

**Bowerman-Loreley Beach Community Association • Brookstone  
Condominium Association • Campus Hills Community Association  
Chartley Townhouse Association • Combined Communities Advocacy Council  
of Greater Randallstown • Eastfield-Stanbrook Civic Association • Ellicott  
Mills Homeowners Association • Fellowship Forest Community Association  
Greater Baltimore Group of the Sierra Club • Greater Jacksonville Association  
Greenbrier Community Association • Green Towson Alliance • Miramar  
Landing Homeowners Association • Oakwood Village Community  
Association of Randallstown • Perry Hall Improvement Association • Ralston  
Community Association • Rockaway Beach Improvement Assoc. Inc. • Sparks  
Glencoe Community Planning Council • Stoneybrook Community Council  
Association • Towson Communities Alliance**

June 9, 2020

Honorable John A. Olszewski, Jr.  
Honorable Tom Quirk  
Honorable Izzy Patoka  
Honorable Wade Kach  
Honorable Julian E. Jones  
Honorable David Marks  
Honorable Cathy Bevins  
Honorable Todd K. Crandell  
400 Washington Avenue  
Towson, Maryland 21204

**RE: Baltimore County Public Health, Property Value, Well-Water, & Fire-  
Explosion Danger Safety Zones for New Gas Stations**

Dear County Executive Olszewski, Councilman Quirk, Councilman Patoka, Councilman Kach,  
Councilman Jones, Councilman Marks, Councilwoman Bevins, and Councilman Crandell:

We, the undersigned, on behalf of the organizations we represent, urge you to amend the Baltimore  
County Zoning Regulations (BCZR), to guide new gas stations to locations where the benefits can  
be gained without jeopardizing public health and the environment.

Over the last decade a number of new studies have shown that the public health and aquatic  
resource impacts of gas stations are far greater than previously thought. These impacts go well  
beyond the traditional concern of leaking underground storage tanks. The impacts result from  
benzene and other harmful compounds released to the air from storage tank vents and at the pump  
during refueling. Also, it's been found that significant amounts of gasoline are spilled at the pump

and the gasoline can travel through the concrete pads present at most pumps to contaminate ground- and surface-waters.

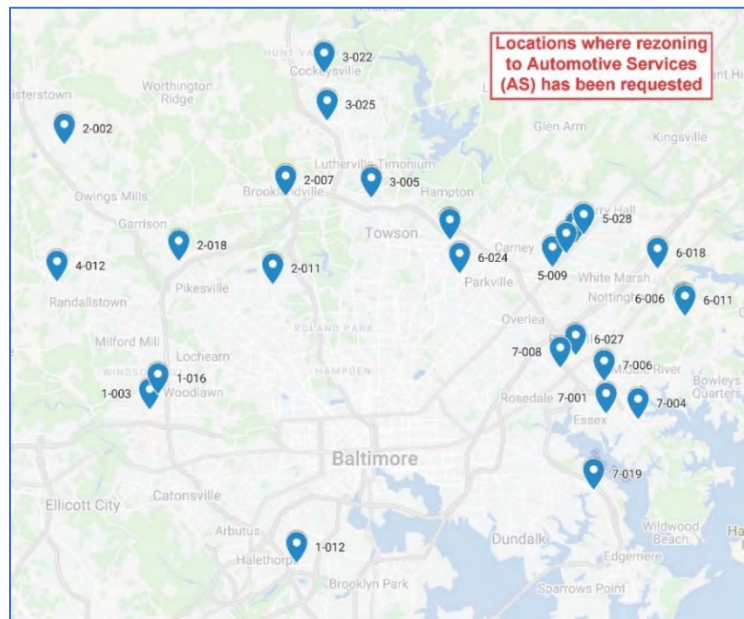
While the Baltimore County Zoning Regulations do contain some requirements that address these impacts, the safeguards are inadequate. For example, the regulations require a 100-foot safety zone between gas station pumps and residential zoning districts, but not from tank vents. Current research shows that tank vents are an even greater threat to public health and emissions at the pump exacerbate the impact. The research summarized in this letter shows that adverse health effects extend to those living, working, worshipping, or learning at a distance of 500-feet or more from a gas station.

Unfortunately, there are no control measures required for new gas stations that can reliably resolve the public health and environmental impact. Because of this, we urge you to update the Baltimore County Zoning Regulations with the following amendments to guide new gas stations to sites where we can gain the benefits without sacrificing public health and the environment:

- require a minimum safety zone of 500-feet between a new gas station and any residentially zoned property, house of worship, public or private school, hospital or assisted living facility, or day care center,
- prohibit new gas stations where adjacent properties are served by wells and public water is not available, and
- delete the BCZR provisions allowing a new gas station to avoid the safety zone and other protection requirements if a special exception is granted.

### 2020 Comprehensive Zoning Map Process May Lead to Many New Gas Stations

The 2020 Comprehensive Zoning Map Process (CZMP) log of issues lists 27 requests to rezone properties to Automotive Services (AS). The map to the right shows that these 27 properties are spread throughout the most densely populated areas of Baltimore County. Seven of the petitioners have a stated intention of adding fuel pumps if AS zoning is granted, three do not, while the remaining 17 petitions are unclear as to whether pumps would be added. However, industry experts say it's likely a number of these 17 properties will be proposed as gas stations. As explained later in this letter, *our*



*proposed amendments will not preclude all of these possible, new gas stations; just those that pose an undue threat to public health, safety and the environment.*

### Health Risk

A number of compounds injurious to human health are released from gas stations during vehicle fueling and from underground storage tank vents. These compounds include: benzene, toluene, ethyl benzene, and xylene (BTEX).<sup>1</sup> Measures to reliably resolve these adverse health effects are not employed at new gas stations.

Benzene is the gasoline constituent most harmful to human health. Adverse health effects of benzene include nausea, cancer, anemia, increased susceptibility to infections, and low birth weight. According to the *World Health Organization Guidelines for Indoor Air Quality*<sup>2</sup> **there is no safe level for benzene**. The following research documents the extent of benzene releases from gas stations as well as adverse health effects:

- A 1993 study published by the Canadian petroleum industry found average benzene concentrations of up to 461 parts per billion (ppb) at the gas station property boundary.<sup>3</sup>
- A 2001 study noted median ambient benzene levels of 1.9 ppb in houses up to 328 feet from a service station.<sup>4</sup>
- A 2003-2004 study conducted in France documented a significant relationship between childhood leukemia and living near a gas station.<sup>5</sup>
- A 2010 study conducted in Spain documented elevated air pollution within 100 meters (328 feet) of a gas station.<sup>6</sup>
- In 2012, Brazilian researchers found that air quality was significantly degraded up to 150 meters (492 feet) from gas stations.<sup>7</sup>

A copy of these and other referenced studies are attached to the end of this letter.

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<sup>1</sup> Hydrocarbon Release During Fuel Storage and Transfer at Gas Stations: Environmental and Health Effects available online at: <https://www.ncbi.nlm.nih.gov/pubmed/26435043>

<sup>2</sup> The WHO guidelines are available online at: <https://www.ncbi.nlm.nih.gov/books/NBK138708/>

<sup>3</sup> Exposure of the general population to gasoline available online at: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1520004/>

<sup>4</sup> Exposure to Methyl Tertiary Butyl Ether and Benzene in Close Proximity to Service Stations available online at: <https://www.tandfonline.com/doi/abs/10.1080/10473289.2001.10464339>

<sup>5</sup> Acute childhood leukemia and residence next to petrol stations and automotive repair garages: the ESCALE study (SFCE) available online at: <https://www.ncbi.nlm.nih.gov/pubmed/19213757>

<sup>6</sup> Assessing the impact of petrol stations on their immediate surroundings available online at: <https://www.ncbi.nlm.nih.gov/pubmed/20810207>

<sup>7</sup> The impact of BTEX emissions from gas stations into the atmosphere available online at: <https://www.sciencedirect.com/science/article/pii/S1309104215304384>

In 2005, the California Air Resources Board probably became the first agency in the U.S. to recommend a minimum public health safety zone between new gas stations and “sensitive land uses.” The recommendation appeared in *Air Quality and Land Use Handbook: A Community Health Perspective*<sup>8</sup>. The pre-2005 studies referenced above and other research prompted the Board to recommend a minimum 300-foot separation distance between new gas stations and “sensitive land uses such as residences, schools, daycare centers, playgrounds, or medical facilities.”

The State of California is widely recognized as having some of the most effective air pollution control requirements in the nation. Yet even with California controls a minimum separation is still required to protect public health.

The U.S. Environmental Protection Agency echoed concerns about the health risk associated with gas station emissions in their *School Siting Guidelines*<sup>9</sup>. The USEPA recommended screening school sites for potential health risk when located within 1,000 feet of a gas station.

The last section of this letter contains a sampling of the public health safety zones for new gas station adopted by other U.S. jurisdictions. Most call for a greater separation than the 300 feet recommended by the California Air Resources Board. The increasing safety zone distances were prompted by the growing body of research showing that adverse health effects extend further and further from gas stations. In fact, a 2019 study<sup>10</sup> of U.S. gas stations found that benzene emissions from underground gasoline storage tank vents were sufficiently high to constitute a health concern at a distance of up to 518-feet. Also, the researchers noted:

*“emissions were 10 times higher than estimates used in setback regulations [like that in the California handbook] used to determine how close schools, playgrounds, and parks can be situated to the facilities [gas stations].”*

Prior to the 2019 study it was thought that most of the benzene was released at the pump during fueling. A 2015 paper<sup>11</sup> noted the following bit of irony with regard to vapor recovery and harmful emissions from gas station storage tanks:

*“It is important to note that vapor recovery at the nozzle can cause vapor releases at the storage tank, because vapors recovered at the nozzle are typically directed into the storage tank. The storage tank, in turn, can “breathe” and potentially release recovered vapors immediately or at a later time. A tank sucks in relatively uncontaminated air as the liquid fuel level drops in the tank due to vehicle refueling, and it releases vapors through the vent pipe into the atmosphere if the gas pressure increases and exceeds the cracking pressure of the pressure/vacuum valve, when fuel evaporates into unbalanced gas in the headspace.”*

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<sup>8</sup> The CARB handbook is available online at: <https://www.arb.ca.gov/ch/handbook.pdf>

<sup>9</sup> The USEPA *School Siting Guidelines* are available online at: [https://www.epa.gov/sites/production/files/2015-06/documents/school\\_siting\\_guidelines-2.pdf](https://www.epa.gov/sites/production/files/2015-06/documents/school_siting_guidelines-2.pdf)

<sup>10</sup> *Vent pipe emissions from storage tanks at gas stations: Implications for setback distances*, available online at: <https://www.sciencedirect.com/science/article/pii/S0048969718337549>

<sup>11</sup> *Hydrocarbon Release During Fuel Storage and Transfer at Gas Stations: Environmental and Health Effects* available online at: <https://www.ncbi.nlm.nih.gov/pubmed/26435043>

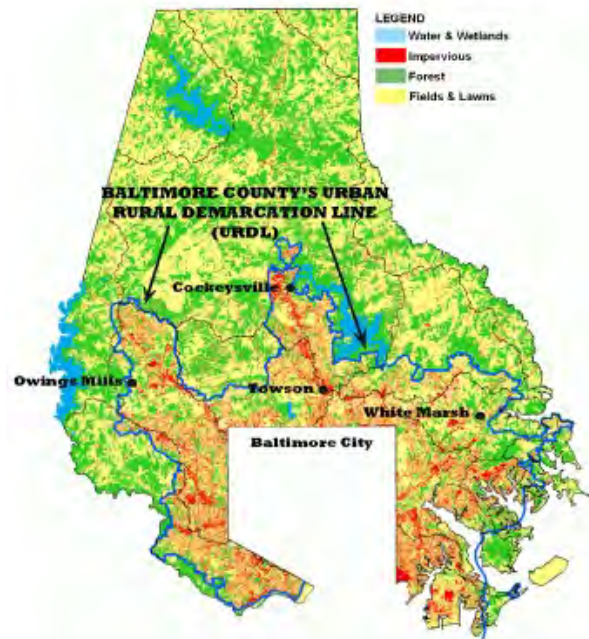
The 2015 paper contained the following summary regarding the health implications of living, working or learning near a gas station:

*“Health effects of living near gas stations are not well understood. Adverse health impacts may be expected to be higher in metropolitan areas that are densely populated. Particularly affected are residents nearby gas stations who spend significant amounts of time at home as compared to those who leave their home for work because of the longer period of exposure. Similarly affected are individuals who spend time close to a gas station, e.g., in close by businesses or in the gas station itself. Of particular concern are children who, for example, live nearby, play nearby, or attend nearby schools, because children are more vulnerable to hydrocarbon exposure.”*

The 2015 study along with other research papers will be found attached at the end of this letter. If you wish we can seek to arrange for you to speak with the scientists who performed these studies.

### **Groundwater Contamination Potential**

Thousands of Baltimore County residents rely on groundwater via wells to provide for their household needs. Allowing new gas stations on the rural lands outside the area served by public water can pose an unreasonable risk. The Urban-Rural Demarcation Line (URDL) shown in the map to the right is the outer limit of public water service for most of Baltimore County



In the past, leaks from fuel storage tanks and the pipelines connecting tanks to pumps were considered the primary source of groundwater contamination. Most Baltimore County residents likely think of Jacksonville when this topic comes to mind.<sup>12</sup>

While the design of both tanks and connecting lines has improved dramatically over the past couple of decades, a recent Johns Hopkins University study (conducted in Baltimore) found that an average of 40 gallons of gasoline is annually spilled at the pumps of a typical gas station.<sup>13</sup> Of greater concern to well owners is that the JHU researchers also found that a significant portion of the spilled gasoline can migrate through the concrete pads present at most gas station pump islands. Once the gasoline travels through the concrete, groundwater contamination may occur. Of

<sup>12</sup> See the Maryland Department of the Environment webpage *Groundwater Remediation Continues in Jacksonville, Maryland* online at: <https://mde.maryland.gov/programs/ResearchCenter/eMDE/Pages/vol4no1/jacksonville.aspx>

<sup>13</sup> See *Small spills at gas stations could cause significant public health risks over time* available online at: <https://www.sciencedaily.com/releases/2014/10/141007103102.htm>

course, the spilled gas which doesn't migrate to groundwater be washed off by stormwater into nearby surface waters.

So how far should a gas station be from a well or surface waters to reduce the likelihood of contamination to a reasonable level? Well, the key question is actually how far can one anticipate that a plume of spilled gasoline will travel underground.

One review of scientific studies of plume travel indicated that the 90th percentile distance is 400 feet.<sup>14</sup> Add another 100 feet for installing grout curtains or other containment measures and a gas station should be no closer than 500 feet to a well, wetland, spring, stream, river, pond, lake, reservoir or tidal waters. However, a 500-foot safety zone may not be sufficient given Baltimore County hydrogeology. For example, the Maryland Department of the Environment tested wells for contamination within a half-mile (2,640 feet) of the Jacksonville station where 26,000 gallons of gasoline was released.<sup>15</sup>

The JHU study and other research shows that the best way to preserve the County's high-quality waters is to prohibit new gas stations in areas where residents rely on wells. We should follow the lead of Harford County and prohibit new gas stations near homes on wells in areas not served with public water.

