Spatial distribution and sources of atmospheric polycyclic aromatic hydrocarbons in Curaçao

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Paul C. Hoetjes

Department of Environment
Ministry of Public Health, Environment and Nature
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Submitted by:

Erin Pulster, M.S.
Dana L. Wetzel, Ph.D.

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Prepared by:

Erin L. Pulster, M.S.
and
Dana L. Wetzel, Ph.D.

Environmental Forensics Laboratory
1600 Ken Thompson Parkway
Sarasota, FL 34236

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1. Introduction

1.1 The Presence of Polycyclic Aromatic Hydrocarbons in the Wider Caribbean

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. However, these factors have created levels of environmental pollution that are of concern regionally, even in the absence of empirical data to document levels and effects of contamination on the health of the environment (e.g., coral reefs), fishery resources and other wildlife, as well as humans. 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.

The presence of hydrocarbons (i.e., polycyclic aromatic hydrocarbons - PAHs) in this region is one of the most significant threats or potential risk factors to environmental and human health (UNEP, 1999). Industrial point sources contribute 90% of the oil pollution loads entering the WCR coastal areas, mainly from approximately 100 oil refineries operating in this region (UNEP, 1994). One of the largest and oldest refineries in the WCR, Isla Refineria, opened in 1918 and is located within the densely populated capital of Willemstad, Curaçao on the shores of Schottegat Bay. Although, the refinery was considered obsolete in the mid-1980s, it is still in use today processing ~320,000 barrels per day and has not been able or required to comply with environmental standards and permit requirements (Curaçao Legal Portal, 2008).

1.2 The Big Question: Vehicular or Refinery Emissions?

A legacy of human health and environmental issues is the basis of a historical debate and conflict between the public and the local government. Communities downwind of Isla Refineria and Schottegatweg Ring, the major thoroughfare circling the refinery and the bay, are suspected to experience higher than average frequencies of headaches, nausea, chronic lung ailments, asthma and cancer (van der Torn, 1999, Behind the Shine, 2003, GCM, 2009). Most of these health complaints originate from local schools. The degree of acute health effects from emissions appears to fit the health-scale for disaster response (van der Torn, 1999). Sulphur dioxide, is ~4 times higher than maximum concentrations accepted anywhere else in the world, and exceeds the normal annual average by 60% (Curaçao Legal Portal, 2008). In 2009, a court order required the refinery to reduce the excessive sulphur dioxide emissions and particulates starting January 1, 2010. Anecdotal information from court proceedings inferred that the refinery insists the adverse health effects are caused from heavy motor vehicle traffic emissions from the major thoroughfare alongside the refinery (P. Hoetjes, MINA, personal communication). However, a lack of concrete data makes it difficult to assess the impact that both motor vehicle traffic and refinery emissions have on human health and the marine environment. Two main questions need to be answered with regard to petrochemical emissions and the public health of Curaçao: First, what is the main source of atmospheric petroleum constituents contributing to the human health problems, motor vehicular emissions (MVE) or refinery emissions? Second, what are the human health risks based on current levels of air pollution?

The presence of high levels of polycyclic aromatic hydrocarbons (PAHs) in the WCR is one of the most significant threats or potential risk factors to human health and the environment (UNEP, 1999). The main sources of PAHs in urban ambient air are from incomplete combustion from predominantly anthropogenic sources like vehicular emissions and industrial emissions using fossil fuel and biofuel, and also from vegetation fires. The major unresolved dispute in Curaçao is whether the petrochemical emissions are solely due to motor vehicle emissions or whether the major contribution comes from one of the largest oil refineries in the WCR, Isla Refineria (USONA, 2008).

There is no question that vehicular traffic has become an increasingly dominant contributor to air pollution globally (Samet, 2007). The adverse health effects associated with elevated exposures to MVEs near busy roadways has emerged as a significant public health concern (Samet, 2007; White et al., 2005). The principal air pollutants associated with vehicle combustion engine sources are carbon monoxide, nitrogen oxides, particulate matter, ozone, and black carbon (Samet, 2007; White et al., 2005). Motor vehicle emissions have been associated with increased risk for multiple adverse health effects including asthma and allergic diseases, cardiac effects, respiratory symptoms, reduced lung function, growth, reproductive impairment, premature mortality, and lung cancer (Smargiassi et al., 2009; Lee et al., 2006; White et al., 2005; Lee et al., 2002; Fusco et al., 2001).

The petroleum manufacturing process associated with refineries generates vast amounts of pollution consisting of particulate matter, sulfur dioxide, nitrogen oxides, benzene and PAHs. Particulate PAHs are a class of semi-volatile compounds that are formed during combustion which are known or suspected carcinogens. Limited information is available on PAH contributions from refineries to ambient air, however epidemiology studies evaluating lung cancer and respiratory disease have shown geographic gradients with highest mortality in areas closest to petrochemical, steel production and other industrial areas (Bhopal et al., 1998). High sulfur dioxide levels were implicated in the acute morbidity and mortality associated with the severe pollution episodes in Donora (Pennsylvania), London, and New York in the 1940s, 1950s and 1960s, respectively (Smargiassi et al, 2009; American Thoracic Society Committee of the Environmental and Occupational Health Assembly, 1996).

While protecting the human population from deleterious exposure to atmospheric petroleum contamination is vital, the environmental health of Schottegat Harbor area ecosystem also needs to be addressed. During World War II an overproduction of asphalt from the refinery processes was pumped out of the refinery creating a 200-acre artificial lake of oil, known today as Asphalt Lake. It is estimated that 1.5 million tons was dumped in the lake during the war. Additional asphalt and other byproducts, in particular those of lubricating oil refining processes, were deposited into a chemical waste lake at the same location of the asphalt lake. In the Harbor, there are vast areas of tar covered beaches (Debrot et al., 1995; Richardson et al., 1987), oil slicks in mangroves, massive fish kills, fish smelling and tasting of petroleum, and degraded coastal coral reef communities (Gast et al., 1999). The reefs surrounding Curaçao have previously been characterized as being at high risk (UNEP, 2004). In the Caribbean, 22% of coral reefs have already been degraded with strong links to harmful anthropogenic contributions, including industrial pollution (UNEP, 2004). Schottegat Harbor is a critical feeding area for

hundreds of shore and seabirds, including the endangered common tern (Buckley & Buckley, 2000). Commercially valuable species (e.g., blue crabs and spiny lobsters), baitfish and popular sport fish (e.g., tarpon, ladyfish and snook) are also found in abundance within the harbor.

Oil pollution is known to pose deleterious effects on aquatic ecosystems, ranging from primary producers to top level predators. Sediments contaminated with PAHs have been found to be both genotoxic and embryotoxic (Cachot et al., 2006). Yong & Tam (2007) reported physiological damage and high mortality rates in mangroves after 90 days of lubricating oil exposure. Cytochrome P4501A induction in oil-exposed pink salmon embryos was related to a variety of lethal and sublethal effects, including decreased survival, reduced growth and abnormalities (Carls et al., 2005). Cod fish subjected to chronic exposure of PAHs also resulted in genotoxicity (Holth et al., 2009). Oil inhalation, skin contact and ingestion have recently been associated with the decline of two killer whale populations (Matkin et al., 2008). In humans, cancer and DNA damage has been directly linked with PAH exposure (Perez et al., 2008).

Given the significance of this current public health risk in Curaçao, there is an urgent need to (a) verify the point source of the petrochemical emissions; (b) establish baseline levels and extent of contamination, (c) conduct a formal human health and environmental risk assessment, and (d) initiate appropriate mitigation measures (MINA, 2009). To date, these important steps have not been undertaken. The amount of chronic exposure to petrochemical emissions in Curaçao and other parts of the WCR experience and the scarcity of data in this region warrant the imminent development for studies in this region.

