_2 have illustrated decreases. For instance, a 50% decrease in annual
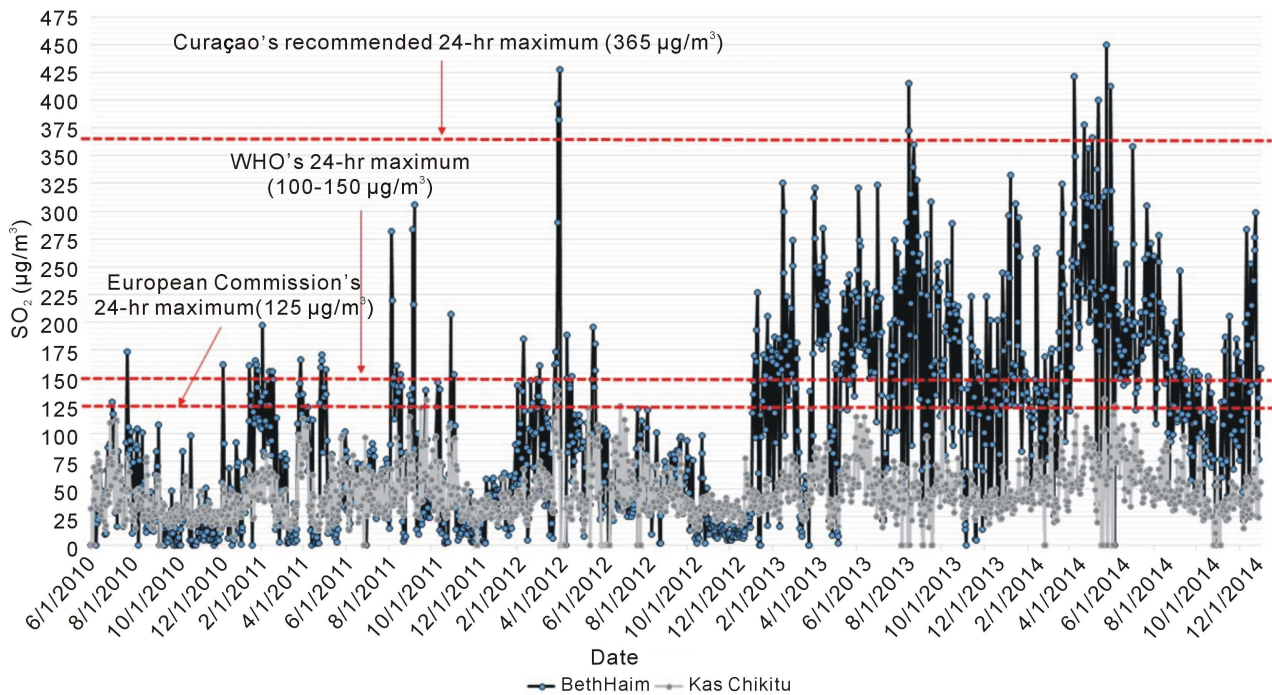
Figure 1. Daily 24-hour mean concentrations of SO_2 (µg/m³) measured at the Beth Haim and Kas Chikitu air monitoring stations in Curaçao from June 1, 2010 through December 31, 2014.
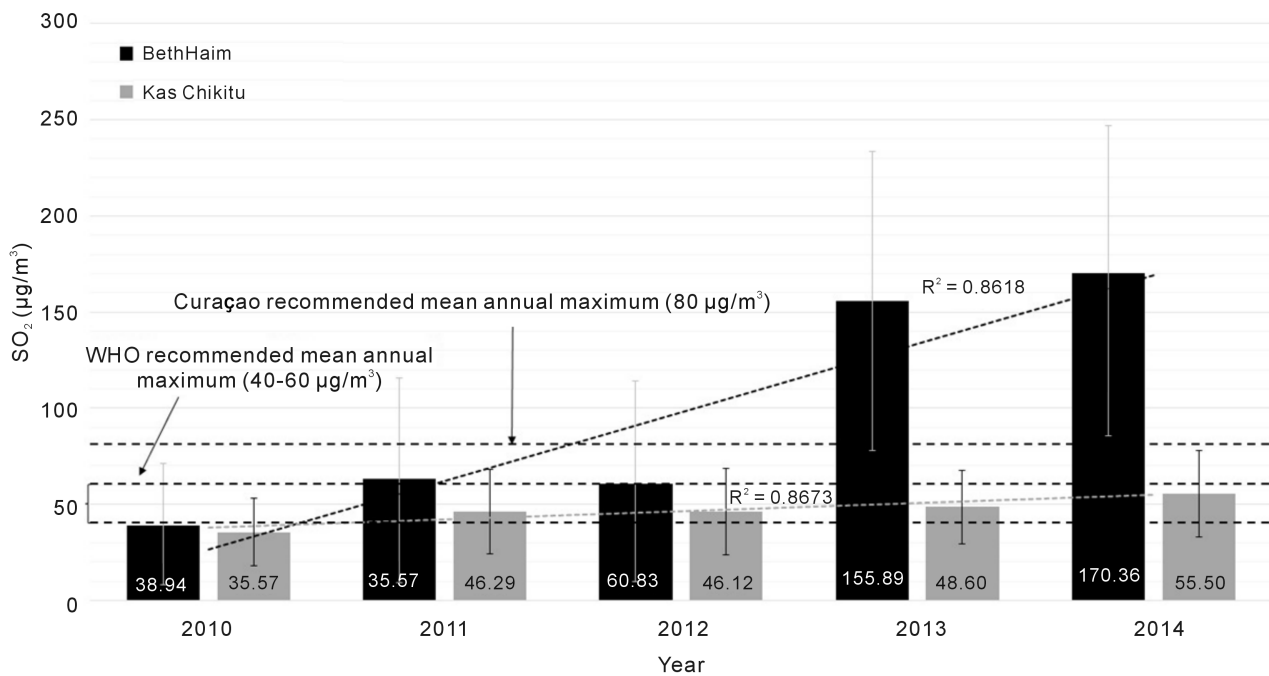