### **Property Value & Fire-Explosion Danger**

The U.S. Department of Housing & Urban Development restricts FHA insured mortgages for homes within 300 feet of a tank holding more than 1,000 gallons of gasoline or other flammable-explosive materials. All gas stations have storage tanks holding far more than 1,000 gallons. This restriction appears in the box to the right and is from Section 2-2M of the HUD *Handbook Valuation Analysis for Single Family One- to Four-Unit Dwellings*<sup>16</sup>.

The following excerpt from another U.S. Department of Housing & Urban Development<sup>17</sup> document shows that while gas station fires-explosions may not be common, they do occur often enough to be a concern for nearby residents:

(2-2) The lender, who is ultimately responsible for rejecting the site, relies on the appraiser's site analysis to make this determination. Guidelines for determining site acceptability follow. The appraiser is required to note only those readily observable conditions.

M. STATIONARY STORAGE TANKS  
Stationary Storage tanks containing flammable or explosive material pose potential hazards to housing, including hazards from fire and explosions. If the property is within 300 feet of a stationary, storage tank containing more than 1000 gallons of flammable or explosive

<sup>14</sup> See Technical Justification for Groundwater Plume Lengths, Indicator Constituents, Concentrations, and Buffer Distances (Separation Distances) to Receptors available online at: <http://www.waterboards.ca.gov/ust/policy/techjust071211.pdf>

<sup>15</sup> See the Maryland Department of the Environment webpage *Groundwater Remediation Continues in Jacksonville, Maryland* online at: <https://mde.maryland.gov/programs/ResearchCenter/eMDE/Pages/vol4no1/jacksonville.aspx>

<sup>16</sup> The Section 2-2M of the HUD Handbook is available online at: [https://www.hud.gov/program\\_offices/administration/hudclips/handbooks/hsg/4150.2](https://www.hud.gov/program_offices/administration/hudclips/handbooks/hsg/4150.2)

<sup>17</sup> The HUD fire-explosions report is available online at: <https://www.hud.gov/sites/documents/stations.pdf>

*“During the five-year period of 2004-2008, NFPA [National Fire Protection Association] estimates that U.S. fire departments responded to an average of 5,020 [fires] in service or gas station properties per year. These fires caused an annual average of two civilian deaths, 48 civilian fire injuries, and \$20 million in direct property damage.”*

As noted in the last section of this letter, Santa Rosa County, Florida requires a minimum 500-foot safety zone between new gas station storage tanks and residentially-zoned properties. The current Baltimore County Zoning Regulations require a mere 100-foot setback between just pumps (fuel dispensers) and residential districts ***with no minimum setback for storage tanks.***

### **Need for New Gas Stations Declining**

The number of gas stations in the U.S. has declined from more than 200,000 in 1994 to slightly more than 111,000 today. According to U.S. Census Bureau data, the number of gas stations in Baltimore County declined 16% between 2005 and 2016. As more and more hybrid and electric cars hit the marketplace, and other vehicles improve their miles/gallon by using lighter bodies and more fuel-efficient technology, the demand for fuel will further decrease. So, from a public policy perspective, it's not like we need more gas stations. In fact, the number of gas stations continues to decline.

Each new hypermarket, which most new gas station-convenience stores are, typically will close five conventional gas stations within their trade area as evidenced by Main Street in Reisterstown, MD. This effect was reinforced by the following results from a Community & Environmental Defense Services (CEDS)<sup>18</sup> analysis of Maryland gas station closures in the vicinity of a major hypermarket:

- There had been 173 stations located in the vicinity of 52 Maryland hypermarket stores,
- Of these 173 stations, 47% had closed, and
- 38% of the stations closed ***after*** a hypermarket store opened in the vicinity.

To put these findings in context, U.S. Census Bureau data shows that in 2005 there were 1,693 gas stations in Maryland. By 2016 the number had dropped to 1,537 for a decrease of 9%. However, 38% of gas stations in the vicinity of a hypermarket store closed after it opened. In other words, gas stations in the vicinity of hypermarkets ***closed at a rate four times higher than the statewide average.***

### **Proposed BCZR Amendments Will NOT Preclude New Gas Stations in Baltimore County**

As noted earlier in this letter, 27 petitions to rezone properties to Automotive Services (AS) have been submitted through the 2020 Comprehensive Zoning Map Process (CZMP). It is likely most of the petitioners intend to develop their property with a gas station if AS rezoning is granted. The enhanced gas station safety zones proposed in this letter were applied to these 27 properties. Of the 27 rezoning petition properties:

- All are in areas served with public water so the proximity to wells criteria would not preclude a gas station,
- However, 15 would ***not*** meet the proposed 500-foot sensitive land use safety zone,

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<sup>18</sup> For further information regarding the CEDS perspective on gas stations visit: <https://ced-s.org/convenience>

- 6 *would meet* the safety zone, and
- The remaining 6 are on sites large enough that tanks and pumps might be situated at points 500 feet from the nearest sensitive land use.

This analysis clearly shows that the proposed BCZR enhanced safety zone amendments will not prohibit future gas stations. Instead, the amendments will guide new gas stations to sites where we can enjoy the benefits these retail establishments provide without exposing area residents to public health and safety impacts.

### **Proposed BCZR Amendments Have Been Adopted by Many Other Counties-Cities**

Following are a few examples of the many similar regulations adopted by other cities and counties:

- [Montgomery County, MD](#): Any Filling Station facility designed to dispense a minimum of 3.6 million gallons per year must be located at least 500 feet from the lot line of any land with a dwelling unit; public or private school; park; playground; day care center; any outdoor use categorized as a Civic and Institutional use or a Recreation and Entertainment use; or any wetland, stream, river, flood plain, or environmentally sensitive area. (Section 3.5.13.C.2.c)
- [Harford County, MD](#): Prohibits new gas stations in rural areas in general and in any area where adjacent properties are not served with public water. (Section 267-60C(2)(e))
- [Rocky Hills, CT](#): A 1500-foot separation is required between new gas stations and a school, hospital, church, theater, public library or building for public assembly. These setbacks appear in Section 6.1, of the Rocky Hill Zoning Regulations.
- [Santa Rosa County, FL](#): In no case shall hazardous or potentially hazardous materials be stored or located in residential zones or within five hundred (500) feet of any residential zone, except for those materials used as fuel by emergency generators for communications towers as provided for in Section 7.01.15 or for public and private utilities. In which case, no hazardous or potentially hazardous materials may be stored within two hundred (200) feet of any residential structure. (Section 7.01.14.D.3.c.)
- [Blaine, MN](#): Gasoline sales must be up to one thousand (1,000) feet from public school buildings. (Section 30.14(c))

Sincerely,

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**2015 Study**  
**Hydrocarbon Release During Fuel Storage and Transfer at Gas**  
**Stations: Environmental and Health Effects**

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# Hydrocarbon Release During Fuel Storage and Transfer at Gas Stations: Environmental and Health Effects

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**Abstract** At gas stations, fuel is stored and transferred between tanker trucks, storage tanks, and vehicle tanks. During both storage and transfer, a small fraction of unburned fuel is typically released to the environment unless pollution prevention technology is used. While the fraction may be small, the cumulative release can be substantial because of the large quantities of fuel sold. The cumulative release of unburned fuel is a public health concern because gas stations are widely distributed in residential areas and because fuel contains toxic and carcinogenic chemicals. We review the pathways through which gasoline is chronically released to atmospheric, aqueous, and subsurface environments, and how these releases may adversely affect human health. Adoption of suitable pollution prevention technology should not only be based on equipment and maintenance cost but also on energy- and health care-saving benefits.

**Keywords** Gas stations · Vapor emissions · Fuel spills · Adverse health effects · Pollution prevention

## Introduction

The primary function of gas stations is to provide gasoline and diesel fuel to customers, who refill vehicle tanks and canisters.

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This article is part of the Topical Collection on *Air Pollution and Health*

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Operating a gas station requires receiving and storing a sufficient amount of fuel in storage tanks and then dispensing the fuel to customers. During delivery, storage, and dispensing of fuel at gas stations, unburned fuel can be released to the environment in either liquid or vapor form. Fuel is a complex mixture of chemicals, several of them toxic and carcinogenic [1]. Of these chemicals, the health consequences of chronic benzene exposure are best understood. Occupational studies have linked benzene exposures to numerous blood cancers, including acute myeloid leukemia and acute non-lymphocytic leukemia [2]. Concerns have been raised that gasoline vapor exposures incurred by gas station attendants [3] and tanker truck drivers [4] may result in health risks.

The potential for fuel released to the environment at gas stations, in the form of liquid spills or vapor losses, to elicit adverse health outcomes could be substantial due to the widespread distribution of gas stations across communities and the intensive usage of vehicle fuel in industrialized nations. For example, the USA consumed about 137 billion gallons of gasoline, or about 430 gallons per US citizen, in 2014 [5]. If only a small fraction of this gasoline was to be released to the environment in the form of unburned fuel, for instance 0.1 %, then about 1.6 L of gasoline would be released per capita per year in the USA. In Canada, a study estimated that evaporative losses at gas stations in 2009 amounted to 58,300,000 L [6]. With a population of about 34 million, we estimated that about 1.7 L of gasoline was released per capita per year in Canada from evaporative losses, without counting the liquid spills. While personal intake of this quantity of gasoline would result in serious adverse health effects, environmental dilution can decrease personal exposure. An overarching question is under which conditions dilution in the aqueous and atmospheric environments can limit personal exposures to acceptable levels. For example, cumulative adverse health effects could be more pronounced in metropolitan areas where more people

are exposed and where the density of gas stations is larger than in rural areas.

Engineers and regulators have paid a lot of attention to leaking underground storage tanks (LUSTs) and leaky piping between storage tanks and gasoline-dispensing stations, which can result in catastrophic fuel release to the subsurface [7]. For instance, double-walled tanks have become standard in order to minimize accidental release of liquid hydrocarbon. Technologies that prevent pollution due to non-catastrophic and unreported releases of hydrocarbon that occur during fuel storage and transfer (hereafter referred to as “chronic releases”), however, have not been uniformly implemented within the developed world. The state of California in the USA has the strictest policies to minimize chronic releases, either in liquid or in vapor form. Other US states and industrialized nations, however, have not uniformly adopted California’s standards, potentially because comprehensive economic and public health analyses to inform policy making are not available. This paper focuses on chronic hydrocarbon releases at gas stations (including both liquid spills and vapor losses), their contributions to human exposures and potential health risks, and factors that influence the adoption of suitable pollution prevention technology.

### Chemical Composition of Fuel

Fuels have historically contained significant fractions of harmful chemicals, some of which have been documented as contributing to morbidity and mortality in exposed persons. Crude oil, from which fuels have historically been refined, already contains toxic chemicals such as benzene [8]. Fuel additives including anti-knocking agents and oxygenates have historically also been a health concern [9]. Fuel composition has changed over time, primarily due to environmental and health concerns [9]. Fuel composition also depends on geographic location and fuel type (e.g., conventional versus reformulated gasoline) [10]. In the 1920s, lead was added to gasoline as an anti-knocking agent to replace added benzene because of its carcinogenicity [11]. Due to the massive release of lead to the environment and its neurotoxicity [12], lead was replaced in the 1970s by less toxic anti-knocking agents including methyl tert-butyl ether (MTBE) [13]. To reduce formation of ground-level ozone and associated adverse respiratory health effects [14], cleaner burning of fuel was sought in the 1990s by adding oxygenates to gasoline. This was accomplished by increasing the concentrations of MTBE, which acts

as an oxygenate [9]. However, MTBE accidentally released to the subsurface [15] contaminated downstream drinking water wells relatively quickly, moving almost with the speed of groundwater, because MTBE is hydrophilic and poorly biodegradable [16]. MTBE was later on identified as a potential human carcinogen [16]. In the USA, MTBE was therefore phased out in the 1990s; at the same time, refineries began supplementing fuel with ethanol as an oxygenate [17].

In current gasoline formulations, benzene, toluene, ethylbenzene, and xylene (BTEX) and particularly benzene are the most studied chemicals and are currently believed to be of greatest health concern [18]. Table 1 shows that fuels have historically contained large fractions of toxic and carcinogenic chemicals. In many countries, lead and MTBE are no longer used. Benzene levels in gasoline are currently much lower in most countries (e.g., on average 0.62 % by volume in the USA), though the chronic health effects of benzene and other BTEX chemicals at relevant exposure levels are not well understood.

### Chronic Release and Environmental Transport of Contaminants from Fuel

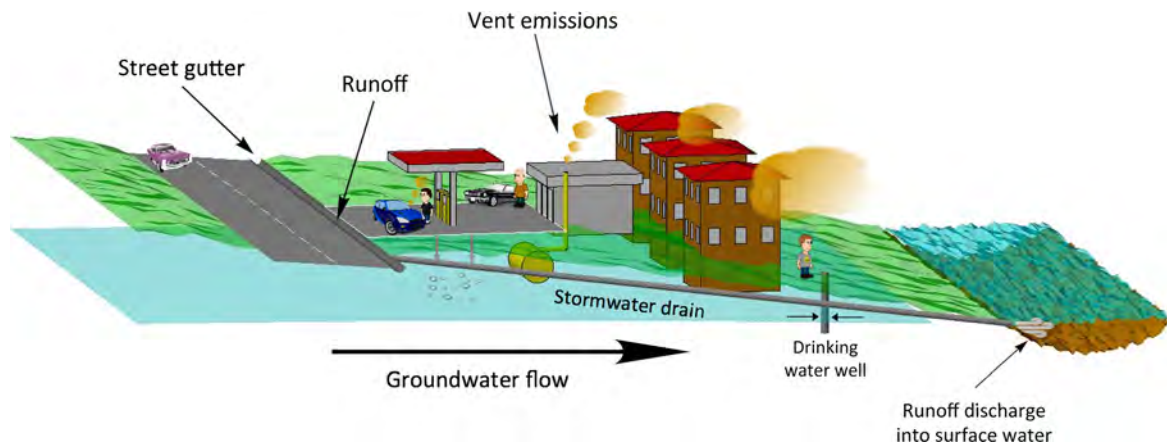
At gas stations, fuel can be released in both liquid and vapor phases during delivery, storage, and dispensing. Direct vapor release is usually associated with atmospheric pollution, while liquid spillage is commonly associated with soil and groundwater contamination. However, spilled liquid fuel also evaporates into the atmosphere. Hypothetically, hydrocarbon vapors can also condense back into liquid form; however, this appears to be unlikely due to quick dilution in a typically turbulent atmosphere. Figure 1 depicts how releases of unburned fuel contaminate the atmospheric, subsurface, and surface water environments (omitting LUST and leaky piping as well as marine gas stations which may release fuel directly to surface water).

#### Liquid Fuel Spills

Liquid fuel spills at the nozzle have received less attention than liquid releases due to LUSTs. These fuel spills occur when the dispensing nozzle is moved from the dispensing station to the vehicle tank and vice versa, when the automatic shutoff valve fails, due to spitback from the vehicle tank after the shutoff has been activated, and when the customer tops off the tank.