1.3 Project Objectives

Exposure assessments are the first critical step for many applications, including compliance with legal standards, disease diagnosis and treatment, risk assessment and management, and occupational and environmental epidemiology. The underlying assumption is that there is a causal relationship between the amount of exposure and the extent of the observed health effect (Hammad & Manocha, 1995). This project focused on conducting a first step to a much larger human health and environmental risk assessment that is needed. The primary objectives of this study were to:

1) Deploy passive air samplers along transects that extend radially from the refinery and along the major thoroughfares to establish baseline levels of select petrochemicals in air samples;

2) Ascertain the point source of the air pollution (i.e., vehicular vs. refinery emissions) using diagnostic ratios;

3) Verify areas with the highest impact from emissions, and identify any exceeding current thresholds for petroleum emissions;

This exposure assessment project has identified the primary source of contamination, established baseline concentrations of petrochemical emissions in ambient air samples, and determined if levels exceeded current thresholds in the targeted sampling area.

2. Materials & Methods

2.1 Site Selection and Study Design

Curaçao is an island in the southern Caribbean, ~40 miles off the Venezuelan coast. It was part of the Netherland Antilles until its dissolution in 2010 and is therefore currently considered a constituent country of the Kingdom of the Netherlands. 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 annual average weather conditions in 2011 consisted of ~27°C degree temperatures with 79% humidity and an average wind speed of 19.4 km/h. The island is approximately 29 - 32 kilometers in length, 5 -13 kilometers wide and a total land mass area of ~443 km^2. The population of ~152,000 consists of >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 Refineria.

Fifteen sampling sites were selected based on their proximity to Isla Refineria, Schottegatweg Ring, and along westerly transects from the ring outward to approximately 6 km west (downwind) of the refinery (Table 1; Figure 1). In addition, the three major communities (Heinjte Kool/Buena Vista, Marchena/Wishi, Habaai) involved in the 1999 Environmental Service of Curacao Health Assessment were included in this study (van der Torn, 1999). This assessment was conducted as a result of health complaints from communities directly exposed to refinery emissions. Passive air samplers were deployed in 13 residential neighborhoods or geozones with a total estimate of 12,000 residents (Table 2).

2.2 Passive Air Samplers (PAS)

Polyurethane foam (PUF) vapor collection substrates (P/N TE-1014; 1.27 cm thick x 13.97 cm diameter; density 0.029 g/cm^3) were purchased from Tisch Environmental (Village of Cleves, OH, USA). Prior to deployment, PUFs were individually packed into a 66mL extraction cell and pre-cleaned with acetone and hexane using an Accelerated Solvent Extractor (ASE 300, Dionex, Sunnyvale, CA, USA). The ASE was programmed for three sequential cycles with the temperature of 100°C, pressure of 1500 psi, static time of 5 min, and a 60% flush volume, and a purge time of 60 sec.

These pre-cleaned PUF vapor collection substrates were then sealed in solvent rinsed aluminum foil and in air tight containers to avoid contamination during transit to the island and sampling locations. The PUFs were suspended within dome-type passive air samplers (PAS, Fig. 2) and deployed in triplicate at each of the 15 sites, with the exception of one site (Parasasa) deployed in duplicate (n=43). Samplers were deployed for ~9 weeks (65 ± 1 day) from 28 February – 6 May, 2011. At the end of the deployment period, the PAS's were retrieved and the PUFs were resealed and transported back to Mote Marine Laboratory where they were stored at -20°C until analysis.

2.3 PUF Extractions and Analysis

The triplicate PUFs from each of the 15 sites were extracted and analyzed separately. Individual PUFs were placed into a 66mL stainless steel accelerated solvent extraction (ASE) cell and spiked with deuterated PAH surrogate standards and ortho-terphenyl (OTP) to monitor recoveries and validate the extraction and clean-up procedures. Each PUF was extracted using 100% methylene chloride under the same ASE conditions as above. The PUF extracts (~80 mL) were reduced to ~1-2 mL using a RapidVap (Labconco Corp., Kansas City, MO, USA) and eluted through an automated GPC system (Fluid Management Systems, Watertown, MA, USA) for further sample cleanup to remove high molecular weight interferences. For further cleanup and separation of polycyclic aromatic hydrocarbons (PAHs), the extract was then eluted with 80:20 CH_2Cl_2/ hexane (v/v) through a neutral silica column (6 g) using a multi-column clean-up system (Automated Power-Prep System, Fluid Management Systems, Watertown, MA, USA). The eluted fraction containing compounds of interest were collected and reduced to 900uL of methylene chloride.

Prior to instrument analysis, all extracts were spiked with two deuterated PAH internal standards (dibenzothiophene-d_8, benzo[e]pyrene-d_{12}) for quantification of targeted analytes. Extracts (1 µL injection volume) were analyzed for approximately 61 polycyclic aromatic hydrocarbons (PAHs), including parent compounds and their homolog, using combined gas chromatography/mass spectrometry (GC/MS; Agilent 7890A/5975C; Agilent Technologies, Inc., Andover, MA, USA). Analyte separation was achieved on a DB-5MS capillary column (30 m x 0.25 µm film thickness x 0.25 mm i.d.; Agilent Technologies, Inc., Andover, MA, USA) with ultrahigh-purity helium as the carrier gas. PAHs were determined in electron impact scan mode (EI) with helium as the carrier gas at 1mL/min. The injector (splitless mode) and transfer line temperatures were set to 300°C and 280°C, respectively. The oven temperature program was as follows: 60°C (0.5 min hold), then 8°C/min to 325°C (3 minute hold) for a total run time of 36.6 minutes. The source and quadrapole temperatures were set to 230°C and 150°C, respectively. All mass spectral data were compared to spectra produced by authentic standards and to previously published library spectra.

2.4 Calculated Air Concentrations

Passive air sampling has previously been shown to be an appropriate substitute for active sampling techniques in a number of regional and global atmospheric PAH monitoring studies (Bohlin et al., 2010; Pozo et al., 2009; Jaward et al., 2004). Consequently, PAS using PUFs is the most widely used technique for monitoring PAHs in both environmental (outdoor) and occupational (indoor) settings (Bohlin et al., 2010; Pozo et al., 2004, 2009). Passive air samplers adsorb chemical constituents that can be used to assess ambient concentrations in the atmosphere. The extent to which chemicals are enriched in the sampling substrate relative to air is dependent on the passive sampler medium (PSM), or the air partition coefficient ($K_{PSM\text{-}A}$). The $K_{PSM\text{-}A}$ and the sampling rates (R) are both necessary to know in order to use PAS quantitatively to assess ambient atmospheric concentrations and both have been previously calculated from field calibration experiments (Harner et al., 2013; Bohlin et al., 2010). The effective air sampling volumes (V_{air}) for the PUFs were determined using the following calculation:

$$V_{air} = Rt$$

where *t* is the mean deployment duration (65 days) and the sampling rate, *R*, is 5 m^3/day (Harner et al., 2013; Bohlin et al., 2010). Ambient air concentrations (C_{air}; ng/m^3) were then calculated using the following formula:

$$C_{air} = \frac{m_i}{V_{air}}$$

where m_i is the mass of the target analyte in the passive samples (ng/PUF).