Figure 2. Mean annual SO_2 concentrations (µg/m³) measured at Beth Haim (■) and Kas Chikitu (■) demonstrate significant temporal trends for the years 2010 through 2014.

average SO_2 concentrations was reported in the Yangtze Delta region of eastern China (2005-2010) and in Europe (2001-2010) [23] [24]. The US also reported an 81% decrease in the daily one hour maximum average for SO_2 concentrations

from 1980-2013 [25]. Decreases were also observed in annual SO_2 concentrations in Mexico City with an 84% decrease between 1986 and 2003 [26]. The annual SO_2 concentrations measured at both the Beth Haim and Kas Chikitu station for the years 2010-2014 are among the highest reported globally (**Figure 3**). The 2014 concentrations measured at Beth Haim were more than 200 times greater than those measured in Nuraminis, Italy (0.72 $\mu g/m^3$) in 2012 (http://www.eea.europa.eu). In addition, the 2013 annual SO_2 concentrations (155.9 $\mu g/m^3$) at the Beth Haim station were over 5 times higher than the 2013 US annual average (29.4 $\mu g/m^3$).
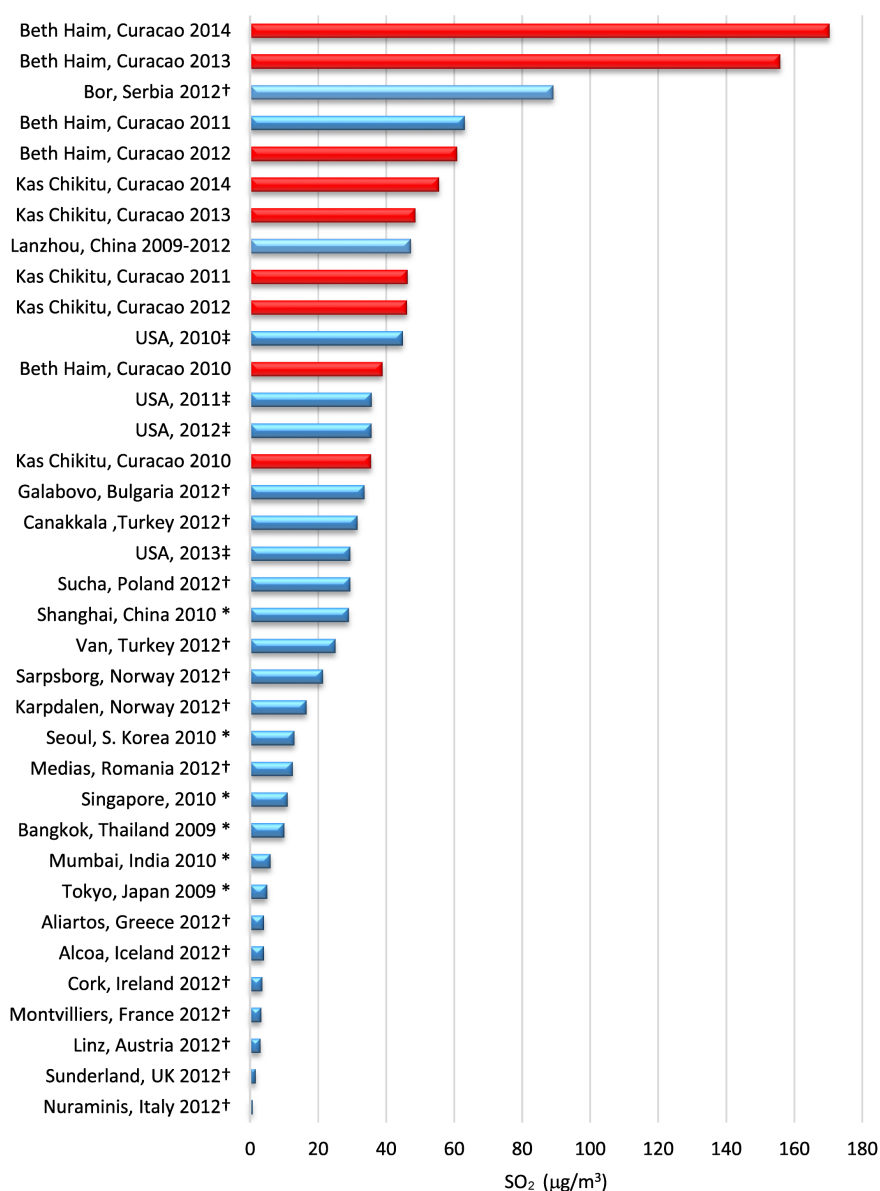

Figure 3. Global comparison of mean annual SO_2 concentrations ($\mu g/m^3$). Sources for the concentrations from other countries are as follows †European Environment Agency, ‡USEPA and *Clean Air Asia Citites ACT. Red bars indicate data relevant to current study.