**Table 1** Historical content of non-negligible amounts of toxic and carcinogenic chemicals in fuel

Chemical of concern	Fraction	Health effects
Benzene	Up to 5 % [75]	Carcinogenic [2]
Lead	Up to 2 g per gallon [76]	Central nervous system [12]
MTBE	Up to 15 % [77]	Potential human carcinogen [78]



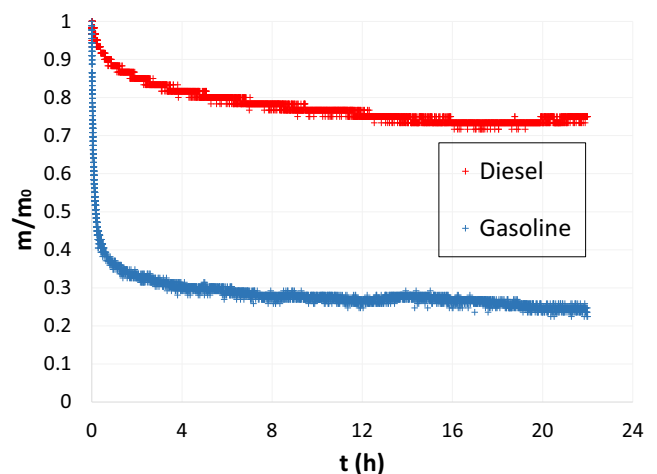
**Fig. 1** Gas stations are embedded into the natural environment and can consequently release pollutants to the atmosphere, the subsurface including soil and groundwater, and surface water

In a study quantifying fuel spill frequencies and amounts at gas stations in California, about 6 L of gasoline was spilled per 16,200 gallons of gasoline dispensed at gas stations without stage II vapor recovery compared to 3.6 L at gas stations per 14,043 gallons of gasoline dispensed at gas stations with stage II vapor recovery (at the nozzle) [19]. This would mean that about 0.007 and 0.01 % of dispensed gasoline are spilled in liquid form during vehicle refueling at gas station with and without stage II recovery (numbers calculated using the assumed fuel density of 6.2 pounds/gallon). On the other hand, a study sponsored by the American Petroleum Institute found that more spills occurred at gas stations with stage II recovery [20].

We have recently performed laboratory experiments to examine the fate of liquid spill droplets. Following our previous protocol [21•], we spilled fuel droplets onto small concrete samples and measured the mass added to the concrete as a function of time. This added mass is the sum of the masses of the sessile fuel droplet and the infiltrated fuel. Figure 2 shows results for diesel and gasoline. After a certain period of time, the sessile droplet vanishes and the measured mass levels off. The remaining mass represents the infiltrated portion. The evaporated mass can be obtained by subtracting the infiltrated mass from the initial droplet mass  $m_0$ . **Evaporation is greater for gasoline, while infiltration is greater for diesel spills. This is because gasoline is more volatile than diesel. Diesel has therefore a higher potential for soil contamination because of the higher infiltrated mass.**

Spilled fuel may move downward in liquid or vapor phase and potentially reach the groundwater table. The physical mechanisms that govern subsurface movement of spilled fuel are the same as for fuel released due to LUST, except that spilled fuel must first penetrate relatively impermeable pavement underneath fuel-dispensing stations. Gasoline and diesel will not penetrate the groundwater table as a liquid, because

they have densities lower than that of water. Released fuel may also evaporate within the sediment, and a portion of it will move downward as a vapor and potentially reach the groundwater table [22]. Whether the fuel reaches groundwater in liquid or vapor form, the fuel will then partition into groundwater and become a dissolved chemical that is carried away by molecular diffusion and groundwater flow and associated hydrodynamic dispersion [23]. **Therefore, the spills can contaminate downstream drinking water wells** [24]. Biodegradation can decrease contaminant concentrations significantly; however, its efficiency depends on many factors including the chemical composition of the fuel and the presence of suitable microbial species that can metabolize a given contaminant, bioavailability, and electron acceptor availability [25]. Partitioning of the contaminant into other phases will cause



**Fig. 2** Results from laboratory experiments, in which we spilled a mass  $m_0=1$  g of diesel or gasoline onto concrete samples. The measured mass  $m$  represents the masses of the sessile droplet and infiltrated liquid

retarded transport of the contaminant within groundwater. For instance, hydrophobic contaminants such as benzene tend to sorb to the sediment. For this reason, large-scale contamination of aquifers and associated adverse health effects due to the ingestion of contaminated drinking water from these aquifers are often considered a lesser concern for hydrophobic contaminants [16].

Stocking et al. [26] evaluated the potential of groundwater contamination due to small one-time releases of liquid gasoline. In a case study, they assumed a spill volume much bigger than the ones typically measured by the study of gas stations in California [19], i.e., 0.5 L, and they concluded the risk to groundwater to be small. This analysis, however, did not include consideration of a key mechanism for fuel spillage; namely, that much smaller droplets are typically released during vehicle refueling [19]. To address this question, Hilpert and Breyse [21•] calculated cumulative spill volumes due to repeated small spillages that occur at gasoline-dispensing facilities and estimated that a gas station selling about 400,000 L of gasoline per month would spill at least 150 L each year. They also developed a model that shows that the fraction of spilled gasoline that infiltrates into the pavement increases as the droplet size decreases. Therefore, repeated small spills could be of greater concern for groundwater contamination than an instantaneous release of the cumulative spill volume; thus, a risk to groundwater may not be as small as previously estimated.

Laboratory experiments and modeling have shown that gasoline from small-volume spills can infiltrate into the concrete that usually covers the ground underneath gasoline-dispensing stations—despite the low permeability of concrete and the high vapor pressure of gasoline [21•]. It is unlikely that liquid fuel fully penetrates a concrete slab to contaminate the underlying natural subsurface due to the low permeability of concrete [27], although preferential pathways for fluid flow such as cracks and faulty joints between concrete slabs can allow for such liquid penetration. It has been hypothesized that evaporation of infiltrated gasoline and subsequent downward migration of the vapor through the concrete may lead to contamination of underlying sediment and groundwater [21•]. Consistent with these two proposed pathways of subsurface contamination, soil/sediment underneath concrete pads of a gas station in Maryland was contaminated by diesel oil and gasoline (leaky piping could have also contributed to the contamination) [28].

Runoff water that flows over pavement can also get contaminated with hydrocarbons spilled onto the pavement [29–31], and such contamination has specifically been linked to gas stations [32–34]. If a spill occurs while runoff occurs, the hydrocarbon can be expected to float on top of the water sheet, because gasoline, diesel oil, and lubricants are typically less dense than water (light non-aqueous phase liquids or LNAPLs). While runoff water is not directly ingested, it is

funneled into the stormwater drainage system, and may be released to natural water bodies, often without treatment. Whereas volatilization decreases contaminant levels in the stormwater within hours depending on the exact environmental conditions [35], and biodegradation will further decrease levels, significantly contaminated stormwater might be released to natural water bodies if they are close by. Finally, fuel spilled at marine gas stations may directly enter natural water bodies.

#### Vapor Fuel Releases

Fuel evaporative losses have received more attention than liquid fuel spills (even though they are related) [6, 36]. These losses are related to the fact that the headspace above liquid fuel in vehicle and storage tanks tends to approach thermodynamic equilibrium with the liquid. Consequently, almost saturated gasoline vapors can be released to the atmosphere when tanks are refueled, unless a suitable vapor recovery system is in place. Since saturated gasoline vapors have a density that is three to four times larger than the one of air, i.e., 4 kg/m<sup>3</sup>, and the density of liquid gasoline is about 720 kg/m<sup>3</sup> [37], about 0.5 % of liquid gasoline dispensed to a tank is released to the atmosphere if the entire headspace is in equilibrium with the liquid fuel. This is true for any type of tank, whether it is a vehicle tank, a canister, an underground storage tank (UST), or an above-storage tank. The percentage loss is less if a tank received clean air relatively recently, e.g., when the fuel level in a storage tank drops because of gasoline-fuel dispensing.

It is important to note that vapor recovery at the nozzle can cause vapor releases at the storage tank, because vapors recovered at the nozzle are typically directed into the storage tank. The storage tank, in turn, can “breathe” and potentially release recovered vapors immediately or at a later time. A tank sucks in relatively uncontaminated air as the liquid fuel level drops in the tank due to vehicle refueling, and it releases vapors through the vent pipe into the atmosphere if the gas pressure increases and exceeds the cracking pressure of the pressure/vacuum valve, when fuel evaporates into unequilibrated gas in the headspace.

As discussed in the “Liquid Fuel Spills” section above, we note that liquid spills also contribute to air pollution because spilled droplets form sessile droplets on pavement that can then evaporate into the atmosphere. On concrete, most of spilled gasoline droplets evaporate into the atmosphere (Fig. 2). This, however, does not mean that the small fraction that infiltrates into the concrete is not of concern.

#### Exposure and Risks to Human Populations

Gas stations exist as part of the built environment and are widely distributed across communities. As a result, they may be surrounded by residential dwellings, businesses, and other

buildings such as schools. Operation of gas stations may thus create opportunities for a variety of human populations to be exposed to vapors during station tank filling and vehicle refueling. These human populations can be broadly grouped into three groups: populations exposed occupationally as a result of employment in various capacities at the service station; those exposed as customers engaging in vehicle refueling; and those passively exposed either by residing, attending school, or working near the refueling station. The exposures to benzene and other components of refueling vapors and spills experienced by these populations vary based on a number of factors, including the size and capacity of the refueling station, spatial variation in pollutant concentrations in ambient air, climate, meteorological conditions, time spent at varying locations of the service station, changing on-site activity patterns, physiological characteristics, and the use of vapor recovery and other pollution prevention technologies.

Employees at service stations (such as pump attendants, on-site mechanics, and garage workers) are among those with greatest exposure to benzene originating from gas stations [3]. These receptors spend the most time on site (potentially reflecting approximately 40 h per week, for decades) and intermittently spend time where vapors from the pump are at their highest concentrations, with benzene concentrations measuring between 30 and 230 ppb in the breathing zone [38–40]. Gas station patrons can also be exposed to vapors when refueling. Compared to station employees, their exposures are brief and transient. A Finnish study reported a median time spent refueling of approximately 1 min, whereas 3 min was the median duration in the USA [41, 42]. The same US study reported an average benzene personal exposure concentration at the pump of 910 ppb, with the strongest predictors of benzene levels being fuel octane grade, duration of exposure, and season [42].

Those occupying residences, businesses, and other structures neighboring gas stations can also be exposed to fuel vapors originating in the gas station, though typically at lower concentrations than those measured at the pump. While vapor concentrations will drop as the distance from the service station increases, exhaust fumes from waiting customers and fuel delivery trucks can also contribute to vapors in proximity to gas stations. A small number of studies have examined benzene concentrations at the fenceline of the service station and beyond. A study published by the Canadian petroleum industry found average benzene concentrations of 146 and 461 ppb at the gas station property boundary in summer and winter, respectively [43]. A South Korean study examined outdoor and indoor benzene concentrations at numerous residences within 30 m and between 60 and 100 m of gas stations and found median outdoor benzene concentrations of 9.9 and 6.0  $\mu\text{g}/\text{m}^3$  (about 3.1 and 1.9 ppb), respectively. Median indoor concentrations at these locations were higher, reaching 13.1 and 16.5  $\mu\text{g}/\text{m}^3$  (about 4.1 and 5.2 ppb), respectively

[44]. Another study found median ambient benzene levels of 1.9 ppb in houses both <50 and >100 m from a service station [45]. Yet, another study [46] found that benzene and other gasoline vapor releases from service stations can be discerned from traffic emissions as far as 75 m from service stations and that the contribution of service stations to ambient benzene is less important in areas of high traffic density. This is because vehicle exhaust is usually the most abundant volatile organic compound (VOC) in urban areas, often followed by gasoline vapor emissions from fuel handling and vehicle operation [47].

Beyond contact with surface-level gasoline vapors, fuel releases may result in other exposure pathways. Soil and groundwater contamination is common at gas stations. Drinking water wells proximate to gas stations, which in rural areas are often the only drinking water source, can become contaminated, potentially exposing well users to benzene and other chemicals [48, 49]. In addition, runoff from rain and other weather events can carry spilled hydrocarbons, which can contaminate surface waters; those using surface waters, either recreationally or for other purposes, may be exposed to these contaminants through dermal contact or incidental ingestion.

In the USA, the Environmental Protection Agency (EPA) regulates releases of benzene under the Clean Air Act as a hazardous air pollutant, and benzene is listed as number 6 on the 2005 priority list of hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act and any release greater than 10 pounds triggers a reporting requirement. Different quantitative toxicity metrics exist for benzene inhalation. The EPA Integrated Risk Information System (IRIS) has published a reference concentration of 0.03  $\text{mg}/\text{m}^3$  (about 9.4 ppb), corresponding to decreased lymphocyte counts [50], whereas the NIOSH recommended exposure limit (REL) is a time-weighted average concentration (for up to a 10-hour workday during a 40-hour workweek) of 0.319  $\text{mg}/\text{m}^3$  (about 100 ppb) [51].

While research attention has been paid to measurement of gasoline vapor constituent concentrations in air at and near service stations, less is known about the health consequences faced by those that are exposed to gasoline vapors. Of the limited literature examining these exposures, service station workers have received the greatest attention, and exposure is often assessed as a function of job title, rather than specific measurements of vapor constituent concentrations. An older study looking broadly at leukemia incidence in Portland, Oregon, found that gas station workers were at significantly increased risk for lymphocytic leukemia [52]. A proportionate mortality ratio analysis of all deaths recorded in New Hampshire among white men from 1975 to 1985 found elevated leukemia mortality in service station workers and auto mechanics [53]. The type of leukemia was not specified. An Italian occupational cohort study of refilling attendants that examined risks among workers at smaller gas stations reported



non-significant increases in mortality for non-Hodgkin's lymphoma and significantly elevated mortality for esophageal cancer in men, as well as increased brain cancer mortality in both sexes [54]. A different cohort of 19,000 service station workers in Denmark, Norway, Sweden, and Finland examined an array of cancer end points and found increased incidence for multiple sites (nasal, kidney, pharyngeal, laryngeal, and lung) among workers estimated to be occupationally exposed to benzene in the range of  $0.5\text{--}1\ \mu\text{g}/\text{m}^3$  (0.16–0.31 ppb). Non-significant increased incidence was found for acute myeloid leukemia in men and for leukemia different from acute myeloid leukemia and chronic lymphocytic leukemia in women [55]. A case–control study of multiple occupations including subjects from the USA and Canada found significant increases in rates of total leukemia and acute myeloid leukemia but not acute lymphocytic leukemia in gas station attendants [56]. A 2015 review of studies examining potential relationships between benzene exposures and hematopoietic and lymphatic cancers among vehicle mechanics yielded inconclusive results, although it suggested that if an effect was to exist, it would be small and difficult to rigorously ascertain with existing epidemiologic methods [57].