2.5 Quality Assurance and Quality Control (QA/QC)

A performance-based quality-assurance and quality-control program, which included the parallel analysis of procedural blanks and matrix spikes was implemented to ensure data of the highest quality. Quality assurance and quality control guidelines follow TDI-Brooks International, B&B Laboratories Inc., EPA 8270D and NOAA established criteria for PAH analysis. Five custom calibration standards ranging in concentration from 25 to 1000 ng/mL were used. Prior to sample analysis, the initial calibration passed the following established criteria: R^2 = 0.99 - 1 for all compounds and surrogates and the % RSD was ≤ 20% for all relative response factors (Table 3). The GC response was monitored using a mid-level (250 ng/mL) continuing calibration standard, passing acceptable criteria (% RSD ≤ 25% for 90% of the analytes; ≤ 35% for 10% of the analytes; see Table 3). Procedural blanks were checked to confirm they were clear of targeted analytes. Acceptable blanks were considered to contain no more than three times the MDL for two or more target analytes. The method of detection limit (MDL) is defined as three times the standard deviation of the mean concentration of each analyte detected in the blanks. Only two of 21 parent PAHs were detected in the blanks (naphthalene and phenanthrene). The MDLs were 22 and 196 ng/PUF for naphthalene and phenanthrene, respectively. Half the instrument detection limits (IDL) were used for the compounds that were not detected in blanks. Instrument detection limits ranged from 0.06 to 0.24 ng/mL (Table 4).

Sample analyte concentrations were quantified based on the concentration and response of the internal standards (dibenzothiophene-d_8 and benzo[e]pyrene-d_{12}). All samples and method blanks were spiked with OTP and four (4) deuterated PAH surrogate compounds prior to extraction. All samples passed the acceptable surrogate recovery criteria (% recovery 50-150%). The mean recovery of OTP spiked in all samples was 104 ± 6%. The overall recovery for the low and high molecular weight surrogates were 61 ±11%; and 84 ± 9%, respectively. The overall recovery for the matrix spiked with 18 parent PAHs was 82 ± 25%. Individual and standard mixtures of PAHs were purchased from AccuStandard (New Haven, CT, USA).

3. Results and Discussion

3.1 Levels of atmospheric polycyclic PAHs in select sites of Curaçao

Calculated ambient concentrations of PAHs in our sampling areas ranged from 0.25 to 193.99 ng/m^3. The highest levels of PAHs were measured at the two sites directly downwind of Isla Refineria, Habaai (178.62 ± 14.07 ng/m^3) and Marchena (103.17 ± 6.68 ng/m^3) (Table 5, Figure 3). The lowest levels were measured in Blauw/Corosol (0.30 ± 0.06 ng/m^3) which was one of the furthest sites west of the refinery (~6 km). Ambient levels of PAHs were significantly different across locations (p<0.00001) however there were no clear trends from east to west or

with increasing distance from the refinery. Nevertheless, the two sites directly downwind (Habaai & Marchena) of the refinery had concentrations significantly higher than all other sites equaling one to two orders of magnitude higher than the eastern and western most sites, respectively. The consistent direction of the Trade Winds is a critical factor in ambient levels of PAHs downwind of the refinery. These results are supported by a previous study evaluating other emission constituents (total suspended particulate, sulfate, chlorides, lead) which concluded the refinery affects a substantial portion of the western side of the island, and more so, those sites downwind of the refinery (Sanhueza et al., 1982). Lack of associations could be attributed to other confounding factors, such as terrain elevation / physical geography, and sample sizes. In order of decreasing mean concentrations of targeted PAHs, Habaai had the highest levels followed by Marchena > W. Buena Vista > Boka Sami > E. Piscadera Baai > Groot Piscadera > W. Piscadera Baai > Nieuw Nederland > E. Buena Vista > Roosendaal > Rooi Catochi > Marie Pampoen > Parasasa > Blauw/Corosol (Figure 3). In general, the ambient concentration of PAH levels in this study were consistent with other urban and industrial regions found globally, but up to three orders of magnitude higher than some remote and rural areas (Jaward et al., 2004; Motelay-Massei et al., 2005; Santiago et al., 2007). Yet still surprising, most of the sites were on the same order of magnitude as highly industrialized regions of India (23-190 ng/m^3; Kulkarni et al, 2000) and up to an order of magnitude higher than some remote regions of Europe (0.4-70 ng/m^3; Jaward, et al., 2004).

Ambient air samples were dominated by PAH compounds with 3-rings, accounting for 47% of the ΣPAHs, followed by the 2-ringed (38%), 4-ringed (13%), 5-ringed (2%) and the 6-ringed (<1%) compounds (Figure 4). However, the 16 USEPA designated priority PAHs contributed 22-62% of the measurable PAHs in ambient air. Furthermore, carcinogenic or likely carcinogenic PAHs (benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene) accounted for 3-36% of the priority PAHs across the different sites (Figure 5). Interestingly, the highest percentage of carcinogenic PAHs were found at the two sites with the lowest levels of total PAHs in ambient air, Parasasa (35%) and Blauw/Corosol (36%).

3.2 Elucidating emission sources using diagnostic ratios

Identifying and understanding the impact of emission sources is critical for proper risk assessment and management (Tobiszewski & Mamieśnik, 2012). Diagnostic ratios and PAH concentration profiles have been useful in identifying emission sources and their contributions to ambient air concentrations (Slezakova, et al., 2013a,b; Teixeira et al., 2013; Ravindra et al., 2008) to distinguish between different sources, such as petrogenic (hydrocarbons associated with petroleum), pyrogenic (hydrocarbons associated with combustion) or phytogenic (hydrocarbons derived from plants). Using these ratios, studies have been able to differentiate between vehicular and non-traffic emissions, diesel and gasoline combustion, different crude oil processing and biomass burning (Zhang et al., 2008; Ravindra et al., 2008; Pies et al., 2008; Yunker et al., 2002, Katsoyiannis et al., 2007).

Each of the diagnostic approaches has its limitations and uncertainties. For instance, the ratios of anthracene/(anthracene+phenanthrene) [ANT/(ANT+PHE)] may be strongly influenced by photoreactions resulting in ratios close to 1, whereas photoreactions can result in higher values for the fluoranthene/(fluoranthene+pyrene) [FLA/(FLA=PYR)] ration (Kim et al., 2009; Tobiszewski & Mamieśnik, 2012). Consequently, more than one diagnostic ratio should be used to confirm the indicated source(s). Two-thirds of the ratios evaluated in this study suggest the

overwhelming contribution from petrogenic sources (i.e., refinery emissions) to the ambient PAH levels at the majority of sites sampled in Curaçao, including Boka Sami, the furthest site west of the refinery (Table 6). This is consistent with earlier findings by Sanhueza et al. (1982) who used additional atmospheric petrochemical constituents (total suspended particulate, sulfate, chlorides, lead). Blauw/Corosol and Parasasa appear to have PAH contributions primarily from pyrogenic sources such as vehicular emissions. In contrast, Sanhueza et al. (1982) concluded Blauw was highly influenced by refinery emissions based on sulfate levels. This supports the need for evaluating both particulate phases of PAHs and these other constituents when elucidating emission sources. It is also important to note, that interpreting diagnostic ratios should be done with caution as values may change with environmental fate as well as with vapor and particulate phases.

3.3 Interpreting risk

Polycyclic aromatic hydrocarbons are ubiquitous environmental pollutants primarily associated with anthropogenic uses. Consequently, higher levels of PAHs are typical of urban and industrialized regions of the world. Moreover, some PAHs may pose health risks and are currently considered carcinogenic, mutagenic and genotoxic. The World Health Organization (WHO; 2003) has documented a higher incidence of lung cancer in urban areas compared to those in rural areas. Furthermore, a clear association of lung cancer in women and respiratory disease (men and women 0-64 yrs) illustrated gradients with highest mortalities in areas closest to industry (Bhopal et al., 1998). In Curaçao, asthma and other respiratory diseases account for 60% and 46% of the disease incidences reported for children (0-14 years of age) and young adults (15-24 years of age), respectively (Table 7; Central Bureau of Statistics Curaçao, 2011). Without evaluating and controlling for other confounding factors, such as life styles (smoking, diet, employment, etc), neighborhood/geozone, age and gender, being able to delineate clear links with air pollution and disease can be problematic.