3.3. SO$_2$ Compliance with Public Health Guidelines

The maximum annual mean concentrations for SO$_2$ that are currently recommended by Curaçao and WHO are 80 µg/m^3 and between 40 - 60 µg/m^3, respectively. The SO$_2$ annual mean concentrations in 2010, at both the Beth Haim (38.9 µg/m^3) and Kas Chikitu (35.6 µg/m^3) air stations, was the only year concentrations were less than the recommended guidelines, however, it is important to note the measurements were only for a 7 month period (July-December). The 24-hour guidelines issued by the European Commission and Curaçao both recommend 125 µg/m^3 with three permissible excursions. Curaçao recommends the mean 24-hour maximum concentrations do not exceed 365 µg/m^3 more than once per year. In addition, WHO recommends 24-hour maximum concentrations of 100 - 150 µg/m^3. The number of days that exceed the 24-hour guidelines at both stations are also increasing over time. The 24-hour recommended SO2 guidelines were within compliance for the majority of 2010 (95%), 2011 (78%) and 2012 (84%) at the Beth Haim Station (Figure 4). However, 2013 and 2014 exceeded the recommended SO$_2$ guidelines 74% and 81% of the year, respectively. Curaçao allows three excursions per year above the 24-hour maximum recommendation (125 µg/m^3). In 2011, 2012, 2013, and 2014 this value was exceeded 30, 15, 40 and 54 times, respectively. In contrast, the daily SO$_2$ concentrations measured at the Kas Chikitu station were compliant for the majority of each of the years measured in this study [2010 (99%). 2011 (98%), 2012 (96%), 2013 (98%) and 2014 (95%)]. The only year that exceeded the number of permissible excursions was 2012, with a total of 4 days exceeding 125 µg/m^3.

3.4. Potential Risks of SO$_2$ Inhalation

Many epidemiological studies have reported relative risk (RR) estimates, hazard ratios (HR) and odds ratios (OR) for associations between mortality and morbidity and SO$_2$, yet results are somewhat inconclusive (Figures 5-7) [27]-[41]. This study primarily focused on literature published within the last five years since there are several meta-analyses and reviews covering literature published prior to 2010.