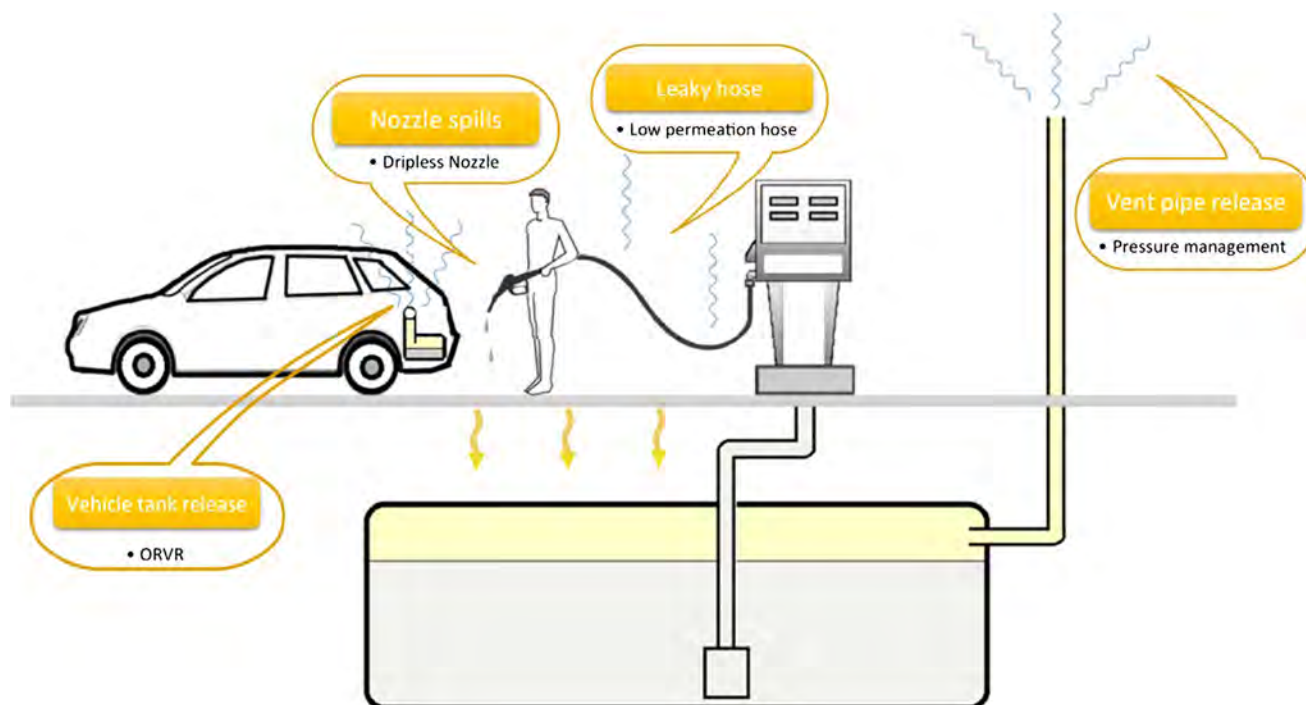
The health consequences of nearby residents of gas stations have not been studied. However, it is known that contaminated groundwater can affect large numbers of people if the groundwater is used as drinking water, as was the case in Camp Lejeune (North Carolina, USA) where thousands were

exposed to a range of chemicals including gasoline released from LUSTs [58]. A study of Pennsylvania residents residing in close proximity to a large gasoline spill from a LUST found evidence of increased leukemia risks [49, 59••]. The health consequences of chronic fuel releases at gas stations that can, for example, occur due to ingestion of contaminated groundwater, fuel vapor intrusion from contaminated soil and groundwater into dwellings [60], and atmospheric vapor releases during fuel transfer and storage have not been studied. While limited measurements of ambient concentrations of vapor constituents in communities were identified, literature searches did not identify studies of the health consequences of inhalation exposures to gasoline vapors among community residents [61].

### Pollution Prevention

Pollution prevention technologies have been developed that can efficiently reduce the releases of unburned fuel to the environment that routinely occur during fuel storage and transfer (see Fig. 3):

1. Stage I vapor recovery collects vapors that would be expelled from USTs during fuel delivery [62]. Without stage I vapor recovery, about 80 kg of gasoline vapor would be released from a  $40\ \text{m}^3$  UST if one assumes a saturated vapor density of  $4\ \text{kg}/\text{m}^3$  [37] and vapors in the headspace



**Fig. 3** There are several sources of chronic release of unburned fuel at gas stations that occur due to fuel storage and dispensing: vapor release through the vent pipe of the storage tank, vapor release from the vehicle tank during refueling, leaky dispensing hoses, liquid spills during vehicle

refueling, and vapor emissions through evaporation of this spilled fuel. As indicated, suitable pollution prevention technology can minimize the releases. Onboard refueling vapor recovery (ORVR)

to be at half saturation. Stage I vapor recovery can thus prevent substantial fuel vapor releases that would occur within a short period of time. Such releases might expose tanker truck drivers and persons in the proximity of a gas station to significant doses of fuel vapors. Stage I vapor recovery is accomplished by establishing a closed loop between the UST and the tanker truck. Through a fuel delivery hose, liquid fuel is pumped into the UST, while a vapor recovery hose directs vapors displaced from the UST into the headspace of the tanker truck. Stage I vapor recovery is currently required for high-throughput gas stations in all states in the USA and in most countries.

2. Stage II vapor recovery technology can efficiently collect vapors expelled from vehicle tanks during refueling, thereby minimizing personal exposure of customers and workers to fuel vapors during dispensing of gas [63]. Recovered vapors are directed into the UST. Two technologies for stage II vapor recovery have been developed, the vacuum-assist method and the balance method. In the vacuum-assist method, contaminant-laden air is actively removed/pumped from the nozzle into the UST. In the balance method, displaced vapors are passively withdrawn by connecting the vapor recovery hose to the inlet of the vehicle tank via an airtight seal. The pressure increase in the headspace of the vehicle tank provides a driving force that seeks to push the vapors into the storage tank. Stage II vapor recovery has been required in many states of the USA and in other countries, although there is currently an effort to decommission stage II vapor recovery (see below).
3. Technology development at the hose and nozzle level can also contribute to reduced fuel releases. Low-permeation hoses, for instance, limit the release of gasoline vapors through the wall of the refueling hoses [64]. Dripless nozzles have been developed to minimize liquid spills that occur when the nozzle is moved between the fill pipe and the dispensing unit.
4. Passenger vehicles and trucks can be equipped with on-board refueling vapor recovery (ORVR) systems which direct vapors that, during vehicle refueling, would be released to the atmosphere into an activated carbon-filled canister in the vehicle [65, 66]. Collected vapors are later reintroduced into the vehicle's fuel system. However, canisters, motorcycles, and boats are not equipped with ORVR.
5. Impermeable liners underneath the concrete pads can reduce the risk of soil and groundwater contamination once environmental fuel releases, in liquid or vapor phase, have occurred. However, this technology might eventually result in air pollution, because liquid fuel that is hindered from moving downward in the concrete pad will tend to saturate the pavement and eventually evaporate into the atmosphere.
6. Finally, unburned fuel vapor can be released from an UST when the tank pressure exceeds the cracking pressure of

the pressure/vacuum valve and it can be prevented by two pressure management techniques, burning or separation of air and fuel vapors. Released air/fuel vapors can be burned, however, which results in the release of combustion-related pollutants into the atmosphere. Alternatively, a semi-permeable membrane can be used to separate the air from the fuel vapors. Depressurization of the tank is then achieved by releasing the relatively clean air through the pressure/vacuum valve to the atmosphere.

When it comes to evaluating the efficiency of vapor recovery during liquid transfer between tanks, it is of utmost importance to consider potential releases from all tanks; they form a system. Otherwise, the overall efficiency of stage II vapor recovery cannot be understood. For instance, stage II vapor recovery based on the vacuum-assist method can negatively interfere with ORVR. In that case, no vapors are released from the vehicle tank and the stage II pump draws relatively clean air from the atmosphere into the storage tank. In the UST, this air will become saturated with fuel vapors that evaporate from the stored fuel. This results in pressurization of the UST and release of contaminant-laden air if the tank pressure exceeds the cracking pressure of the pressure/vacuum valve of the UST. This might occur immediately or at a later point in time. However, there are stage II systems that do not negatively interfere with ORVR including the balance method.

Estimates for the efficiency of pollution technologies are usually provided by the manufacturers. However, adoption of these technologies by gas station owners usually relies on the certification and quantification of efficiencies by independent parties. In the USA, the California Air Resources Board and EPA typically assume this role [36]. Consultants and environmental agencies have used these estimates to determine current releases of unburned fuel to the environment and to evaluate the effects of pollution prevention technology [67].

While many studies have found health benefits from pollution prevention technology intended to minimize chronic gasoline spills, these studies typically do not quantify overall financial benefits and costs. Instead, only equipment and maintenance cost are typically considered [68]. Adopting the new equipment can reduce fuel losses and reduce environmental cost and health risks. However, this new equipment comes with non-trivial upfront costs. It is therefore a concern that the related policy-making process of chronic fuel spills relies only on non-comprehensive cost estimates. Studies are needed that account for health care cost due to released pollutants and energy-saving benefits due to pollution prevention. Such econometric studies have, for example, been performed in the context of pollutant emissions from coal-fired power plant and commercial real estate development [69•, 70]. At times, there is also the perception that pollution prevention

costs are only carried by the specific industry [71]. Adoption of the environmentally friendly technology could be slow when the firms have long equipment replacement cycles or when the firms do not have sufficient information to evaluate whether or not a switch to an environmentally friendly technology is in their private interests. It is, however, not clear that this apparent investment, in the form of prevention cost, might also be partly shouldered by customers and that this apparent cost might actually (at least in the long run) be beneficial to customers, gas station workers, nearby residents, and other populations that spend significant amounts of times in the proximity of gas stations (e.g., school children in nearby schools). Policy intervention is often expected to expedite the adoption of such environmental friendly technologies, in order to reduce the difference in the private and social values of adoption.

Efforts are currently underway that could potentially allow decommissioning stage II vapor recovery in the USA due to the widespread use of ORVR in the motor vehicle fleet [68]. However, the remaining legacy fleet without ORVR and all motorcycles and boats (lacking ORVR) can produce significant emissions during vehicle refueling, emissions that could be avoided by stage II vapor recovery. For the State of Maryland, it has been estimated that fuel consumption of non-ORVR-equipped vehicles was about 10 % in 2015 (Table 4 in [67]). These emissions can result in direct hydrocarbon exposures among vehicle owners during vehicle refueling as well as in passive exposure of other populations. A comprehensive cost analysis of the decommissioning of stage II recovery represents an opportunity to inform policy makers on their recommendation with regards to stage II recovery.

## Conclusions

Even if only a small fraction of unburned fuel is lost during vehicle refueling and fuel storage, the cumulative release of fuel to the environment can be large if large total amounts of fuel are dispensed at gas stations. For instance, about 0.01 % of fuel can be spilled during the refueling process and up to about 0.5 % can be lost in vapor form if equilibrated gasoline vapors are released from a tank to the atmosphere during refueling (worst-case scenario). For a medium-size gas station, which sells 400,000 L of gasoline per month, this results in 480 L of spilled gasoline and in 24,000 L of liquid gasoline that is annually released in vapor form to the environment. Even though dilution can reduce concentrations of released contamination, research is needed to assess whether such releases represent an environmental health concern.

The potential for pollution prevention, moreover, is substantial. Technology has already been developed and partially employed that can efficiently decrease vapor losses and liquid spills. Particularly, when it comes to vapor losses, it is crucial to consider not only vapor recovery at the vehicle tank/nozzle

but also at the storage tank, since vapors recovered at the nozzle are directed into the storage tank, from which they might be potentially released. While California has implemented the strictest regulations when it comes to preventing chronic hydrocarbon releases at gas stations, other highly industrialized states and nations do not employ the same standards for different reasons. For instance, pressure/vacuum valves on vent pipes of fuel storage tanks are not common in Canada, because they might freeze in the wintertime, potentially causing a tank implosion [6].

Relatively little research has been done on potential soil and groundwater contamination due to chronic releases of liquid fuel during vehicle refueling. Unlike catastrophic releases, such as LUST, chronic spills are not reported. Limited field investigations suggest that spilled fuel may penetrate concrete underneath dispensing pads to contaminate underlying sediment. However, it is possible that such soil contamination occurs routinely over the life span of a gas station and that this contamination pathway is masked or erroneously explained by leaks in the piping from the USTs to the dispensers. Overall, large-scale soil and groundwater contamination by fuel appears to be a lesser problem, because many of the toxic compounds in fuel are hydrophobic (including BTEX) and can therefore be expected not to travel too far in groundwater. However, customers, gas station workers, and nearby residents may get exposed to the hydrocarbons if groundwater is used as a drinking water supply or if fuel vapor intrusion in dwellings occurs.

Health effects of living near gas stations are not well understood. Adverse health impacts may be expected to be higher in metropolitan areas that are densely populated. Particularly affected are residents nearby gas stations who spend significant amounts of time at home as compared to those who leave their home for work because of the longer period of exposure. Similarly affected are individuals who spend time close to a gas station, e.g., in close by businesses or in the gas station itself. Of particular concern are children who, for example, live nearby, play nearby, or attend nearby schools, because children are more vulnerable to hydrocarbon exposure [72].

Potential future changes in fuel composition might pose new environmental health challenges as there is a history of adding even large amounts of toxic substances to fuel (Table 1). Changes in fuel composition could occur due to an increasing usage of biofuels, or to comply with air quality standards, which might also change over time. Chemicals newly added to fuel or changes in chemical concentrations can have unforeseen ramifications. One could argue that future fuel composition changes will be performed with more care; however, it was only in the 1990s, decades after the Safe Drinking Water Act (SDWA) was passed in 1974, that MTBE was added to gasoline without critically evaluating its transport behavior in groundwater and toxicity, a mistake which

nowadays is considered avoidable [73]. Interestingly, ethanol, which has largely replaced MTBE, can inhibit biodegradation of BTEX, which is not the case for MTBE [74]. Given the complexities of chemical fate and transport in the environment and the potential for insufficient toxicity testing, using appropriate pollution prevention technology that minimizes release of unburned chemicals with known and unknown adverse health effects during fuel storage and transfer seems a wise, long-term, and cost effective idea given ever-changing fuel compositions.

Finally, employing efficient pollution prevention technology might be economically advantageous. The evaluation of economic benefits of pollution prevention technology needs to account not only for the cost of implementation and maintenance of such technology but also for public health burdens due to released pollutants and energy-saving benefits due to valuable hydrocarbons not wastefully released to the environment.

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#### Compliance with Ethics Guidelines

**Conflict of Interest** Markus Hilpert, Bernat Adria Mora, Jian Ni, Ana Rule, and Keeve Nachman declare that they have no conflict of interest.

**Human and Animal Rights and Informed Consent** This article does not contain any studies with human or animal subjects performed by any of the authors.