3.3.1 Toxic Equivalency Factors

Toxic equivalency factors (TEFs) can be used as a practical tool for regulatory purposes in predicting toxicity and calculating the relative contribution of individual PAHs to the total carcinogenicity of measured PAHs. Toxic equivalent concentrations are obtained by multiplying ambient concentrations of each of the PAHs which have available assigned TEFs. The TEFs used in the calculations for this study came from Larsen and Larsen (1998). In the ambient air from the sampling areas in Curaçao, fluoranthene and B[a]P equivalents accounted for 39 and 40% respectively, of the carcinogenicity of quantified PAHs (Table 8). The mean B[a]P equivalents in the ambient air sampled (0.0001 – 0.046 ng/m^3) were similar to those observed in Norway (0.00002-0.072 ng/m3) yet lower than those observed in Sweden (0.0063-1.7 ng/m^3; Boström et al., 2002). It is important to note, the calculated toxic equivalencies are only the sum of the PAHs (*n*=11) that had available TEFs and therefore may underestimate the carcinogenic risk from the other PAHs present in ambient air.

3.3.2 Carcinogenic risk estimates

Carcinogenic risks from PAH inhalation can be assessed using the United States Environmental Protection Agencies (USEPA) methodology for screening levels of chemical contaminants in residential air (USEPA, 1989; USEPA, 2009). Risks are estimated as the incremental probability of an individual to develop cancer over a lifetime as a result of exposure to a particular

carcinogen (USEPA, 1989). Guidelines suggest the acceptable lifetime risk for developing cancer is one in a million (10^{-6}). Carcinogenic risks for residents in our select study area were estimated only for the mean PAHs (*n*=8) for which an inhalation unit risk value was available (Table 9). Overall, the total lifetime risk (70 years) for exposure to eight PAHs was estimated at 1.5 in 10,000,000, which is an order of magnitude less than the recommended USEPA guidelines. However, only the vapor phase of PAHs was measured in this study thereby underestimating potential risk to both the vapor and particulate matter phases. In addition, PAH exposures combined with certain life styles (i.e., smoking, alcohol, diet, exercise, etc) may increase potential cancer risks to these atmospheric pollutants (Castro et al., 2011; Slezakova et al., 2013a,b).

The carcinogenicity of PAHs is associated with the complexity of the molecule (i.e., number of aromatic rings in the compound), metabolites of PAHs and the potential for DNA binding. Currently guidelines are not available for PAH mixtures; therefore, an indicator of carcinogenic PAHs is used for estimations. Typically the most potent of the carcinogenic PAHs (B[a]P) is used as the indicator. Fluoranthene is used as a complementary indicator due to its carcinogenicity and abundance in ambient air (Boström et al., 2002). Based on a WHO risk assessment, ambient levels of B[a]P should not exceed current guidelines of 0.1 ng/m^3, which is equivalent to a theoretic excess lifetime risk of 1 in 100,000 ($1x10^{-5}$). Most of the sites sampled in Curaçao were below the detection limit for B[a]P and the guidelines for fluoranthene with the exception of the Habaai location, which had levels equivalent to the WHO guidelines for B[a]P (0.1 ng/m^3) and exceeded the 2 ng/m^3 recommended guideline for fluoranthene (3.5 ng/m^3).

Conclusions

This first assessment research project, successfully completed the three primary objectives of this study which were to 1) deploy passive air samplers along transects that extend radially from the refinery and along the major thoroughfares to establish baseline levels of PAHs in air samples; 2) ascertain the point source of the air pollution (i.e., vehicular vs. refinery emissions) using diagnostic ratios; and 3) verify areas with the highest impact from emissions, and identify any sites exceeding current thresholds for petroleum emissions.

Ambient levels of atmospheric PAHs in targeted areas of Curaçao were consistent with those recorded in other urban and industrial areas globally, yet up to three orders of magnitude higher than some remote and rural areas. Although there were no clear trends in PAH levels from east to west or with increasing distance from the refinery, levels were statistically different across sites. However it is highly probable the consistent trade winds are accountable for the highest observed levels at the two sites (Habaii and Marchena) directly downwind and closest to Isla Refineria. Moreover, these two sites contained benzo[a]pyrene levels that were equivalent to suggested health based guidelines (0.1 ng/m^3) and had fluoranthene levels that surpassed the recommended guidelines (2 ng/m^3; Boström et al., 2002). Diagnostic ratios highly suggested the ambient levels of PAHs were of petrogenic origin (i.e., likely from the refinery).

Sixteen of the designated priority pollutants by the USEPA accounted for up to 62% of the PAHs in ambient air and up to 30% were carcinogenic PAHs. Although calculated TEFs and carcinogenic risk were relatively low and below recommended guidelines, the absolute concentrations of some compounds (B[a]P and fluoranthene) were equivalent or exceeded WHO guidelines for theoretical excess risk. Considering 60% of children (0-14yrs) in Curaçao suffer

from asthma or other respiratory diseases, this preliminary study underscores the need for expanding this research to include both gaseous and particulate matter phases and other hazardous constituents (i.e., sulfur dioxide), as well as developing and applying a more rigorous health evaluation of the health status of the residents of Curaçao.

Clean air is considered to be a basic requirement of human health and well-being, yet air pollution continues to pose a significant threat to health worldwide with more than 2 million premature deaths attributed to urban outdoor and indoor pollution (WHO, 2005). Meffe et al. (1999) have suggested that conservation involves an ideal relationship between humans and nature. That relationship should safeguard the viability of all biota (including humans) and the ecosystems on which they depend, while allowing human benefit, for present and future generations, through various consumptive and non-consumptive uses. The critical components for success include a visionary, proactive approach, and the will to find some a balance between human activities and nature that allows both to be sustained for the long term. Conservation works best when decisions and policies are based on good science. Our scientific data support earlier findings (van der Torn, 1999; van der Auweraert et al., 2001; Sanhueza et al., 1982) indicating that a single human venture (a refinery) may impair the health and well-being of local people and potentially the sustainability of local, economically vital ecosystems (coral reefs). We hope that Curacao's decision makers use our data to inform management decisions that will provide broad benefits to and reduce risks for Curaçao's people and ecosystems.

Recommendations

Although, excess risk for cancer was estimated to be below current USEPA guidelines other indicators of carcinogenicity from atmospheric PAHs were equivalent or exceeded European guidelines. Furthermore, additional emission constituents (e.g., sulfur dioxide and particulate matter) have been shown to exceed air quality standards dating back to over three decades (van der Auweraert et al., 2001; Sanhueza et al., 1982). These results, combined with evidence of associated respiratory diseases and cancer with urban air pollution, suggest continued monitoring in Curaçao is highly recommended and emphasize the need for further research. Therefore, our recommendations are as follows:

1. Expand air monitoring for vapor and particulate phases for both petrogenic and pyrogenic constituents, including but not limited to sulfur dioxide, sulfates, lead, particulate matter, and PAHs;
2. Conduct environmental studies measuring PAHs in a variety of biota and matrices (i.e., fish, water, sediment);
3. Conduct a more complete human health risk assessment to include dermal, inhalation and dietary exposures;
4. Conduct a more rigorous epidemiological study evaluating associations between disease and point sources across neighborhoods or geozones;
5. Evaluate current air quality guidelines and regulations in Curaçao.

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help us understand some of the societal issues and impacts from Isla Refineria on local communities.

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Appendix A: Tables

Table 1. Passive air sampling locations, coordinates, geographic information and direction in relation to Isla Refineria.