Many of the studies reported relative risk estimates that were either close to or included unity or had large confidence intervals (Figure 5). A study evaluating air pollution effects on residents of central Taiwan, reported positive relative risk estimates (RR: 1.043, 95% CI: 1.018 - 1.098) for associations between SO$_2$ (12.6 µg/m^3 winter mean concentration) and all-cause mortality during the winter months [27]. Similarly, the health impacts were assessed in the megacity of Iran and also reported positive associations (RR: 1.004, 95% CI: 1.003 - 1.0048) between all-cause mortality and SO$_2$ concentrations (89.2 µg/m^3 annual mean) [33]. Lai *et al.* [28] conducted a meta-analysis of research between 1989 and 2010 reporting health effects on Chinese populations in China, Taiwan and Hong Kong, which also resulted in positive associations (RR: 1.007, 95% CI: 1.0045 - 1.0097) between SO$_2$ (14 - 213 µg/m^3 annual mean) and all-cause mortality.
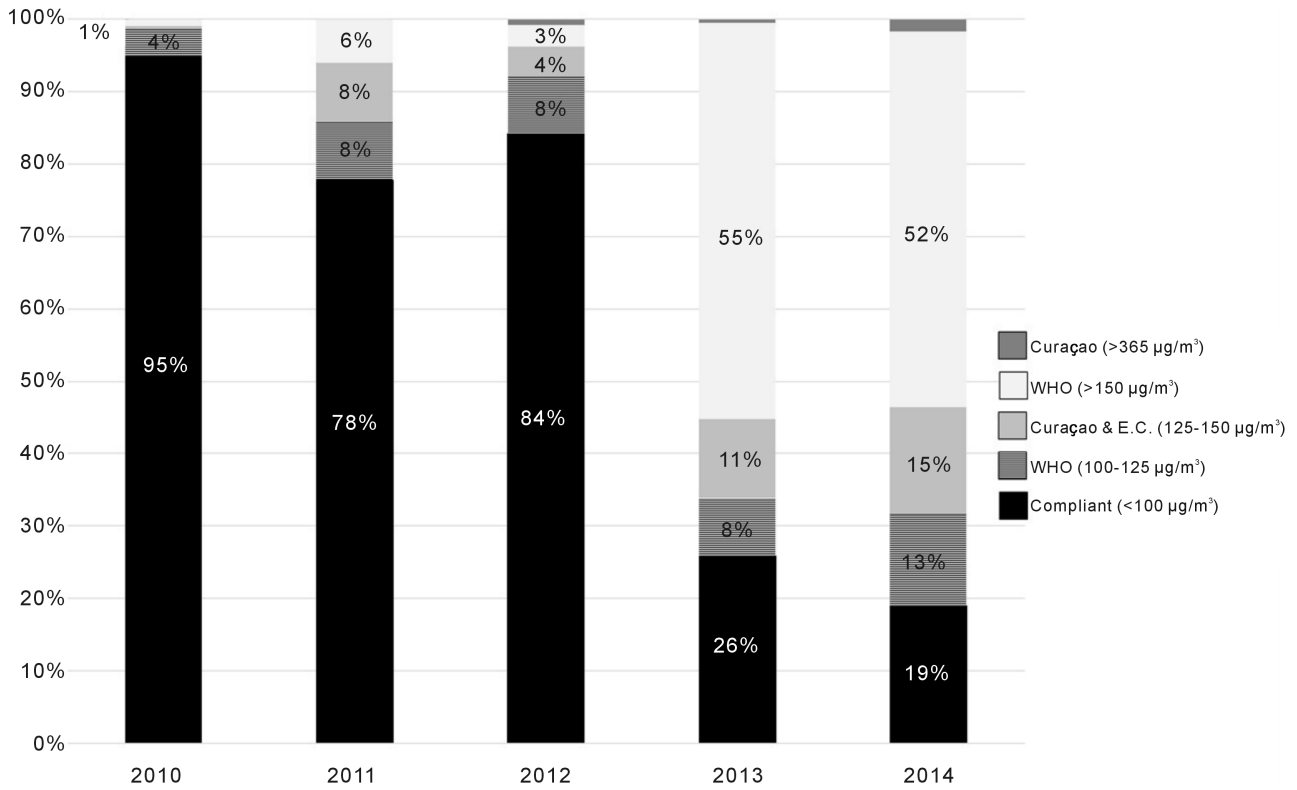
Figure 4. Percentages of each year that were either in compliance or exceeded current maximum 24-hour guidelines for SO_2 concentrations at the Beth Haim air monitoring station.
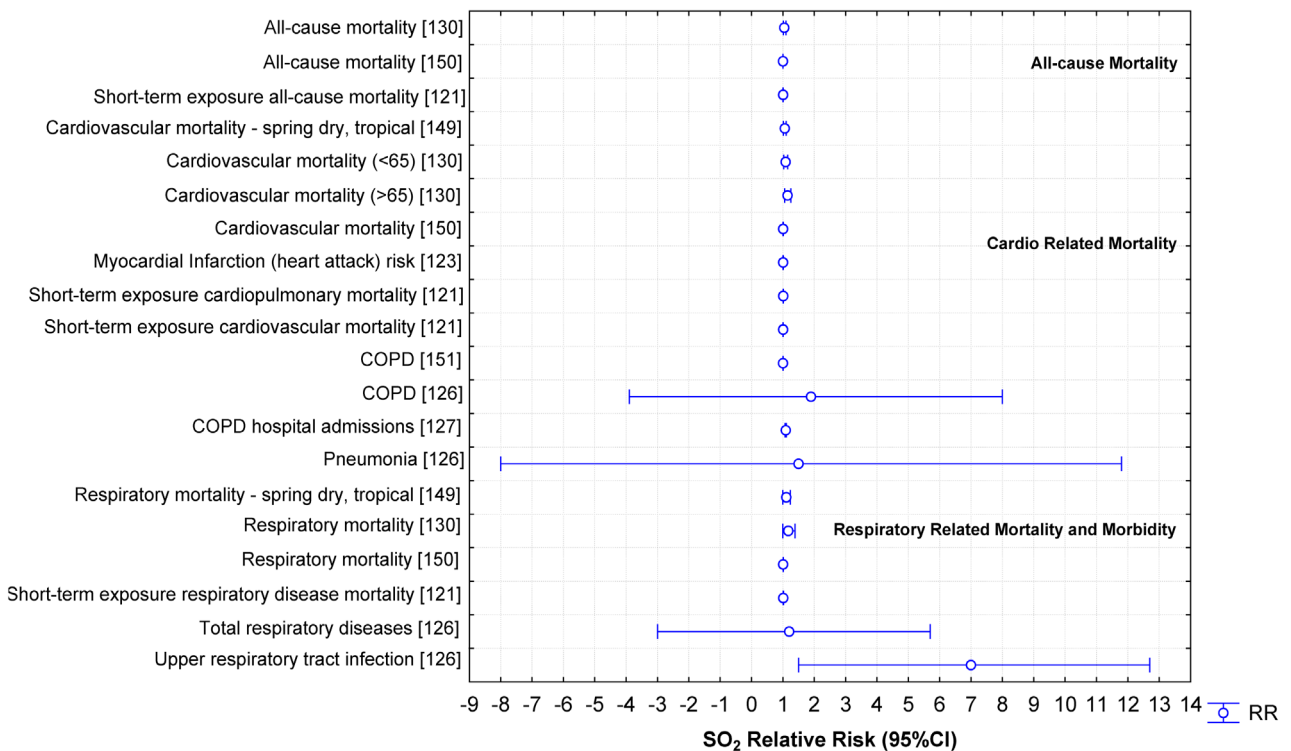