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- Of major importance

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**2019 Study**

**Vent pipe emissions from storage tanks at gas stations:  
Implications for setback distances**



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## Vent pipe emissions from storage tanks at gas stations: Implications for setback distances

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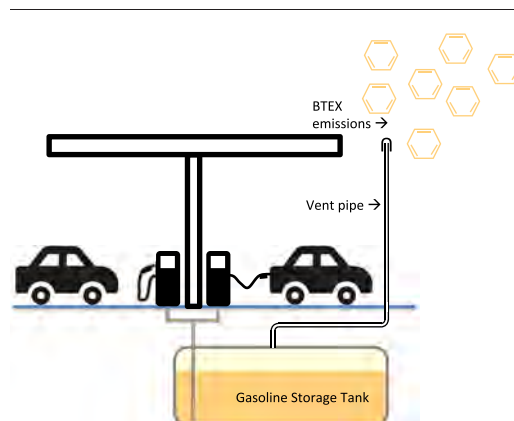
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### HIGHLIGHTS

- At gas stations, fuel vapors are released from storage tanks through vent pipes.
- We measured vent pipe flow rates and tank pressure at high temporal resolution.
- Vent emission factors were >10 times higher than previous estimates.
- Modeling was used to examine exceedance of benzene short-term exposure limits.

### GRAPHICAL ABSTRACT



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### ABSTRACT

At gas stations, fuel vapors are released into the atmosphere from storage tanks through vent pipes. Little is known about when releases occur, their magnitude, and their potential health consequences. Our goals were to quantify vent pipe releases and examine exceedance of short-term exposure limits to benzene around gas stations. At two US gas stations, we measured volumetric vent pipe flow rates and pressure in the storage tank headspace at high temporal resolution for approximately three weeks. Based on the measured vent emission and meteorological data, we performed air dispersion modeling to obtain hourly atmospheric benzene levels. For the two gas stations, average vent emission factors were 0.17 and 0.21 kg of gasoline per 1000 L dispensed. Modeling suggests that at one gas station, a 1-hour Reference Exposure Level (REL) for benzene for the general population (8 ppb) was exceeded only closer than 50 m from the station's center. At the other gas station, the REL was exceeded on two different days and up to 160 m from the center, likely due to non-compliant bulk fuel deliveries. A minimum risk level for intermediate duration (>14–364 days) benzene exposure (6 ppb) was exceeded at the elevation of the vent pipe opening up to 7 and 8 m from the two gas stations. Recorded vent emission factors were >10 times higher than estimates used to derive setback distances for gas stations. Setback distances should be revisited to address temporal variability and pollution controls in vent emissions.

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## 1. Introduction

In the US, approximately 143 billion gal (541 billion L) of gasoline were dispensed in 2016 at gas stations (EIA, 2017) resulting in release of unburned fuel to the environment in the form of vapor or liquid (Hilpert et al., 2015). This is a public health concern, as unburned fuel chemicals such as benzene, toluene, ethyl-benzene, and xylenes (BTEX) are harmful to humans (ATSDR, 2004). Benzene is of special concern because it is causally associated with different types of cancer (IARC, 2012). Truck drivers delivering gasoline and workers dispensing fuel have among the highest exposures to fuel releases (IARC, 2012). However, people living near or working in retail at gas stations, and children in schools and on playgrounds can also be exposed, with distance to the gas stations significantly affecting exposure levels (Terres et al., 2010; Jo & Oh, 2001; Jo & Moon, 1999; Hajizadeh et al., 2018). A meta-analysis (Infante, 2017) of three case-control studies (Steffen et al., 2004; Brosselin et al., 2009; Harrison et al., 1999) suggests that childhood leukemia is associated with residential proximity to gas stations.

Sources of unburned fuel releases at gas stations include leaks from storage tanks, accidental spills from the nozzles of gas dispensers (Hilpert & Breyse, 2014; Adria-Mora & Hilpert, 2017; Morgester et al., 1992), fugitive vapor emissions through leaky pipes and fittings, vehicle tank vapor releases when refueling, and leaky hoses, all of which can contribute to subsurface and air pollution (Hilpert et al., 2015). Routine fuel releases also occur through vent pipes of fuel storage tanks but are less noticeable because the pipes are typically tall, e.g., 4 m. These vent pipes are put in place to equilibrate pressures in the tanks and can be located as close as a few meters from residential buildings in dense urban settings (Fig. 1).

Unburned fuel can be released from storage tanks into the environment through “working” and “breathing” losses (Yerushalmi & Rastan, 2014). A working loss occurs when liquid is pumped into or out of a tank. For a storage tank, this can happen when it is refilled from a tanker truck or when fuel is dispensed to refuel vehicles (Statistics Canada, 2009) if the pressure in the storage tank exceeds the relief pressure of the pressure/vacuum (P/V) valve (EPA, 2008). P/V valve threshold pressures are typically set to around +3 and −8 in. of water column (iwc) (7.5 and −20 hPa). However, P/V valves are not always used, particularly in cold climates, as valves may fail under cold weather conditions (Statistics Canada, 2009).

Breathing losses occur when no liquid is pumped into or out of a tank because of vapor expansion and contraction due to temperature and barometric pressure changes or because pressure in the storage

tank may increase when fuel in the tank evaporates (Yerushalmi & Rastan, 2014; EPA, 2008). Although delayed or redirected by the P/V valve, breathing emissions can be significant and represent an environmental and health concern (Yerushalmi & Rastan, 2014).

Stage I vapor recovery systems, put in place to prevent working losses while delivering fuel to a station, collect the vapors displaced while loading a storage tank, redirecting them into the delivery truck. Stage II vapor recovery systems minimize working losses while delivering gas from the storage tank to the customer's car. During Stage II vapor recovery, gasoline vapors can be released through the vent pipe, if the sum of the flow rates of the returned volume and of the fuel evaporating within the storage tank is greater than the volume of liquid gasoline dispensed (Statistics Canada, 2009). We refer to this scenario as pressure while dispensing (PWD). In theory, a properly designed Stage II vapor recovery system should not have working losses, although in practice this is not typically the case (McEntire, 2000).

Regulations on setback distances for gas stations are based on lifetime cancer risk estimates. Several studies have assessed benzene cancer risk near gas stations (Atabi & Mirzahosseini, 2013; Correa et al., 2012; Cruz et al., 2007; Edokpolo et al., 2015; Edokpolo et al., 2014; Karakitsios et al., 2007). Based on cancer risk estimations, the California Air Resources Board (CARB) recommended that schools, day cares, and other sensitive land uses should not be located within 300 ft. (91 m) of a large gas station (defined as a facility with an annual sales volume of 3.6 million gal = 13.6 million L or greater) (CalEPA/CARB, 2005). This CARB recommendation has not been adopted by all US states, and within states setback distances can depend on local government. Notably, CARB regulations do not account for short term exposure limits and health effects. An important limitation of existing regulations is the use of average gasoline emission rates estimated in the 90s that do not consider excursions (CAPCOA, 1997).

The main objective of this study is to evaluate fuel vapor releases through vent pipes of storage tanks at gas stations based on vent emission measurements conducted at two gas stations in the US in 2009 and 2015, including the characterization of excursions at a high temporal resolution (~minutes) and meteorological conditions at an hourly temporal resolution. In addition, we performed hourly simulations of atmospheric transport of emitted fuel vapors to inform regulations on setback distances between gas stations and adjacent sensitive land uses by comparing modeled benzene concentrations to four 60-min benzene exposure limits: an acute Reference Exposure Level (REL) for infrequent (once per month or less) exposure (WHO, 2010) and Emergency Response Planning Guidelines ERPG-1, ERPG-2 and ERPG-3 (AIHA, 2016). Finally we compared simulated benzene levels to a Minimal Risk Level (MRL) for benzene for intermediate exposure duration (14 to 364 days) (ATSDR, 2018) because that duration window includes our duration of data collection. See Table 1 for the various benzene exposure limits and issuing agencies.

## 2. Methods

Although we provide SI unit conversions, we report some measures in English engineering units (ft, gal, and lb) as regulatory agencies such as CARB use these units.

### 2.1. Sites

Data for this study were obtained from vent release measurements conducted at two gas stations as part of technical assistance to the gas stations to quantify fuel vapor losses through the vent pipes of their storage tanks. A motivation for conducting the measurements was to perform a cost-benefit analysis to compare the economic losses due to the lost fuel versus the cost of technologies that reduce the emissions. The exact location of the two gas stations is not revealed for confidentiality reasons. The gas station managers and staff who authorized the



**Fig. 1.** The three vent pipes (enclosed by the red ellipse) on the right side of the convenience store of a gas station are <10 m away from the residential building. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

Benzene exposure limits, to which we compared simulation results. For unit conversion, we assumed a temperature of 25 °C, i.e., 1 ppm = 3194 µg/m<sup>3</sup> (CAPCOA, 1997).

Agency	Name	Value (ppb)	Value (µg/m <sup>3</sup> )	Exposure duration
California Office of Environmental Health Hazard Assessment (OEHHA)	REL	8	26	1 h
American Industrial Hygiene Association (AIHA)	ERPG-1	50	159,700	1 h
AIHA	ERPG-2	150	479,100	1 h
AIHA	ERPG-3	1000	3,194,000	1 h
Agency for Toxic Substances and Disease Registry (ATSDR)	MRL	6	19	14 to 364 days

ERPG = Emergency Response Planning Guidelines. The primary focus of ERPGs is to provide guidelines for short-term exposures to airborne concentrations of acutely toxic, high-priority chemicals.

collection and analysis of these data have not been involved in the current manuscript.

The first gas station, “GS-MW,” was located in the US Midwest and is a 24-hour operation. The study was conducted from December 2014 to January 2015 for 20 full days, and fuel sales  $\dot{V}_{sales}$  were about 450,000 gal (1.7 million L) per month. Fuel deliveries to the gas station usually took place during the nighttime. The second gas station, “GS-NW,” was located on the US Northwest coast and closed at night. Hours of operation were between 6:00 am and 9:30 pm on weekdays and between 7 am and 7 pm on weekends. That study was conducted in October 2009 for 18 full days, and fuel sales were  $\dot{V}_{sales} \sim 700,000$  gal (2.6 million L) per month.

Both gas stations are considered to be high-volume, because they dispense >3.6 million gal of gasoline (both regular and premium) per year (CalEPA/CARB, 2005), and fuel was stored in underground storage tanks (USTs), which is typical in the US. Both gas stations had Stage II vapor recovery installed using the vacuum-assist method. In that method, gasoline vapors, which would be ejected into the atmosphere as a working loss during refueling of customer vehicle tanks, are collected at the vehicle/nozzle interface by a vacuum pump. The recovered vapors are then directed via a coaxial hose back into the combined storage tank ullage (head space) of the gas station. Stage I vapor recovery was also used at both gas stations during fuel deliveries. Both sites had a 3-inch diameter (7.5 cm) single above-grade vent pipe with below-grade manifold that connected the vent lines from several USTs; the cracking pressures of the P/V valves were set to +3 and –8 iwc (+7.5 and –20 hPa).

## 2.2. Vent emission measurements

To quantify evaporative fuel releases through the vent pipe of a storage tank, the volumetric flow of the mixture of gasoline vapor and air was measured in the vent pipe. A dry gas diaphragm flow meter (American Meter Company, Model AC-250) was used. For each cubic foot (28 L) of gas flowing through the meter, a digital pulse was generated. Every minute, the number of pulses was read out and stored together with date and time on a data logger. Gas flow meters were obtained from a distributor calibrated and equipped with temperature compensation and a pulse meter.

To determine the time-dependent volumetric flow rate  $Q(t)$  of the gasoline vapor/air mixture through the vent pipe, the time series of measured flow volumes were integrated over an averaging period (15 or 60 min) and divided by the duration of that period. I.e.,  $Q(t)$  is given by the number of pulses registered by the gas flow meter in a time window multiplied by 1 cubic foot and divided by the averaging time. The 15-minute averaging time was chosen to visualize time-dependent data, while the 60-minute averaging time was chosen because air pollution simulations were performed at that resolution.

Gas pressure  $p$  in the ullage of the storage tank was measured to assess vent emission patterns. For instance, releases can occur when the pressure exceeds the cracking pressure of the P/V valve in the vent pipe (the dry gas flow meter was fitted with a P/V valve on the outlet). Pressure was measured with a differential pressure sensor (Cerabar PMC 41, Endress + Hauser) every 4 s, and 2-minute average values

were stored. The sensor range was scaled from –15 to +15 iwc (–37 to +37 hPa), with a full scale accuracy of 0.20%. We also obtained 15- and 60-minute averaged tank pressure data  $p(t)$  where averages represent the means of the 2-minute average pressure measurements taken during each time window.

## 2.3. Descriptive analysis

For the 60-minute flow rate, we calculated medians and inter quartile ranges (IQRs). To illustrate diurnal fluctuations in vapor emissions, we created box plots for the 60-minute flow rate distribution that occurred during each hour of the day. Spearman correlation coefficients between the time series for pressure and flow rate were calculated to evaluate whether pressure can be used to infer vent emissions.

To estimate the mass flow rate of gasoline  $\dot{m}_{gas}$  that is released through the vent pipe in the form of a mixture of gasoline vapors and fresh air, we assumed, following the protocol of a study by the California Air Pollution Control Officers Association (CAPCOA) that assessed risks from fuel emissions from gas station (Appendix D-2 (CAPCOA, 1997)), that the density of gasoline vapors in this mixture is given by  $\rho_{gas}^{(v)} = 0.3 \times 65 \text{ lb} / 379 \text{ ft}^3 = 0.824 \text{ kg/m}^3$ , i.e., the molar percentages of gasoline and air were 30% and 70%, respectively. Then the volumetric flow rate  $Q$  can be converted into a mass flow rate of the vaporized gasoline:

$$\dot{m}_{gas} = \rho_{gas}^{(v)} Q \quad (1)$$

To arrive at vent emission factors, we first calculated the mean volumetric flow rate  $\bar{Q}$ , and then the mean mass flow rate  $\bar{m}_{gas} = \rho_{gas}^{(v)} \bar{Q}$ . From the latter, one can calculate the vent emission factor

$$EF_{vent} = \bar{m}_{gas} / \dot{V}_{sales} \quad (2)$$

For  $EF_{vent}$ , CARB uses units of pounds of emitted gasoline vapors (also called total organic gases (TOG)) per 1000 gal dispensed, or more briefly lb/kgal where kgal stands for kilogallons.

As we were not able to measure benzene levels in the tank ullage, we assumed like the CAPCOA study (Section C) that the density of the mixture of gasoline vapors and fresh air was  $\rho_{mix}^{(v)} = 1.05 \text{ lb/ft}^3 = 1.682 \text{ kg/m}^3$  and that the emitted gasoline vapor/air mixture contained 0.3% of benzene by weight (CAPCOA, 1997). Therefore, the mass flow rate of benzene through the vent pipe was estimated as follows:

$$\dot{m}_{benz} = 0.003 \rho_{mix}^{(v)} Q \quad (3)$$

## 2.4. Air pollution modeling

We used the AERMOD Modeling System developed by the US Environmental Protection Agency (EPA) to model the dispersion of benzene vapors released into the environment through vent pipes of fuel storage tanks and from other sources (Cimorelli et al., 2005). AERMOD simulates atmospheric pollutant transport at a 1-hour temporal resolution. 3D polar grids were created with the gas station in the origin and potential receptors at different radial distances (up to 170 m) and angles (10°

increments). The grids were placed at the ground level ( $z = 0$  m), in the breathing zone ( $z = 2$  m), and at the 2nd floor level ( $z = 4$  m) where the vent pipe emissions were assumed to occur. The topography was simplified for modeling purposes consistent with the CAPCOA study (CAPCOA, 1997), i.e., the terrain was assumed to be flat with no buildings present. Vent pipe emissions were modeled as a capped point source. Chemical reactions of benzene were not modeled, as residence times of atmospheric benzene are on the order of hours or even days (ATSDR, 2007), i.e. much longer than the travel time of benzene vapors across the 340-m diameter model domain.