Site	MML ID	Neighborhood/Geozone	Latitude	Longitude	Deployment (Days)	Distance (km)	Direction
1	CUR-11-0030 CUR-11-0031 CUR-11-0032	Habaai	12º 07'22.0"	68º57'00.4"	65	2.52	West
2	CUR-11-0033 CUR-11-0034 CUR-11-0035	Groot Piscadera	12º08'44.8"	68º58'02.6"	65	4.41	West
3	CUR-11-0036 CUR-11-0037 CUR-11-0038	Boca Sami	12º08'26.1"	68º59'23.5"	65	6.68	West
4	CUR-11-0039 CUR-11-0040 CUR-11-0041	W. Piscadera Baai	12º08'18.2"	68º58'21.6"	68	4.78	West
5	CUR-11-0042 CUR-11-0043 CUR-11-0044	Rooi Catochi	12º07'24.1"	68º54'10.0"	64	3.07	East
6	CUR-11-0045 CUR-11-0046 CUR-11-0047	Nieuw Nederland	12° 6'1.96"	68°55'15.46"	64	3.68	Southeast
7	CUR-11-0048 CUR-11-0049 CUR-11-0050	Maria Pampoen	12º05'03.8"	68º55'47.7"	66	6.5	Southeast
8	CUR-11-0051 CUR-11-0052 CUR-11-0053	E. Buena Vista	12º08'33.5"	68º55'55.5"	65	1.14	Northwest
9	CUR-11-0054 CUR-11-0055 CUR-11-0056	W. Buena Vista	12º08'30.2"	68º56'20.9"	65	1.46	Northwest
10	CUR-11-0057 CUR-11-0058 CUR-11-0059	Heintje Kool	12º08'23.4"	68º56'30.1"	64	1.56	Northwest
11	CUR-11-0060 CUR-11-0061 CUR-11-0062	Roosendaal	12º08'34.3"	68º57'11.8"	64	2.86	West
12	CUR-11-0063 CUR-11-0064 CUR-11-0065	Marchena/Wishi	12º07'41.2"	68º57'13.7"	64	2.72	West
13	CUR-11-0066 CUR-11-0067 CUR-11-0068	E. Piscadera Baai	12º08'07.6"	68º57'48.7"	63	3.75	West
14	CUR-11-0069 CUR-11-0070 CUR-11-0071	Blauw / Corosol	12º08'40.5	68º58'53.5	63	5.87	West
15	CUR-11-0072 CUR-11-0073	Parasasa	12º07'21.9"	68º58'08.2"	64	4.48	Southwest

Table 2. Neighborhood/geozone populations sampled in 2011.

Neighborhood	Population
Blauw (Corosol)	1006
Boca Sami	1108
Buena Vista	3892
Groot Piscadera	749
Habaai	407
Nieuw Nederland	276
Parasasa	171
Rooi Catochi	319
Roosendaal	481
Wishi	841
Marchena	584
Maria Pampoen	1319
Piscadera Baai	787
Total Population Sampled	**11940**

Source: Central Bureau of Statistics Curaçao 2011

Table 3. Calibration Standards, quantification and QA/QC parameters

Calibration Compounds	Ref to IS/SS	Quant Ion	Qual Ion	Cal R^2	RRF % RSD (≤20%)	Cont Cal %RSD (≤25% for 90%)
Naphthalene-d_8 (I-1, S-1)	I-1, S-1	136	134	1.00	4	6
Acenaphthene-d_{10} (I-1, S-2)	I-1,S-2	164	162	1.00	4	6
Anthracene-d_{10} (I-1, S-3)	I-1, S-3	188	184	1.00	7	18
Benzo[a]anthracene-d_{12} (I-2,S-4)	I-2,S-4	240	236	1.00	6	24
Perylene-d_{12} (I-2, S-5)	I-2, S-5	264	260	1.00	10	22
Naphthalene	I-1,S-1	128	127	1.00	6	6
Acenaphthylene	I-1,S-2	152	153	1.00	4	26
Acenaphthene	I-1,S-2	154	153	1.00	5	7
Fluorene	I-1,S-2	166	165	1.00	3	8
Dibenzothiophene	I-1,S-3	184	152	1.00	4	1
Phenanthrene	I-1,S-3	178	176	1.00	10	1
Anthracene	I-1,S-3	178	176	1.00	4	13
Fluoranthene	I-2,S-3	202	101	1.00	10	12
Pyrene	I-2,S-3	202	101	1.00	10	18
Benzo[B]fluorene	I-2,S-3	216	nd	1.00	9	31
Napthobenzothiophene	I-2,S-3	234	nd	1.00	6	15
Benzo[A]anthracene	I-2,S-4	228	226	1.00	6	17
Chrysene	I-2,S-4	228	226	1.00	8	6
Benzo[B]fluoranthene	I-2,S-4	252	253	1.00	3	18
Benzo[K]fluoranthene	I-2,S-4	252	253	1.00	11	17
Benzo[E]pyrene	I-2,S-4	252	253	1.00	4	11
Benzo[A]pyrene	I-2,S-4	252	253	1.00	3	19
Perylene	I-2,S-5	252	253	0.99	4	16
Indeno[1,2,3,-cd]pyrene	I-2,S-4	276	277	1.00	7	18
Dibenzo[a,h]anthracene	I-2,S-4	278	279	1.00	17	12
Benzo[g,h,i]perylene	I-2,S-4	276	277	1.00	7	4

Table 4. Instrument detection limits (IDL) calculated from seven injections of a 750 pg/mL PAH standard mix.

Analytes	RT	Quant Ion	Conf Ion	IS/SS	Mean Response	STDEV	% RSD (<20%)	IDL (ng/mL)
Naphthalene	8.970	128	127	I-1,S-1	1266	85	7	0.26
Acenaphthylene	13.445	152	153	I-1,S-2	420	41	10	0.12
Acenaphthene	13.971	154	153	I-1,S-2	353	57	16	0.17
Fluorene	15.500	166	165	I-1,S-2	509	66	13	0.20
Dibenzothiophene	17.937	184	152	I-1,S-3	549	35	6	0.11
Phenanthrene	18.295	178	176	I-1,S-3	689	78	11	0.24
Anthracene	18.447	178	176	I-1,S-3	370	42	11	0.13
Fluoranthene	21.810	202	101	I-2,S-3	490	43	9	0.13
Pyrene	22.449	202	101	I-2,S-3	566	57	10	0.17
Benzo[B]fluorene	23.728	216	226	I-2,S-3	149	20	13	0.06
Napthobenzothiophene	25.130	234	nd	I-2,S-3	281	32	11	0.10
Benzo[A]anthracene	26.050	228	226	I-2,S-4	219	30	14	0.09
Chrysene	26.137	228	226	I-2,S-4	308	58	19	0.17
Benzo[B]fluoranthene	29.020	252	253	I-2,S-4	365	60	16	0.18
Benzo[K]fluoranthene	29.050	252	253	I-2,S-4	197	24	12	0.07
Benzo[E]pyrene	26.697	252	253	I-2,S-4	161	20	12	0.06
Benzo[A]pyrene	29.829	252	253	I-2,S-4	176	30	17	0.09
Perylene	30.032	252	253	I-2,S-5	185	32	17	0.09
Indeno[1,2,3,-cd]pyrene	32.410	276	277	I-2,S-4	162	21	13	0.06
Dibenzo[a,h]anthracene	32.494	278	279	I-2,S-4	174	20	11	0.06
Benzo[g,h,i]perylene	32.941	276	277	I-2,S-4	247	29	12	0.09

Table 5. Calculated mean concentrations of PAHs (ng/m3) from each of the study sites in Curaçao in 2011. Concentrations below the detection limit were replaced with ½ the IDL.

Table 6. Comparison of diagnostic ratios used to elucidate emission source(s) of atmospheric PAHs in Curaçao.