Figure 5. Relative risk estimates (95% CI) for SO_2 associated mortality and morbidity from published literature.
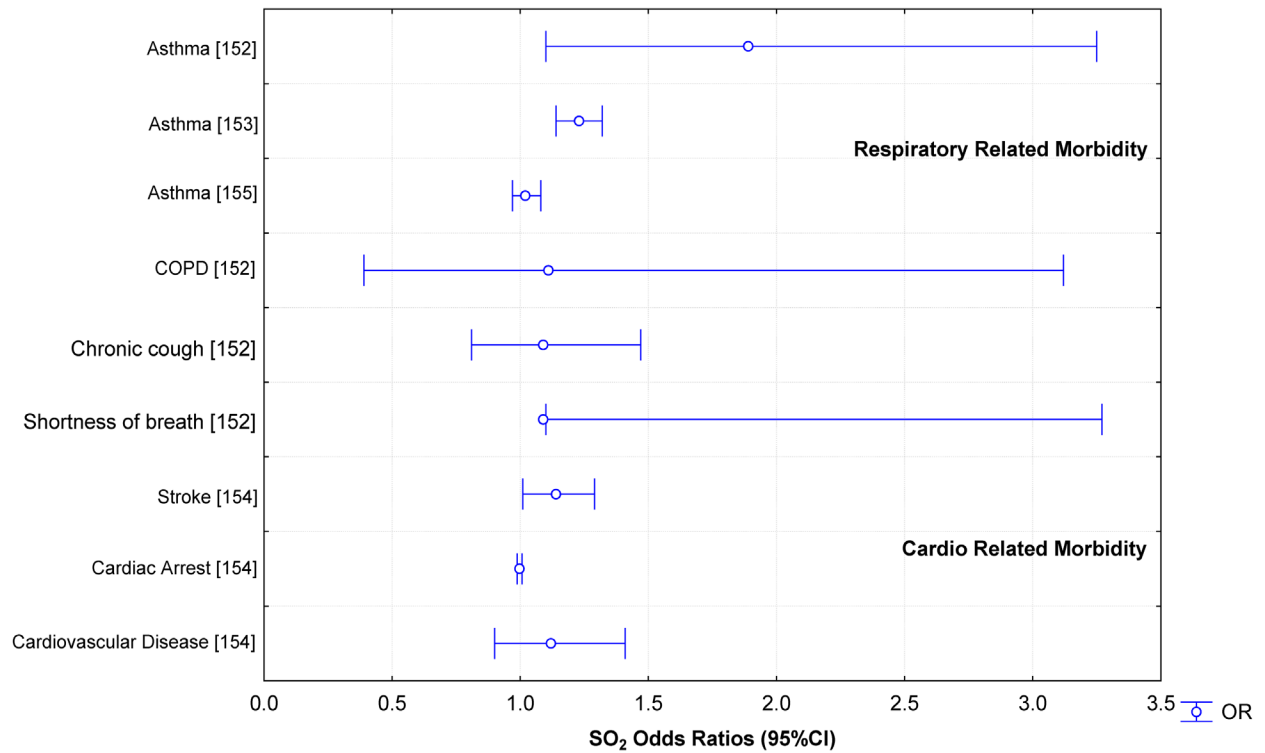
Figure 6. Odds ratios (95% CI) for SO$_2$ associated morbidity from published literature.
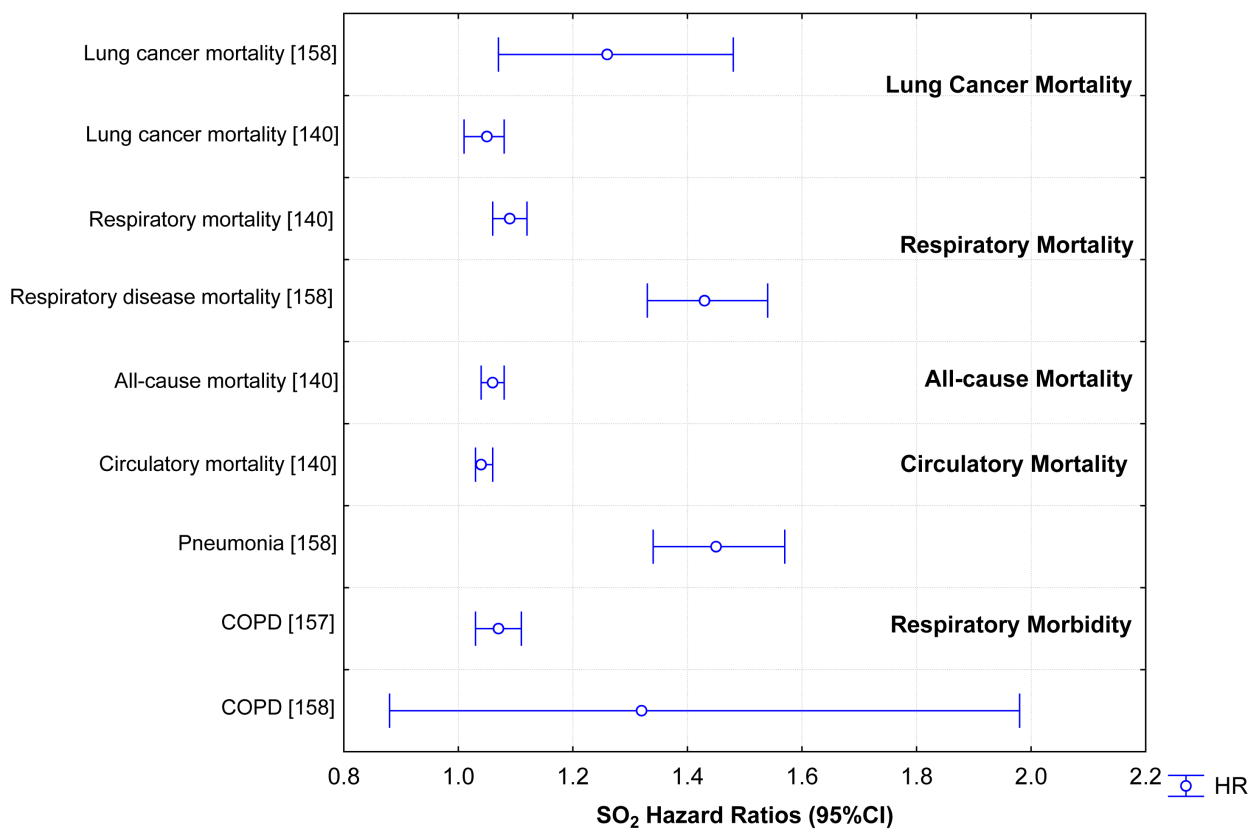

Figure 7. Hazard ratios (95% CI) for SO$_2$ associated morbidity from published literature.