For the period of time when vent emission measurements were made, we obtained meteorological data at a 1-hour temporal resolution that are representative for the geographic locations of the two gas stations. Table SI-1 provides descriptive statistics of that data. The time series were used in AERMOD to model the transport of benzene in the temporally varying turbulent atmosphere. We also used the 1-hour average time series of benzene emission rates (Eq. (3)) as an input into AERMOD.

To evaluate at each grid point whether OEHHA's acute REL or AIHA's ERPG levels were exceeded at least once, we determined maximum 1-hour average benzene concentrations that were simulated for about three weeks. To evaluate how often the OEHHA REL was exceeded at each grid point in the breathing zone, we created plots indicating the number of exceedances and the day when the maximum benzene level was observed.

To facilitate comparison to published benzene measurements around gas stations, we determined for each simulated radial distance from a gas station the mean of the average concentrations simulated for each ten degree increment on the radius around the gas station.

### 3. Results: vent releases

#### 3.1. Times series of tank pressure and flow rate

Fig. 2 shows the time-series data for the volumetric flow rate  $Q$  of the gasoline vapor/air mixture through the vent pipe and tank pressure  $p$  that we collected at the two gas stations. At GS-MW, little vapor was typically released in the late night and in the very early morning, while releases were generally much higher during the daytime and evenings, presumably when more fuel was dispensed (Fig. 2a). Occasionally, no vapor releases occurred for several hours. While we do not have access to time of fuel delivery records, field visits indicate that time periods with no releases coincide with fuel deliveries. For instance, fuel delivery likely occurred on January 6 at 7 pm (see Fig. 3a; an amplification of data shown in Fig. 2a). As a result, the UST pressure dropped by about 10 hPa, far below the cracking pressure of the P/V valve. The decreased gas pressure in the ullage increased until the cracking pressure of the P/V valve was reached. A very small vapor release ( $\sim 2$  L/min) was observed briefly on the next day at 2 am. The vapor flow rate becomes relatively large again,  $\sim 12$  L/min, only after 6 am, i.e., 11 h after fuel delivery.

Fig. 3b amplifies a major vapor release at GS-MW. The UST pressure significantly exceeded the cracking pressure of the P/V valve and rose rapidly up to 37 hPa, which coincides with vapors being released at a high flow rate (15-min average) of about 470 L/min.

At GS-NW, vapor releases followed a quite different pattern (Fig. 2b). Contrary to GS-MW, vapor releases occurred in a cyclical pattern, and tended to be higher in the late night and in the very early morning when the gas station was closed.

#### 3.2. Statistics of vapor emissions

The average volumetric flow rate  $\bar{Q}$  through the vent pipe for the entire period of time during which measurements were taken was  $\bar{Q} = 7.9$  L/min for GS-MW and  $\bar{Q} = 15.4$  L/min for GS-NW, which is

consistent with the higher sales volume  $\dot{V}_{sales}$  of GS-NW. These emissions consist of a mixture of gasoline vapors and air. Using Eq. (1), the volumetric flow rates were converted into average mass flow rates of gasoline:  $\bar{m}_{gas} = 0.39$  kg/h for GS-MW and  $\bar{m}_{gas} = 0.76$  kg/h for GS-NW. Using Eq. (2), we determined a vent emission factor  $EF_{vent} = 0.17$  kg per 1000 L = 1.4 lb/kgal for GS-MW and  $EF_{vent} = 0.21$  kg per 1000 L = 1.7 lb/kgal for GS-NW.

The medians (IQRs) for the 60-minute averaged flow rate  $Q$  (L/min) were 6.1 (1.9, 10.9) for GS-MW and 16.0 (12.7, 18.4) for GS-NW. For GS-MW, the mean is larger than the median, indicating a more skewed distribution of flow rates when compared to GS-NW. Also the first quartile is much lower than the median for GS-MW, indicating that there are periods of time during which little emissions occurred. Conversely, GS-NW was releasing emissions more consistently.

Fig. 4a shows boxplots illustrating the distribution of flow rate  $Q$  for each hour of the day at GS-MW. Less vapor was released between 10 pm and 4 am, even though the gas station was in operation, albeit at lower activity levels. The flow rate  $Q$  at GS-NW (Fig. 4b) had fewer outliers, and the highest outlier was an order of magnitude lower than the highest one at GS-MW. Emissions were highest between 1 and 3 am, when the gas station was closed.

The Spearman correlation coefficients between tank pressure  $p$  and vent flow rate  $Q$  were  $r = 0.58$  for GS-MW and  $r = 0.85$  for GS-NW. Thus, vent releases are moderately and strongly correlated with tank pressure, respectively. Table 2 summarizes statistical properties of vent emissions at the two gas stations.

## 4. Results: air pollution modeling

### 4.1. Emission sources and rates

Vent pipe emissions of benzene were modeled at a 1-hour temporal resolution as described in Section 2.4. However, they are not the sole source of gasoline emissions at gas stations. Accidental spills from nozzles regularly occur near the dispensers, "refueling losses" can occur when gasoline vapors are released from the vehicle tank during refueling due to the rising liquid levels in the tanks, fuel vapors are released from permeable dispensing hoses, and "fugitive" or leakage emissions occur with driving force derived from storage tank pressure. In Section A of Supporting material, we detail how these other emission sources were modeled. Table 3 summarizes estimated mean emission rates. Note that the vent pipe losses are much greater than other losses.

### 4.2. Predicted benzene levels

Fig. 5 shows for both gas stations and at each grid point the maximum 1-hour average benzene concentration observed during the simulated periods in time. Benzene levels depend significantly on elevation within a 50-meter radius around the centers of the gas stations. Close to the centers of the gas stations, benzene levels are higher at the 4-m elevation and at ground level due to vent pipe emissions, which represent the largest emission source (Table 3). Further than 50 m away from the center, the vertical concentration differences become less obvious due to dispersion causing vertical mixing of benzene vapors.

At GS-MW, the 1-hour acute REL of  $26 \mu\text{g}/\text{m}^3$  was exceeded 160 m away from the center of the gas station, at the location ( $x = 158$  m,  $y = 28$  m) both at ground level and in the breathing zone. At grid points with a distance  $>50$  m from the center of the gas station, the REL was exceeded at most once (Fig. SI-1a). However, the exceedance at different grid points did not occur on the same day (Fig. SI-1b). Within the 20 days during the measurement campaign, exceedances occurred on the 4th and 13th of January.

At GS-NW, the furthest REL exceedance occurred at 50 m from the center of the gas station at the grid point ( $x = -38$  m,  $y = 32$  m) as

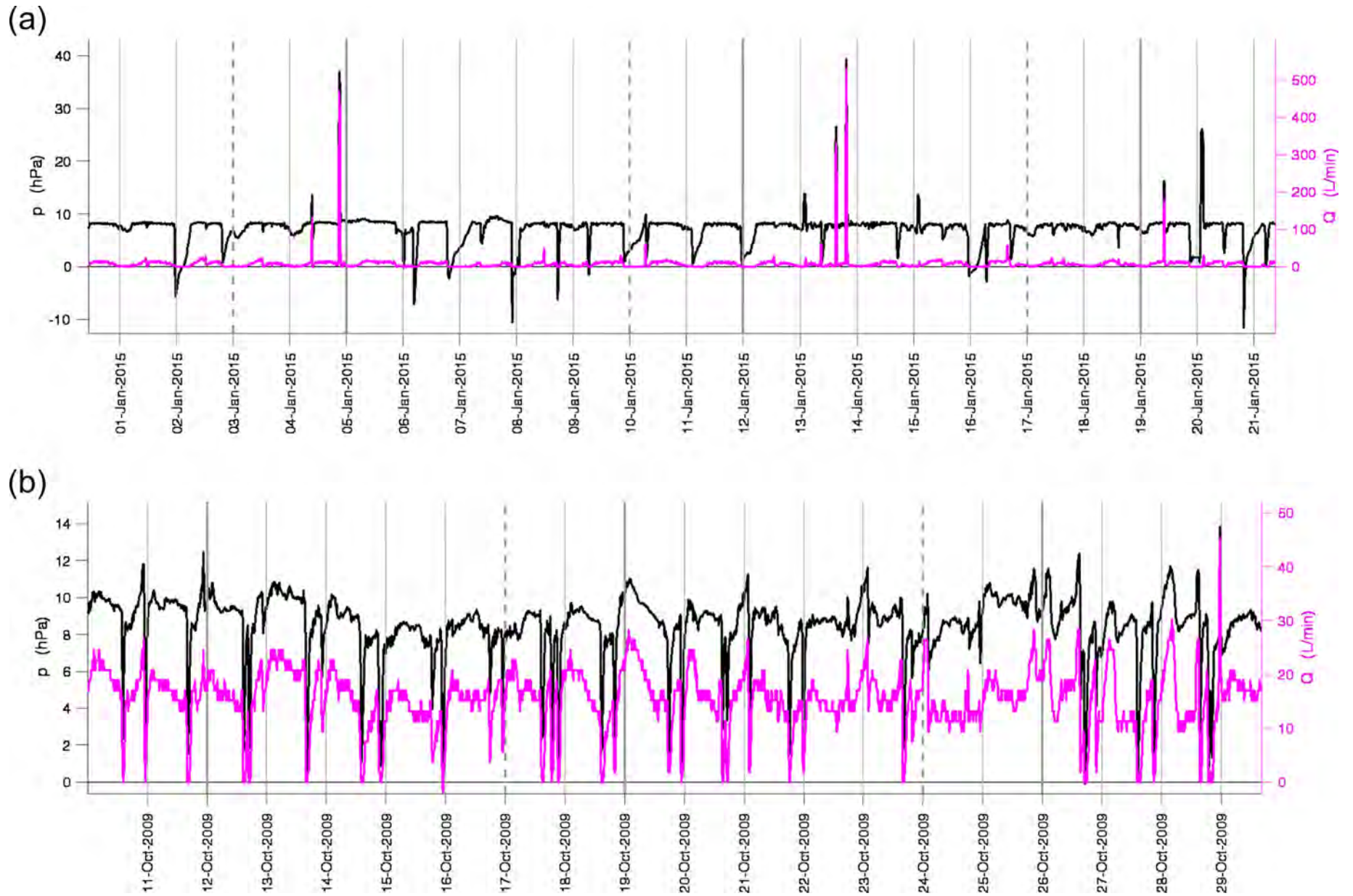
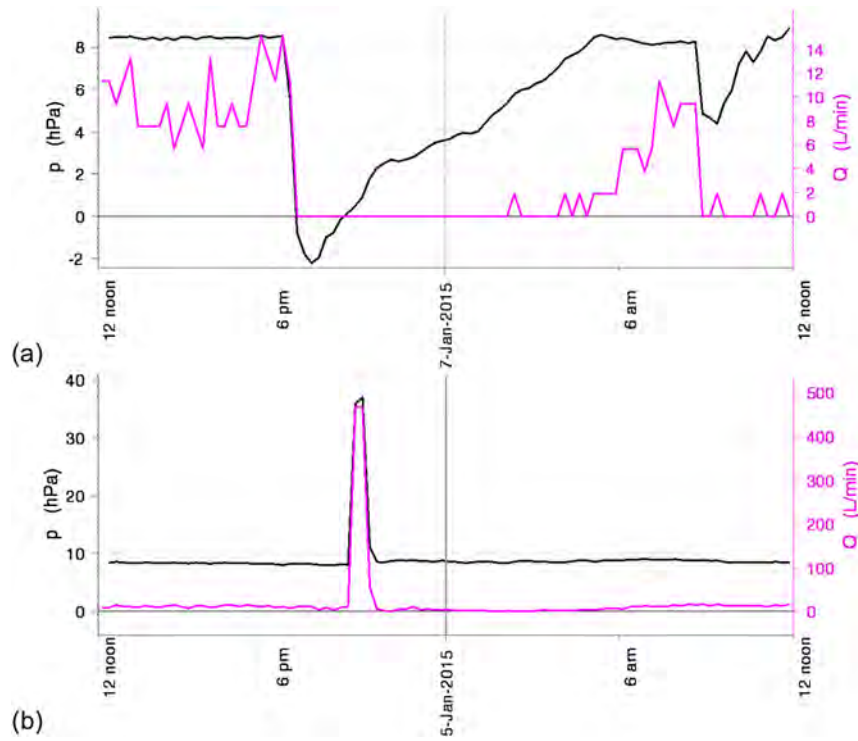
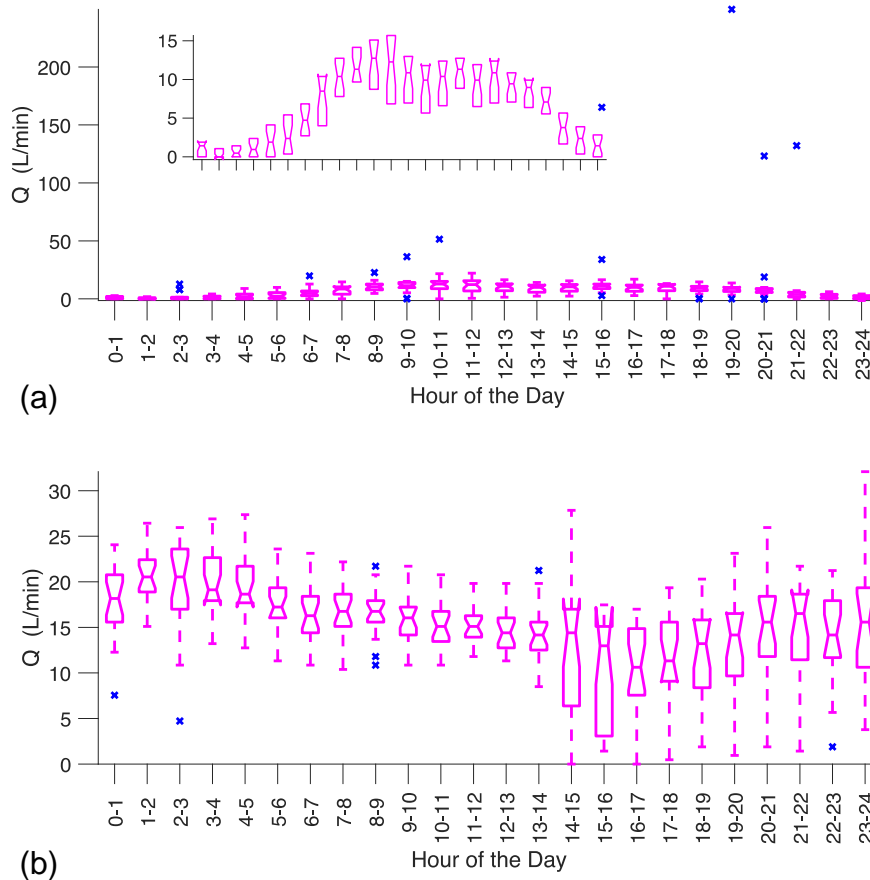


Fig. 2. Time series of ullage pressure  $p$  (left ordinate) and volumetric flow rate  $Q$  (right ordinate) for (a) GS-MW and (b) GS-NW. Horizontal tick marks indicate midnights. The vertical dashed and thick solid gray lines enclose weekends.