Neighborhood/Geozone	ΣLMW/ΣHMW	ANT/(ANT+PHE)	PHE/ANT	FLA/(FLA+PYR)	FLA/PYR	BaA/(BaA+Chr)	FL/(FL+PYR)	FL/PYR	Ind/(Ind+Bghi)
Habaai	3.88	0.03	36.97	0.57	1.35	0.42	0.26	0.35	0.35
Groot Piscadera	3.81	0.03	37.14	0.57	1.35	0.40	0.29	0.40	0.43
Boka Sami	4.31	0.03	37.62	0.59	1.43	0.52	0.43	0.77	0.40
W. Piscadera Baai	5.66	0.02	40.22	0.59	1.44	0.35	0.58	1.35	0.40
Rooi Catochi	4.53	0.02	59.28	0.65	1.85	0.41	0.41	0.70	0.40
Nieuw Nederland	3.94	0.03	38.05	0.62	1.63	0.39	0.37	0.59	0.40
Maria Pampoen	2.24	0.03	34.45	0.70	2.33	0.35	0.36	0.56	0.40
E. Buena Vista	2.54	0.04	25.37	0.58	1.36	0.34	0.25	0.33	0.40
W. Buena Vista	3.85	0.03	34.68	0.55	1.23	0.37	0.26	0.35	0.40
Heintje Kool/Buena Vista	2.79	0.03	32.26	0.56	1.25	0.33	0.24	0.31	0.40
Roosendaal	3.54	0.03	34.37	0.58	1.36	0.35	0.36	0.57	0.40
Marchena	5.36	0.03	28.89	0.53	1.11	0.33	0.36	0.55	0.40
E. Piscadera Baai	3.88	0.03	34.18	0.56	1.27	0.29	0.38	0.61	0.40
Blauw/Corosol	0.87	0.35	1.85	0.43	0.76	0.35	0.54	1.18	0.40
Parasasa	0.82	0.35	1.85	0.54	1.19	0.35	0.54	1.18	0.40
Dominant Source	*Petrogenic (>1)*[a]	*Petrogenic (<0.1)*[b]	*Petrogenic (>10)*[c]	Diesel (>0.5)[d]	*Vehicular (0.6)*[f]	Petrogenic (<0.2); Combustion & Vehicular Emissions (>0.35)[e]	*Petrol emissions (<0.5)*; Diesel emissions (>0.5)[d]	*Petrogenic (<1); Combustion (>1)*[c]	*Petroleum Combustion (0.2-0.5)*[e]

[a] Zhang et al., 2008; [b] Pies et al., 2008; [c] Budzinski et al., 2007; [d] Ravindra et al., 2008 ; [e] Yunker et al., 2002; [f] Neilson, 1998

ΣLMW/ΣHMW=sum of low molecular weight PAHs (2-3 rings)/sum of high molecular weight PAHs (4-6 rings); ANT=Anthracene, PHE=Phenanthrene; FLA=Fluoranthene; PYR=Pyrene; BaA=Benzo[a]anthracene; CHR=Chrysene; FL=Fluorene; BaP=Benzo[a]Pyrene; BghiP=Benzo[g,h,i]perylene; Ind=Indeno[1,2,3,-cd]pyrene

Table 7. Incidences of common diseases by age group in Curaçao.

	Age Groups											
Population by most common diseases	**0-14 yrs**				**15-24 yrs**				**25-44 yrs**			
	Male	**Female**	**Total**	**%**	**Male**	**Female**	**Total**	**%**	**Male**	**Female**	**Total**	**%**
High blood pressure	50	48	98	3	65	114	179	7	959	1615	2574	32
Diabetes	17	35	52	2	37	46	83	3	314	415	729	9
Glaucoma/pressure in the eyes	16	18	34	1	34	30	64	3	138	238	376	5
Asthma/chronic bronchitis/CARA	1157	768	1925	60	550	582	1132	46	492	1178	1670	21
Cancer	10	11	21	1	13	5	18	1	15	54	69	1
Sickle cell	72	87	159	5	76	101	177	7	120	257	377	5
Heart problems	114	106	220	7	92	109	201	8	187	313	500	6
Consequences of heart attack	6	6	12	0	8	9	17	1	26	25	51	1
Consequences of brain hemorrhage	8	6	14	0	8	4	12	0	17	33	50	1
Serious kidney problems	16	10	26	1	9	10	19	1	74	83	157	2
Dementia/Alzheimer	3	2	5	0	5	0	5	0	17	7	24	0
Other	371	293	664	21	224	338	562	23	528	833	1361	17
Total	1840	1390	3230	100	1121	1348	2469	100	2887	5051	7938	100

Population by most common diseases	**45-64 yrs**				**65+ yrs**				**Total**			
	Male	**Female**	**Total**	**%**	**Male**	**Female**	**Total**	**%**	**Male**	**Female**	**Total**	**%**
High blood pressure	3863	6583	10446	43	2770	5095	7865	36	7707	13455	21162	35
Diabetes	1747	2697	4444	18	1627	2701	4328	20	3742	5894	9636	16
Glaucoma/pressure in the eyes	656	991	1647	7	911	1406	2317	10	1755	2683	4438	7
Asthma/chronic bronchitis/CARA	457	1068	1525	6	231	376	607	3	2887	3972	6859	11
Cancer	110	278	388	2	197	182	379	2	345	530	875	1
Sickle cell	139	327	466	2	54	86	140	1	461	858	1319	2
Heart problems	780	1125	1905	8	1041	1430	2471	11	2214	3083	5297	9
Consequences of heart attack	223	189	412	2	325	275	600	3	588	504	1092	2
Consequences of brain hemorrhage	225	169	394	2	341	364	705	3	599	576	1175	2
Serious kidney problems	221	238	459	2	199	225	424	2	519	566	1085	2
Dementia/Alzheimer	60	59	119	0	323	603	926	4	408	671	1079	2
Other	823	1308	2131	9	474	844	1318	6	2420	3616	6036	10
Total	9304	15032	24336	100	8493	13587	22080	100	23645	36408	60053	100

Source: Central Bureau of Statistics Curaçao (Census 2011)

Table 8. Mean Curaçao and site PAH concentrations (ng/m^3), B[a]P equivalents and percent contribution of 11 PAHs to the B[a]P equivalents calculated in ambient air during 2011.