Several studies reported positive associations between SO_2 and cardio related mortality and risk [27] [28] [30] [31] [33]. A Canadian study reported positive associations (RR: 1.061, 95% CI: 1.018 - 1.105) between SO_2 (15.72 μg/m^3 spring mean) and cardiovascular mortality during the spring when the weather was described as dry and tropical [30]. The meta-analysis evaluating air pollution effects on Chinese populations also reported positive associations between short-term SO_2 exposure (14 - 213 μg/m^3 annual mean) and cardiopulmonary (RR: 1.01, 95% CI: 1.009 - 1.015) and cardiovascular mortality (RR: 1.007, 95% CI: 1.004 - 1.01) [28]. A meta-analysis of 34 studies concluded statistically significant positive associations (RR: 1.01, 95% CI: 1.003 - 1.017) with SO_2 and increased risks of myocardial infarction [31].

The relative risks reported for chronic obstructive pulmonary disease (COPD) and respiratory mortality or morbidity appear to be likewise inconclusive. Significant positive associations between SO_2 and COPD were reported in Shiraz (674.9 μg/m^3 annual mean; RR: 1.095, 95% CI: 1.07 - 1.11) and Tabriz, Iran (19 μg/m^3 annual mean; RR: 1.0044, 95% CI: 1.0 - 1.011) [32] [34]. In contrast, a study reported no significant associations (RR: 1.9, 95% CI: 0.9 - 8) with COPD in the heavily polluted city of Lanzhou, China where the mean SO_2 concentrations (79 μg/m^3 annual mean) are four times higher than those reported in Tabriz, Iran and almost an order of magnitude lower than those reported in Shiraz, Iran [29]. No significant associations were found between respiratory mortality and SO_2 in Canada (RR: 1.11, 95% CI: 0.996 - 1.238) and Taiwan (RR: 1.176, 95% CI: 0.998-1.384) [27] [30]. In contrast, significant positive associations were reported in Iran (RR: 1.01, 95% CI: 1.006 - 1.014) and in a 26 study meta-analysis study (RR: 1.012, 95% CI: 1.0058 - 1.0199) [28] [33].

A number of studies also reported odds ratios for various morbidities (Figure 6). Amster *et al.* [35] reported positive associations between asthma (OR: 1.89, 95% CI: 1.1 - 3.25) and shortness of breath (OR: 1.09, 95% CI: 1.1 - 3.27) with total ambient SO_2 concentrations of 6.6 μg/m^3, yet interestingly, no significant associations were observed with higher SO_2 (43 μg/m^3) concentrations related to specific coal-fired power plant events. A meta-analysis evaluating effects from long-term air pollution exposure reported no significant associations (OR: 1.02, 95% CI: 0.97 - 1.08) between SO_2 and asthma prevalence and wheezing in children [38]. Conversely, in a cross-sectional study consisting of over 23,000 Chinese children, significant positive associations (OR: 1.23, 95% CI: 1.14 - 1.32) were reported between SO_2 (50.3 μg/m^3 annual mean) and asthma [36].

The hazard ratios reported for mortality and various respiratory morbidities also illustrated weak and inconsistent associations with SO_2 and various endpoints (Figure 7). The National English Cohort study, consisting of over 800,000 participants, reported statistically significant positive associations (HR: 1.05, 95% CI: 1.01 - 1.08) between lung cancer mortality and SO_2 [42]. Similarly, a Japanese cohort study, consisting of over 63,000 study participants, also reported significant positive associations (HR: 1.26, 95% CI: 1.07 - 1.48) between lung

cancer mortality and SO_2, although the confidence interval range is relatively wide [41]. Hazard ratios were also reported for respiratory mortality and COPD. Both a National English Cohort (HR: 1.09, 95% CI: 1.06 - 1.12) and the Japanese Cohort (HR: 1.43, 95% CI: 1.33 - 1.54) studies reported significant positive associations between SO_2 and respiratory mortality [41] [42]. For COPD, significant associations were reported in a National English Cohort study (HR: 1.07, 95% CI: 1.03 - 1.11) yet no significant associations (HR: 1.32, 95% CI: 0.88 - 1.98) were reported in the Japanese cohort study [40] [41].

In summary, the epidemiological studies presented a mix of weak positive associations (*i.e.*, RR, HR, OR < 3.0) between health effects and SO_2 and nonsignificant findings. Potential inconsistencies between studies and results could be due to confounding factors with copollutants and various study designs and methodology, making individual findings difficult to interpret and inconclusive as to the effect of observed levels of SO_2 on health. In general, cardiovascular and respiratory effects and mortality were evaluated in locations with a wide range in annual mean concentrations ranging from 4 to 675 $\mu g/m^3$.

Evidence regarding short-term exposures to SO_2 were inadequate to infer an association with cardiovascular health [43]. As well, the available evidence was inadequate to infer an association between long-term SO_2 exposures and respiratory effects (including asthma), cardiovascular effects and mortality. In the selected epidemiological studies evaluated in a USEPA review, associations between short-term SO_2 exposures and some respiratory effects were observed in locations with mean 24-hour average SO_2 concentrations ranging from 2.62 to 78.6 $\mu g/m^3$, with maximum values ranging from 31.4 to 196.5 $\mu g/m^3$. In addition, some associations with mortality were observed with mean 24-hour average SO_2 concentrations less than 26.2 $\mu g/m^3$.