**Fig. 3.** Amplifications of time series data (15-minute averages) for GS-MW. (a) Tank pressure  $p$  became negative after fuel delivery. As a result, vent emission ceased for several hours. (b) A major vapor release (burst) likely occurred when the cracking pressure of the P/V valve was significantly exceeded at around 9 pm during a non-compliant bulk fuel delivery.



**Fig. 4.** Distribution of vent emissions  $Q$  observed for each hour of the day at (a) GS-MW [insert shows the IQRs of  $Q$ ] and (b) GS-NW gas stations. In (a), outliers make it difficult to recognize variations in median hourly emissions. We therefore plotted in the inset only the IQRs. Boxes indicate median and IQR, whiskers values within 1.5 the IQR, and asterisks outliers.

**Table 2**  
Summary of gas station characteristics and vent emissions.

	GS-MW	GS-NW	Units
Sales volume $\dot{V}_{sales}$	450,000	700,000	gal/month
Volumetric flow rates (of gasoline vapor/air mixture)			
Mean $\bar{Q}$	7.9	15.4	L/min
Median (IQR) of 60-min average	6.1 (1.9, 10.9)	16.0 (12.7, 18.4)	L/min
Maximum of 60-min average	250	32.1	L/min
Vent emission factor $EF_{vent}$	1.4	1.7	lb/kgal
Mass flow rates of gasoline (w/o air)			
Mean $\bar{m}_{gas}$	0.39	0.76	kg/h
Maximum of 60-min average	12.3	1.6	kg/h
Correlation coefficient Between $Q$ and $p$	0.58	0.85	–

shown in Fig. SI-2a. At a distance of 40 m, the REL was exceeded three times at one grid point (260° angle), and at 35 m four times at two grid points (250° and 260° angles) (Fig. SI-2b). At a distance of 20 m, the REL was exceeded at 30 (out of 36) grid points, and on nine different days.

Average benzene levels are shown in Fig. 6 for both gas stations. The MRL is exceeded at the elevation of the vent pipe opening,  $z = 4$  m, up to 7 m away from for GS-MW and up to 8 m from GS-NW. Fig. 7 shows the average benzene concentration as a function of distance at an elevation of 2 m. Close to the center, benzene levels first increase and then decrease.

## 5. Discussion

### 5.1. Vent emission factors

We present unique data on vent emissions from USTs at two gas stations. Emissions can be compared to vent losses assumed by CAPCOA (CAPCOA, 1997). For a gas station with Stage I and II vapor recovery technology and a P/V valve on the vent pipe of the UST (Scenario 6B), the CAPCOA study assumed loading losses of 0.084 and breathing losses of 0.025 lb/kgal dispensed. The total loss of gasoline through the vent pipe is the sum of the two and amounts to a vent emission factor  $EF_{vent} = 0.109$  lb/kgal. Based on actual measurements in two fully functioning US gas stations, we obtained  $EF_{vent}$  values of 1.4 lb/kgal for GS-MW and 1.7 lb/kgal for GS-NW, more than one order of magnitude higher than the CAPCOA estimate. While the difference between our measurements and the CAPCOA estimates may appear surprising, it is important to consider that the CAPCOA estimates are based on relatively few measurements and some unsupported assumptions (Aerovironment, 1994), particularly with regard to uncontrolled emissions due to equipment failures or defects (Appendix A-5 (CAPCOA, 1997)).

### 5.2. Pressure measurements

Tank ullage pressure  $p$  was moderately to strongly positively correlated with vent flow rate  $Q$ , likely because exceedance of the cracking pressure of the P/V valve causes a vent release. Thus pressure

**Table 3**  
Mean benzene emission rates  $\bar{m}_{benz}$  for the two gas stations.

Emission source	Benzene emissions (mg/s)	
	GS-MW	GS-NW
Vent pipe	0.80	1.55
Spillage	0.39	0.65
Refueling	0.41	0.69
Hose permeation	0.06	0.10
Total	1.67	2.90

measurements can be used to infer vent releases. Real-time detection of equipment failures and leaks via so-called in-station diagnostics systems is based on our observed correlations between  $p$  and  $Q$ .

### 5.3. Diurnal fluctuations in vent emissions

Diurnal vent emissions were quite different at the two gas stations. At GS-MW, a 24-hour operation, vent emissions were high during the daytime, presumably due to PWD. Emissions ceased at night, likely because less gasoline was dispensed and fuel deliveries with relatively cool product were frequent. Evaporative losses could also have been lower at night because the cooler delivered fuel would cause slight contraction of the liquid phase with corresponding growth in the ullage volume while at the same time lowering the vapor pressure of gasoline in the UST.

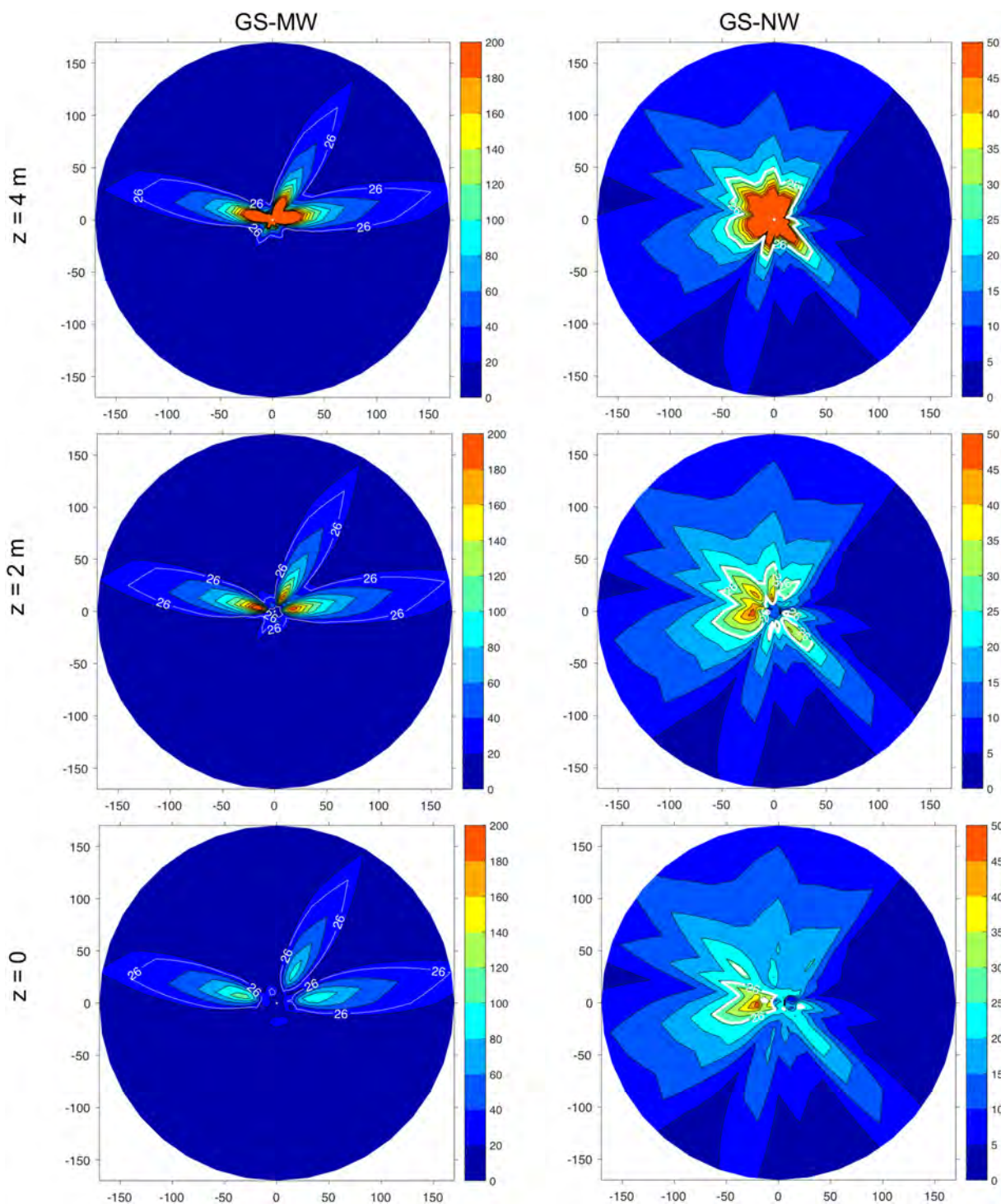
At GS-NW, vent pipe releases occurred most of the time, during the daytime when fuel was dispensed (PWD) and at night when the gas station was closed. Vent releases were higher when the gas station was closed, suggesting that during the day-time Stage II vapor recovery resulted in the injection of vapors into the storage tank that were not completely equilibrated with the liquid gasoline. During night-time, the gradual equilibration of unsaturated air in the ullage of the UST with gasoline vapors could then have caused exceedance of the cracking pressure of the P/V valve and consequently vapor release. It seems counterintuitive that less nighttime emissions occurred at the gas station where fuel was dispensed. However, while fuel is being dispensed, the outgoing liquid creates additional ullage volume, and depending on excess air ingestion rate, a negative pressure could result that lowers vent pipe emissions.

Dispensing fuel to customer vehicles and the associated Stage II vapor recovery system interact with vent emissions and can even cause vent emission during PWD, because the vacuum-assist method can negatively interfere with Onboard Refueling Vapor Recovery (ORVR) installed in customer vehicles (EPA, 2004). However, Stage II vapor recovery is not obsolete. It can be used in conjunction with ORVR to minimize exposure of gas station customers and workers to benzene due to working losses (Cruz-Nunez et al., 2003), particularly when customer vehicles are not equipped with ORVR (e.g., older vehicles, boats, motorcycles) or small volume gasoline containers are refueled. Enhanced Stage II vapor recovery technology can significantly reduce vapor emissions both at the nozzle and from UST vent pipes (CARB, 2013).

### 5.4. Fuel deliveries and accidental vent releases

Based on observations and interpretation of time series of the tank pressure data, it is likely that the peak vent emissions (e.g., Fig. 3b) were partly due to non-compliant bulk fuel drops where the Stage I vapor recovery system either was not correctly hooked up by the delivery driver or to hardware problems with piping and/or valves. This



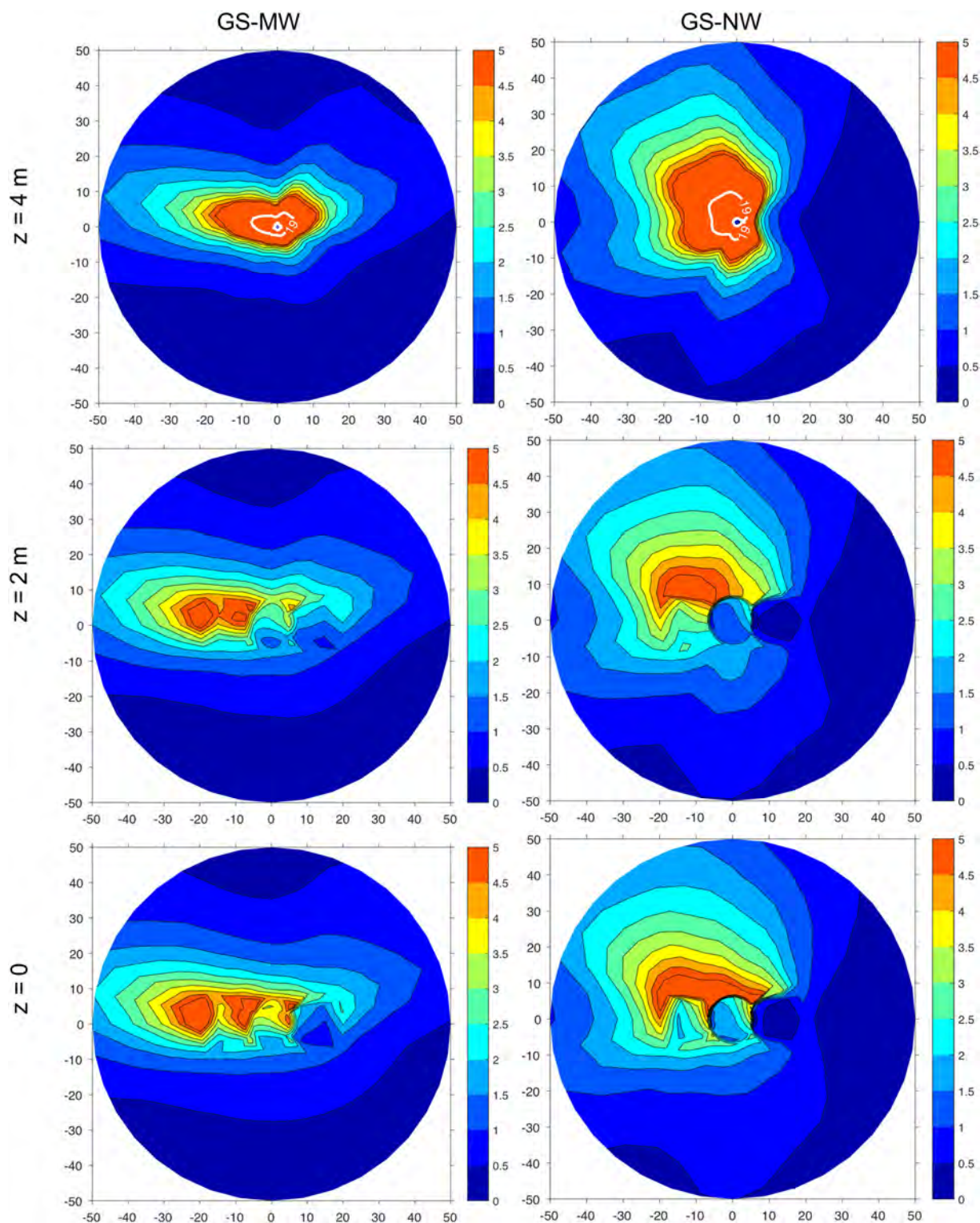


**Fig. 5.** Modeled maximum benzene concentrations for GS-MW and GS-NW at three different elevations  $z$ . The  $x$ - and  $y$ -axes indicate horizontal coordinates in meters. The color indicates benzene levels in units of  $\mu\text{g}/\text{m}^3$ . Left column: time series of benzene emission rates were used. Right column: average benzene emission rate was used in the modeling. The white isoline indicates OEHHA's acute REL of  $26 \mu\text{g}/\text{m}^3 = 8 \text{ ppb}$ .

conjecture is consistent with typical US storage tank volumes (~10,000 to 30,000 gal). Assuming that Phase I vapor recovery did not work at all and that 10,000 gal (~38,000 L) of fuel were delivered, the working loss (volume of gasoline vapor/air mixture released to the atmosphere through the vent pipe) is 38,000 L. It is also reasonable to assume that delivery lasted less than 1 h. According to Table 2, the maximum hourly flow rate through the vent pipe was 250 L/min at GS-MW, which would result in a maximum cumulative vapor release of 15,000 L within this hour. The measured maximum cumulative release underestimates the

assumed working loss of 38,000 L. This could be due to a fuel delivery, which involved dropping fuel from multiple compartments of a tanker truck, with the vapor return hose not being correctly hooked up for only some of the emptied compartments.