								Concentration (ng/m^3)									
PAH	**TEF**	**Curaçao**	**Habaai**	**GP**	**BS**	**WPB**	**RC**	**NN**	**MP**	**EBV**	**WBV**	**HK**	**Roosendaal**	**Marchena**	**EPB**	**B/C**	**Parasasa**
ANT	0.0005	0.244	0.802	0.182	0.191	0.137	0.132	0.161	0.120	0.169	0.227	0.222	0.147	0.745	0.183	0.120	0.120
B[a]A	0.005	0.097	0.397	0.214	0.137	0.045	0.030	0.026	0.045	0.045	0.092	0.091	0.045	0.166	0.028	0.045	0.045
B[a]P	1	0.046	**0.064**	**0.045**	**0.045**	**0.045**	**0.045**	**0.045**	**0.045**	**0.045**	**0.045**	**0.045**	**0.045**	**0.045**	**0.045**	**0.045**	**0.045**
B[b]F	0.1	0.091	0.160	0.090	0.090	0.090	0.090	0.090	0.090	0.090	0.090	0.032	0.090	0.090	0.090	0.090	0.090
B[k]F	0.05	0.040	0.103	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035
B[g,h,i]P	0.02	0.051	0.130	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045
CHR	0.03	0.155	0.548	0.222	0.124	0.085	0.085	0.060	0.085	0.060	0.158	0.220	0.028	0.332	0.142	0.085	0.085
FLA	0.05	0.901	**3.480**	0.834	0.663	0.381	0.776	0.752	0.509	0.817	0.995	1.110	0.584	1.773	0.680	0.065	0.101
IND	0.1	0.032	0.060	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030
PHE	0.0005	7.852	29.652	7.033	7.182	5.495	7.799	6.132	2.239	4.276	7.872	7.159	5.056	21.513	6.245	0.065	0.065
PYR	0.001	0.669	2.576	0.593	0.463	0.264	0.420	0.461	0.218	0.601	0.812	0.886	0.431	1.598	0.537	0.085	0.085
								B[a]P equivalents (ng/m^3)									
PAH	**TEF**	**Curaçao**	**Habaai**	**GP**	**BS**	**WPB**	**RC**	**NN**	**MP**	**EBV**	**WBV**	**HK**	**Roosendaal**	**Marchena**	**EPB**	**B/C**	**Parasasa**
ANT	0.0005	0.0001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
B[a]A	0.005	0.000	0.002	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000
B[a]P	1	0.046	0.064	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045
B[b]F	0.1	0.009	0.016	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.003	0.009	0.009	0.009	0.009	0.009
B[k]F	0.05	0.002	0.005	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
B[g,h,i]P	0.02	0.001	0.003	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
CHR	0.03	0.005	0.016	0.007	0.004	0.003	0.003	0.002	0.003	0.002	0.005	0.007	0.001	0.010	0.004	0.003	0.003
FLA	0.05	0.045	0.174	0.042	0.033	0.019	0.039	0.038	0.025	0.041	0.050	0.055	0.029	0.089	0.034	0.003	0.005
IND	0.1	0.003	0.006	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003
PHE	0.0005	0.004	0.015	0.004	0.004	0.003	0.004	0.003	0.001	0.002	0.004	0.004	0.003	0.011	0.003	0.000	0.000
PYR	0.001	0.001	0.003	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.000	0.002	0.001	0.000	0.000
ΣPAH		0.116	0.304	0.113	0.101	0.085	0.106	0.103	0.089	0.105	0.119	0.121	0.093	0.172	0.102	0.066	0.068
								% B[a]P Contribution									
PAH	**TEF**	**Curaçao**	**Habaai**	**GP**	**BS**	**WPB**	**RC**	**NN**	**MP**	**EBV**	**WBV**	**HK**	**Roosendaal**	**Marchena**	**EPB**	**B/C**	**Parasasa**
ANT	0.0005	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1
B[a]A	0.005	0.4	0.7	0.9	0.7	0.3	0.1	0.1	0.3	0.2	0.4	0.4	0.2	0.5	0.1	0.3	0.3
B[a]P	**1**	**40**	**21.0**	**39.7**	**44.4**	**53.2**	**42.6**	**43.8**	**50.4**	**42.7**	**37.7**	**37.2**	**48.4**	**26.2**	**44.2**	**68.3**	**66.5**
B[b]F	0.1	7.8	5.3	7.9	8.9	10.6	8.5	8.8	10.1	8.5	7.5	2.7	9.7	5.2	8.8	13.7	13.3
B[k]F	0.05	1.7	1.7	1.5	1.7	2.1	1.7	1.7	2.0	1.7	1.5	1.4	1.9	1.0	1.7	2.7	2.6
B[g,h,i]P	0.02	0.9	0.9	0.8	0.9	1.1	0.9	0.9	1.0	0.9	0.8	0.7	1.0	0.5	0.9	1.4	1.3
CHR	0.03	4.0	5.4	5.9	3.7	3.0	2.4	1.8	2.9	1.7	4.0	5.4	0.9	5.8	4.2	3.9	3.8
FLA	**0.05**	**39**	**57.3**	**36.8**	**32.7**	**22.5**	**36.8**	**36.6**	**28.5**	**38.8**	**41.6**	**45.9**	**31.4**	**51.6**	**33.4**	**4.9**	**7.5**
IND	0.1	2.7	2.0	2.6	3.0	3.5	2.8	2.9	3.4	2.8	2.5	2.5	3.2	1.7	2.9	4.6	4.4
PHE	0.0005	3.4	4.9	3.1	3.5	3.2	3.7	3.0	1.3	2.0	3.3	3.0	2.7	6.3	3.1	0.0	0.0
PYR	0.001	0.6	0.8	0.5	0.5	0.3	0.4	0.4	0.2	0.6	0.7	0.7	0.5	0.9	0.5	0.1	0.1
% Total		100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

GP=Groot Piscadera, BS=Boka Sami, WPB=W Piscadera Baai; RC=Rooi Catochi, NN=Nieuw Nederland, MP=Maria Pampoen, EBV=E Buena Vista, WBV=W Buena Vista, HK=Heintje Kool, EPB=E Piscadera Baai, B/C=Blauw/Corosol, ANT=Anthracene, PHE=Phenanthrene; FLA=Fluoranthene; PYR=Pyrene; BaA=Benzo[a]anthracene; CHR=Chrysene; FL=Fluorene; BaP=Benzo[a]Pyrene; BghiP=Benzo[g,h,i]perylene; Ind=Indeno[1,2,3,-cd]pyrene

Table 9. Mean residential inhalation risk to PAHs in Curaçao over a lifetime (70 years).

Chemical	Inhalation Unit Risk $(\mu g/m^3)^{-1}$	Chronic RfC (mg/m^3)	Concentration (µg/kg)	Carcinogenic Risk TR=1.0E-6	Noncarcinogenic Risk HI=1
Benz[a]anthracene	1.10E-04	-	0.0000967	1.11E-08	-
Benzo[a]pyrene	1.10E-03	-	0.0000462	5.30E-08	-
Benzo[b]fluoranthene	1.10E-04	-	0.0000908	1.04E-08	-
Benzo[k]fluoranthene	1.10E-04	-	0.0000396	4.53E-09	-
Chrysene	1.10E-05	-	0.0001545	1.77E-09	-
Dibenz[a,h]anthracene	1.20E-03	-	0.000044	5.50E-08	-
Indeno[1,2,3-cd]pyrene	1.10E-04	-	0.000032	3.66E-09	-
Naphthalene	3.40E-05	3.00E-03	0.0003388	1.10E-08	0.000108
**Total Risk*	-	-	-	*1.50E-07*	*0.000108*