3.5. Meteorological Parameters and SO_2 Concentrations

Daily temperature, humidity, precipitation and wind speeds were analyzed for trends and correlations with SO_2 concentrations. Briefly, the mean temperature (±standard deviation) from 2010 through 2014 was 27.9˚C (±1.2) and although Kruskal-Wallis multiple comparisons revealed annual differences (p < 0.000001) there were no observable trends (R^2 = 0.0007). The mean humidity (77.7% ± 4.1%; R^2 = 0.73) and precipitation (1.70 ± 6.9 mm; R^2 = 0.75) from 2010 through 2014 both demonstrated moderately strong decreasing trends. Mean annual wind speeds (19.6 ± 4.7 km/h) demonstrated a strong increasing trend over time (R^2 = 0.91). This is consistent with increasing global trends in wind speed [44]. Similar to observations seen with PM_{10} concentrations (Pulster, unpublished data), there was a weak to moderately strong correlation between SO_2 concentrations and wind speeds at Beth Haim (r = 0.42) and the Kas Chikitu (r = 0.46) station (**Figure 8**). In addition, SO_2 concentrations were found to have a weak, negative correlation with humidity (Beth Haim r = -0.37; Kas Chikitu r = −0.29) and precipitation (Beth Haim r = −0.12; Kas Chikitu r = −0.15) at both stations.

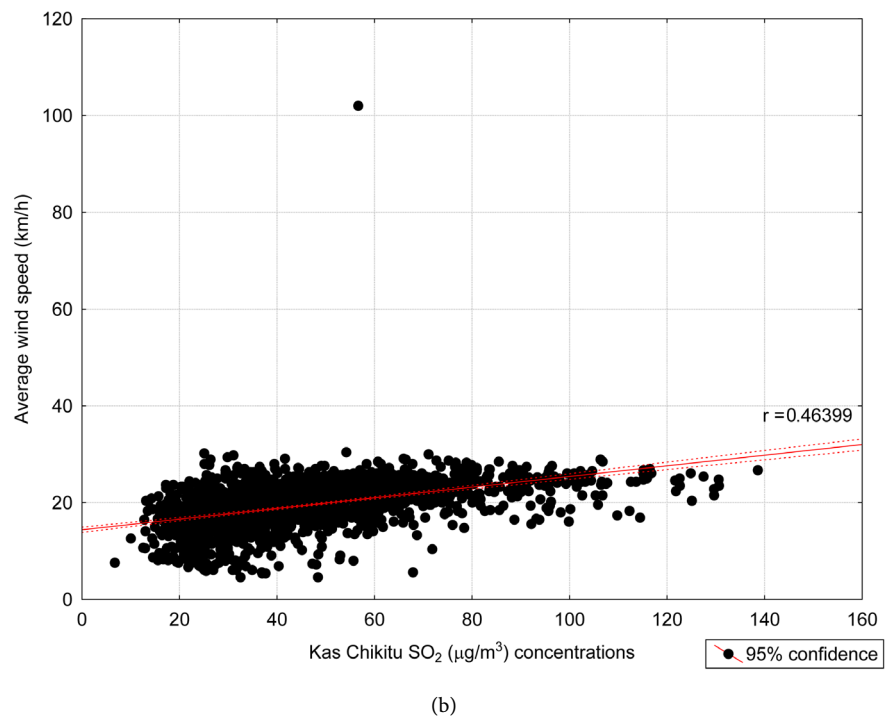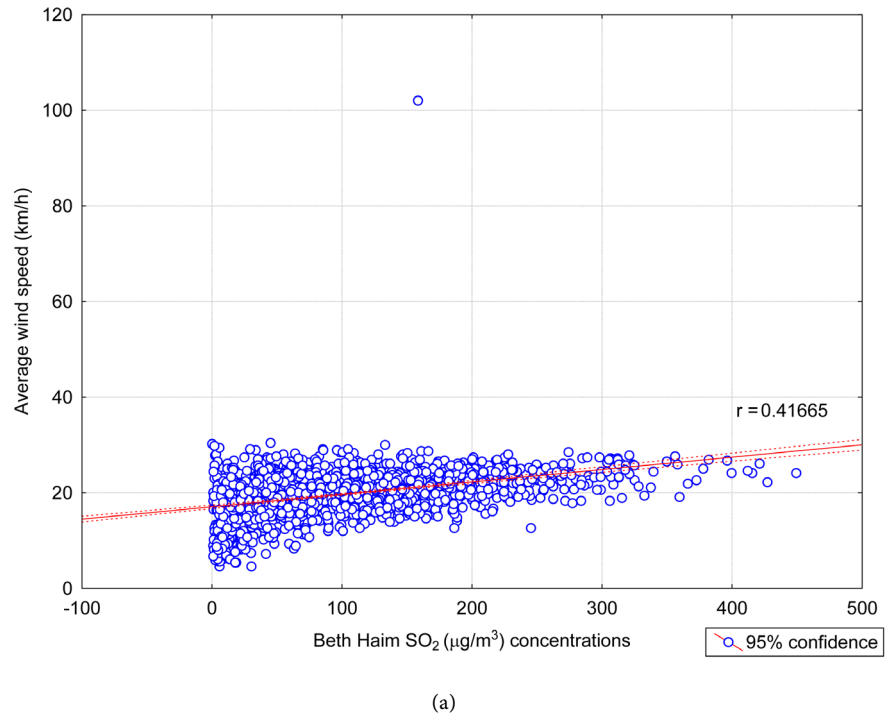**Figure 8.** Regression analysis between wind speeds (km/h) and SO$_2$ concentrations (μg/m^3) at the Beth Haim (a) and the Kas Chikitu (b) air monitoring station measurements from 2010 through 2014.