Appendix B: Figures

Figure 1. Passive air sampling (PAS) locations in Curaçao

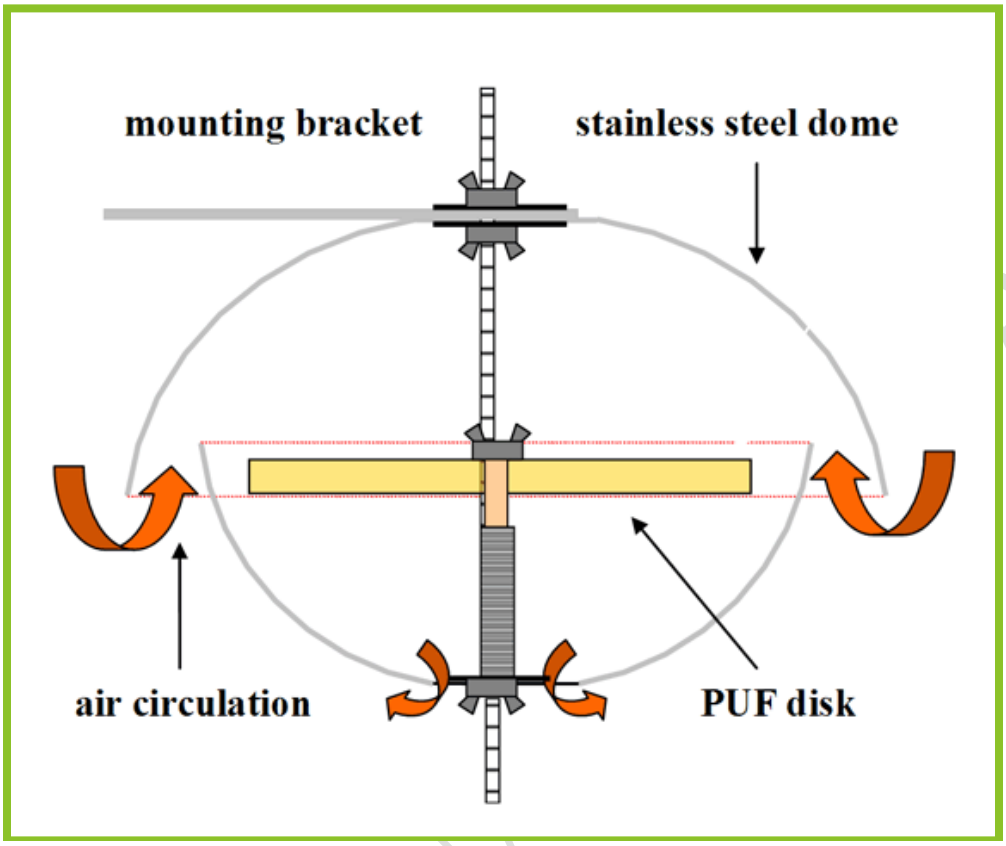

Figure 2. Passive sampler schematic.

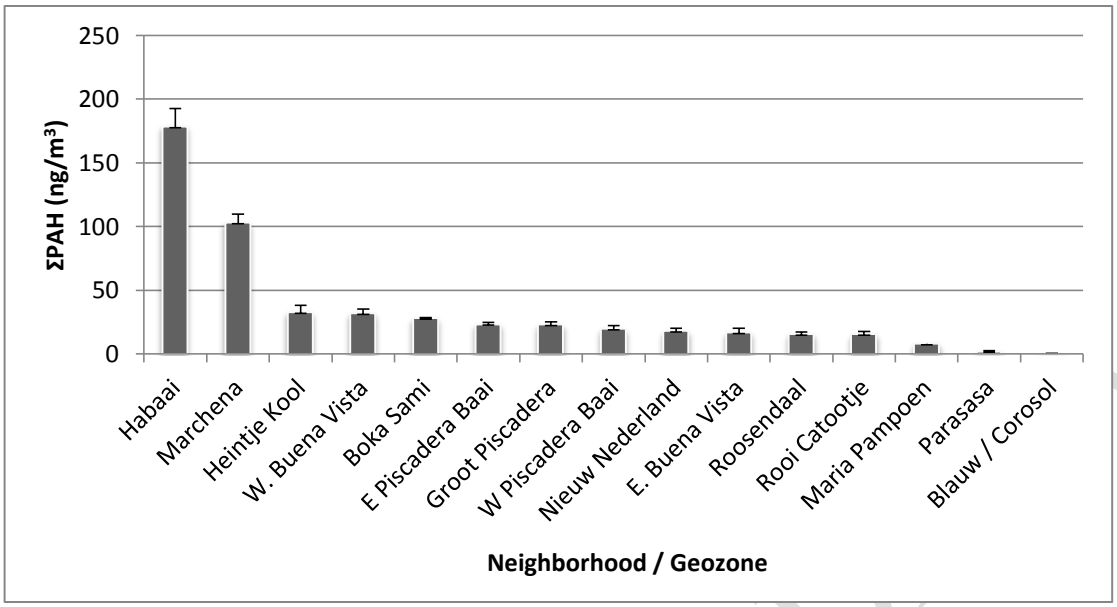

Figure 3. Calculated mean ΣPAHs (ng/m^3) by neighborhood / geozone in order of decreasing concentrations.

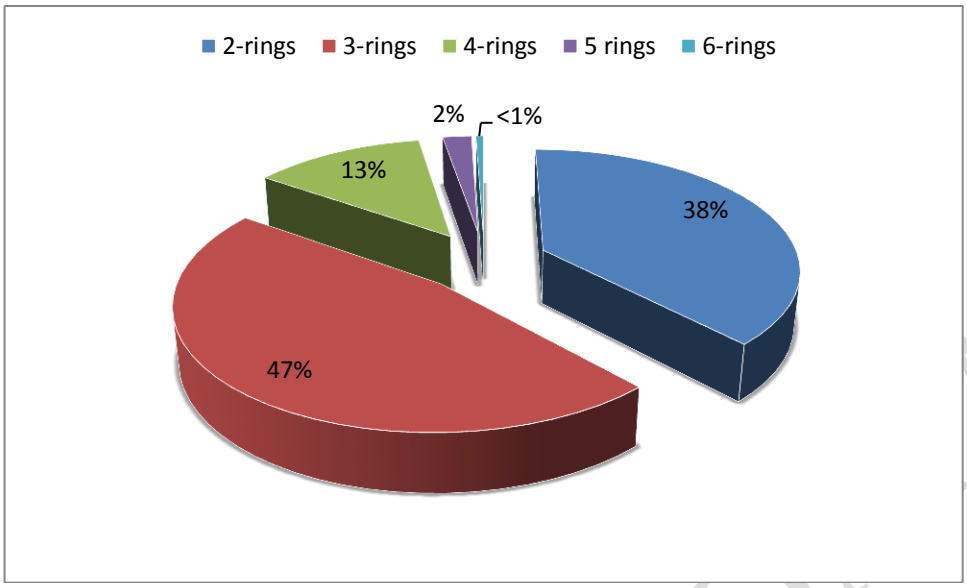

Figure 4. Relative abundance of PAHs in ambient air in Curaçao. Abundances are presented as sums of individual compounds according to the number of aromatic rings.

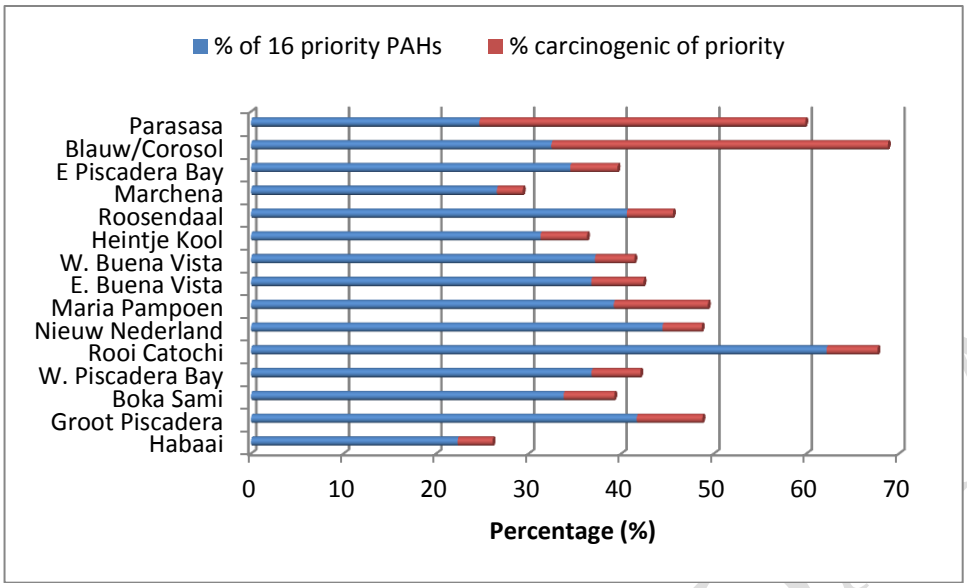

Figure 5. Percentage of the 16 priority PAHs and carcinogenic PAHs at each site sampled in 2011.