There were no correlations found between SO$_2$ and temperature at either the Beth Haim (r = 0.11) or the Kas Chikitu (r = 0.15) station. This is not surprising since the average year round temperature is ~28˚C with very little fluctuation.

Meteorological parameters can influence air pollution concentrations in ambient air, for instance, the frequencies and concentrations of pollution episodes can vary considerably over time and space depending on weather, which indicates the importance of climate change [45] [46]. In some instances, wind speeds can have a dilution effect which has been demonstrated in a study in Hungary, that illustrated increasing wind speeds decreased aerosol concentrations which resulted in decreased pollen related hospital admissions [47]. However, other studies have demonstrated statistically significant impacts from SO_2 and other emissions downwind of oil and gas exploration and production activities [46]. Likewise, this study illustrates that increasing wind speeds were correlated with increasing SO_2 concentrations downwind of the Isla Refineriá's plume trajectory in Curaçao. Furthermore, the previously reported increasing inhalable particulate matter in this region mimics that of the SO_2 suggesting a single source (Figure 9; Pulster, unpublished data). This suggests with increasing wind speeds, pollution plumes and fluxes are also expected to increase, ultimately impacting local populations residing within the refinery's plume trajectory.

4. Conclusions

The objective of this investigation was to conduct an exposure assessment by analyzing levels of SO_2 in ambient air surrounding Willemstad, Curaçao in order to determine if any temporal trends exist in the measured concentrations, to verify if measured levels exceed current public health guidelines and to identify potential health risks. In conclusion, concentrations of SO_2 in Curaçao are among the highest reported globally and demonstrate an increasing trend over time. Levels of SO_2 exceeded the annual and 24-hour guidelines recommended by Curaçao, the European Commission, and the World Health Organization.
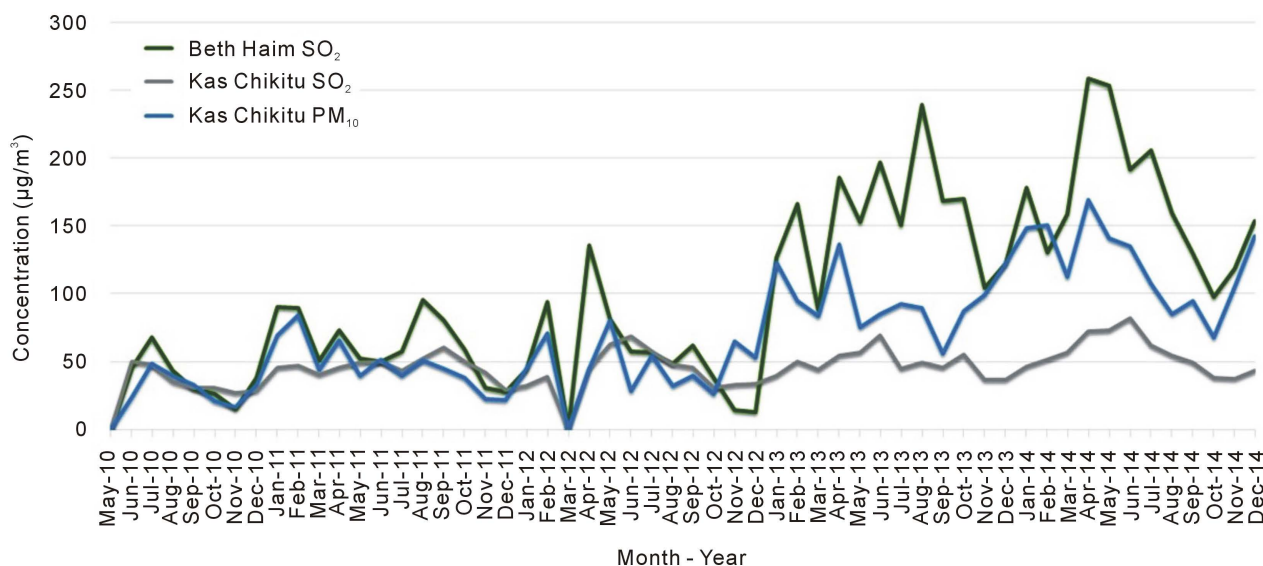

Figure 9. Increasing trends of monthly measurements of SO_2 and PM_{10} at the Beth Haim and Kas Chikitu air stations in Curaçao from 2010 through 2014, suggesting one source.

Furthermore, both the 24-hour and annual mean concentrations of SO_2 measured in Curaçao were within the ranges often associated with cardiovascular and respiratory effects and mortality as a result of short-term exposures. While the epidemiological evidence does not conclusively suggest there is a health risk from these levels of exposure, SO_2 concentrations greatly exceed regulatory and guidance levels and suggest that further emissions control is warranted.

In a recent survey, 60% of 3230 children (ages 0 - 14) in Curaçao had asthma, which is more than four times the global average for children [48]. Since exposures to both SO_2 and PM_{10}, individually and together, have been found to be associated with significant increases in the prevalence of pediatric asthma and asthma related hospital admissions, this should necessitate the need for further evaluation [49] [50]. This warrants a more rigorous epidemiological study in Curaçao involving clinical assessments to evaluate health effects and disease associations with air quality parameters. A complete human health risk assessment is recommended to include dermal, inhalation and dietary exposure pathways. Future research needs in Curaçao include expanding the air monitoring efforts to include areas upwind of the refinery as well as additional petrochemical emissions, including but not limited to sulfur dioxide, particulate matter (PM_{10} and $PM_{2.5}$), benzene, as well as both the vapor and particulate phases of ambient PAHs.

Acknowledgements

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