At GS-MW, UST pressure decreased after fuel delivery (causing vent emissions to cease for several hours) during the climatic conditions prevalent during the observation period, behavior not observed at GS-NW. In practice, it is possible to observe both positive and negative pressure excursions, even during the same fuel delivery (when multiple fuel



**Fig. 6.** Modeled average benzene concentrations for GS-MW and GS-NW at three different elevations  $z$ . The  $x$ - and  $y$ -axes indicate horizontal coordinates in meters. The color indicates benzene levels in  $\mu\text{g}/\text{m}^3$  and the white isoline the MRL of  $19 \mu\text{g}/\text{m}^3 = 6 \text{ ppb}$ .

compartments of tanker trucks are unloaded), when Stage I vapor recovery is in place (personal observation by TT).

##### 5.5. Exceedance of 1-hour exposure limits

AERMOD air pollution modeling suggests that at GS-MW the 1-hour acute REL was exceeded at one grid point 160 m (525 ft) from the center of the gas station once in 20 days (Fig. 5). This distance

is larger than the 300-ft (91 m) setback distance recommended by CARB for a large gasoline dispensing facility (CalEPA/CARB, 2005). Assuming the gas station's fence line is <225 ft. (69 m) from its center (where the vent pipe was assumed to be located), our study shows that sensitive land uses at a distance further than 300 ft from the fence line of the gas station would represent a health concern despite compliance with the CARB guidelines because of non-compliance with the acute REL.

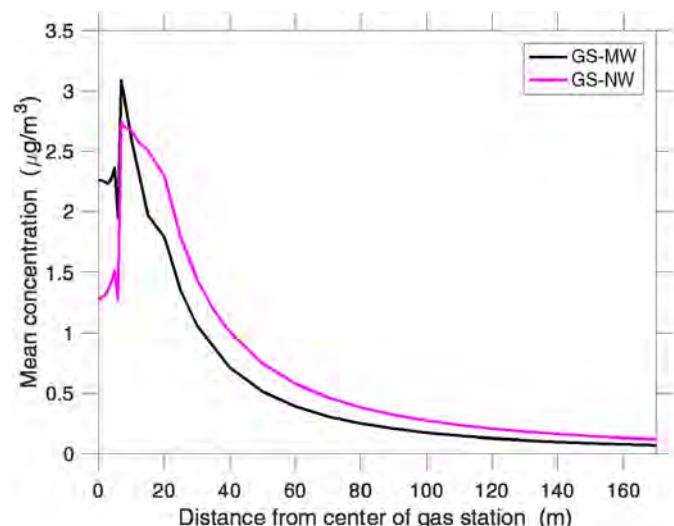


Fig. 7. Mean benzene concentrations as a function of distance from the center of the gas stations.

At any location further than 50 m from the gas station's center, the REL was exceeded at most once during the 20-day measurement campaign (Fig. SI-1a). However, exceedance occurred at several locations, and on two different days (Fig. SI-1b). E.g., at a distance of 120 m from the center, the REL was exceeded at three grid points, and the number of grid points increased with closer proximity to the gas station. This suggests that it was not just a single worst-case scenario or a single accidental vapor release that led to REL exceedance; rather exceedance may occur more frequently than is anticipated. Prevalent wind directions during the measurement campaign explained the directional patterns of exceedances (see the wind rose in Fig. SI-3a).

At GS-NW, despite its higher sales volume, the REL was exceeded only closer than 50 m from the gas station's center. However, exceedance occurred much more frequently (Fig. SI-2), likely because of the higher sales volume of GS-NW. Again, the wind rose for GS-NW (Fig. SI-3b) explains spatial patterns of REL exceedance.

None of AIHA's three ERPG levels were exceeded, meaning that individuals, except perhaps sensitive members of the public, would not have experienced more than mild, transient adverse health effects.

### 5.6. Average benzene levels

The initial increase in average benzene levels when moving away from the gas stations' centers (Fig. 7) is likely due to the vent emissions (at 4 m) which represent the largest benzene source, and which require a certain transport distance until they reach the 2-m level through dispersion. Further away from the gas station, benzene levels are higher for GS-NW than for GS-MW likely because of the higher sales volume of GS-NW. However, close to the center, benzene levels are higher at GS-MW. This can be attributed to the higher wind speeds at GS-NW (Table SI-1), which result in greater initial dilution of emitted pollutants in the incoming airstream and also in greater subsequent pollutant dispersion.

Modeled average benzene concentrations are generally lower ( $\sim 10 \mu\text{g}/\text{m}^3$  or less) than those measured in the surroundings of gas stations, likely because our simulations do not account for traffic-related air pollution (TRAP). For instance, a study published by the Canadian petroleum industry found average benzene concentrations of 146 and 461 ppb (466 and  $1473 \mu\text{g}/\text{m}^3$ ) at the gas station property boundary in summer and winter, respectively (Akland, 1993), values orders of magnitudes higher than ours. A South Korean study examined outdoor and indoor benzene concentrations at numerous residences within 30 m and between 60 and 100 m of gas stations and found median outdoor benzene concentrations of 9.9 and  $6.0 \mu\text{g}/\text{m}^3$ , respectively (Jo &

Moon, 1999), while we simulated benzene levels on the order of  $1 \mu\text{g}/\text{m}^3$  (Fig. 7). In a study on atmospheric BTEX levels in an urban area in Iran, the three highest BTEX levels were measured near gas stations ( $\sim 150$  m away); the measured benzene levels ( $64 \pm 36$ ,  $31 \pm 28$ ,  $52 \pm 26 \mu\text{g}/\text{m}^3$ ) were again much higher than ours simulated at that distance, likely due to TRAP. Our modeled average benzene levels at a distance of about 50 m are on the same order as background benzene levels of  $1.0 \mu\text{g}/\text{m}^3$  that were measured in 2010 in the National Air Toxics Trend Sites (NATTS) network of 27 stations located in most major urban areas in the US (Strum & Scheffe, 2016). However, our modeled levels at a distance of 170 m were 0.07 at GS-MW and 0.12 at GS-NW, a non-negligible addition to urban background levels.

At both gas stations, the MRL was exceeded at the level of the vent pipe opening in the vicinity of the gas stations, up to 7 m away from the vent pipe at GS-MW and 8 m at GS-NW. Therefore there might be an appreciable risk of adverse noncancer health effects for individuals living at the 2nd-floor level relatively close to high-volume gas stations such as GS-MW and GS-NW.

### 5.7. Limitations

A limitation of our study is that data were collected only in fall and winter. Results cannot be easily extrapolated to other seasons, because vent pipe emissions are seasonally dependent, e.g., due to seasonally dependent gasoline formulations and meteorological conditions. However, modeled exceedance of the OEHHA acute REL in the winter season is already of concern, because that REL was developed for once per month or less exposures.

Another limitation is that we did not directly measure benzene levels in the vent pipe, and instead made assumptions about vapor composition that were also made in the CAPCOA study (CAPCOA, 1997) of gas station emissions. In practice it may be difficult to obtain permission from gas station owners to measure benzene levels directly.

In part because we did not want to reveal the locations of the gas stations, we did not use site-specific topography information in the air dispersion modeling and instead assumed flat terrain. While this simplification results in less accurate air pollution predictions for the two sites, using a "generic" gas station is perhaps more representative of other gas station sites, and is consistent with an approach used in a previous study (CAPCOA, 1997).

Finally, our study did not predict benzene levels in indoor environments. Even though indoor air pollution levels may substantially differ from outdoor levels due to indoor sources (e.g., smoking, photocopying) (El-Hashemy & Ali, 2018), our study can still inform exposure levels in indoor environments as outdoor sources may be the main contributors to indoor air pollution, e.g., in buildings situated in urban areas and close to industrial zones or streets with heavy traffic (Jones, 1999). This is relevant to workers and customers in C-stores or other fast-food/gasoline station combination facilities.

## 6. Conclusions

Our study is to the best of our knowledge the first one to (1) report hourly vent emission data for gasoline storage tanks in the peer-reviewed literature and (2) use these data in hourly simulations of atmospheric benzene vapor transport. This allowed us to examine potential exceedance of short-term exposure limits for benzene. Prior studies including CAPCOA's (CAPCOA, 1997) could not do so as average emission rates were used (only meteorological data was used at an hourly resolution).

Our findings support the need to revisit setback distances for gas stations, which are based on >2-decade old estimates of vent emissions (Aerovironment, 1994). Also, CARB setback distances are based on a binary decision, related to whether the gasoline sales volume  $\dot{V}_{\text{sales}}$  is  $>3.6$  million gal per year. Our data support, however, that setback

distances should be a continuous function of sales volume  $\dot{V}_{sales}$  and also include the type of controls installed at the facility. Setback distances should also address health outcomes other than cancer. OEHHA's acute REL for benzene could be used to inform setback distances as it accounts for non-cancer adverse health effects of benzene and its metabolites (Budroe, 2014). ATSDR's MRL could also be considered since it is a health-based limit.

We note that CARB recommended their setback distances in 2005, presumably assuming pollution prevention technology yielding a 90% reduction in benzene emissions (CalEPA/CARB, 2005). Since then, CARB further promoted use of second-generation vapor recovery technology (Enhanced Vapor Recovery, EVR) to reduce emissions further. EVR includes technology that is supposed to prevent fuel vapors in overpressurized tanks from being expelled into the atmosphere (CARB, 2017). To that end, “bladder tanks” have been proposed, into which the gasoline vapor/air mixture is directed as the pressure in the combined ullage space of the storage tank increases, and from which the mixture is redirected into the fuel storage tanks if the ullage pressure becomes negative (when fuel is dispensed). The challenge with such a system is to ensure that the bladder tank capacity is not exceeded by the fuel evaporation rate. Alternatively, fuel vapor release can be reduced by processing the fuel/air mixture through either a semi-permeable membrane which selectively exhausts clean air and returns enriched fuel vapor (Semenova, 2004) or an activated carbon filter which adsorbs hydrocarbons (and water vapor) and exhausts air into the atmosphere, or by combusting the fuel/air mixture which would otherwise be released through the P/V valve. Therefore, current CARB setback distances might be adequate for gas stations in California but less so for the other 49 US states, and other countries—depending on pollution prevention technology requirements.

The larger areal extent of modeled REL exceedance at GS-MW is due to “accidental” releases of gasoline vapors. Even though regulations appear generally not to be driven by accidental releases, at GS-NW such releases likely led on two different days to REL exceedances at distances beyond CARB's recommended setback distances. Policies should address accidental fuel vapor releases that depending on pollution prevention technology (here Stage I vapor recovery) and its proper functioning can occur on a frequent basis (twice at GS-MW within about three weeks).

In future work, potential exceedance of other shorter-term exposure limits should be examined, e.g., the 15-minute short-term exposure limits (STELs) and the 8-hour time-weighted averages (TWAs) used for occupational exposures.

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## Competing financial interest declaration

TT directs a company (ARID), which develops technologies for reducing fuel emissions from gasoline-handling operations. AMR, BAM and MH have no conflicts of interests to declare.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.09.303>.

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## **Other Studies Regarding Health Effects of Gas Stations**

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## Assessing the impact of petrol stations on their immediate surroundings.

Morales Terrés IM<sup>1</sup>, Miñarro MD, Ferradas EG, Caracena AB, Rico JB.

Author information

### Abstract

This paper describes a novel methodology for evaluating the extent to which petrol stations affect their surroundings. The method is based on the fact that the ratio of the concentrations of aliphatic and aromatic hydrocarbon pollutants in the air of the petrol stations and their surroundings (basically determined by vapor emissions from unburned gasoline) differs from the ratio found in urban air, which is mainly influenced by traffic emissions. Bearing this in mind, the spatial limit of influence of petrol stations in any direction would be the first point, moving away from the station, where the ratio becomes equal to the urban background ratio. Application of the methodology involves multipoint measuring campaigns of the air at the studied petrol station and built-up area in general and processing the data with software capable of providing isoconcentration contours. The procedure should help local authorities in terms of land management, so that a "belt" can be established around petrol stations where housing or vulnerable populations and activities such as those in schools, hospitals and community centers should be restricted.

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# Exposure of the General Population to Gasoline

by Gerald G. Akland

This paper summarizes the currently available information on gasoline exposure to the general population. In general, the largest contribution to the time weighted exposures results from exposures while indoors, which are influenced by the outside air, indoor sources, and attached garages. Personal activities, including refueling and commuting, contribute significantly higher exposures but last for only a small portion of the 24-hr time weighted average. The highest exposed group includes those individuals living near large service stations and those with contaminated water supplies.

## Introduction

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary to establish sound regulatory policy. There is an increasing awareness of the need for exposure information as part of this risk-based approach to environmental standard setting. This need is equal for exposure information as it relates to gasoline exposures. Because gasoline contributes to virtually everyone's daily exposure as a result of traffic emissions, there is clearly a need to understand the significance of this exposure as it relates to public health. Accordingly, it is not surprising that the sponsors of the International Symposium on the Health Effects of Gasoline wanted an overview of gasoline exposures to the general population. In particular, the organizers wanted information about what people were being exposed to, when they were exposed, where and for how long, and who made up the "sensitive population subgroups" exposed to all the numerous constituents of gasoline. With this information, the health scientists could debate the toxicological importance of the many constituents of gasoline. This information could then provide a basis for understanding the health risks of gasoline and help prepare us for the inevitable changes in the fuel composition already in progress, including the change to clean fuels. It is therefore the objective of this paper to summarize the available general population exposure information. This task has been made easier as a result of a contract effort by ENVIRON Corporation of Arlington, Virginia, funded by the American Petroleum Institute. The results of this

contract as well as other research were presented in a conference about 1 year ago sponsored by the American Petroleum Institute on Exposures to Gasoline (1).

## Exposure Concepts

"Exposure" has been used in many different ways when applied to environmental or human health effects studies. In this paper, exposure is defined as the joint occurrence of two events: The pollutant of a measurable concentration is present at a particular location at a particular time, and the person is present at the same time and location. Exposure is characterized by who is exposed, to what pollutant, how the exposure occurred (through air, water, soil, food), where the exposure occurred (route—inhala-tion, ingestion, dermal contact) and when (time pattern). This definition is consistent with the definition given by the National Academy of Science report (2) and the recently completed EPA Guidelines on Exposure Assessment (3). Total human exposure accounts for all exposures to a specific contaminant regardless of environmental medium or route of entry (4).

Traditionally, air pollutant exposure has meant exposure to ambient air. Environmental scientists have recognized that measurements at outdoor monitoring sites provide a severely limited estimate of personal exposure. Concerns about the adequacy of ambient measurements have been increased by our recent comprehension of the impact of the proportion of time that most individuals spend indoors. Because we spend most of our time indoors (approximately 90%, i.e., 21.5 hr), it follows that the pollutant levels experienced within these microenvironments weigh heavily on one's total exposure for a given pollutant (5). No matter how toxic a chemical might be, if people do not come into contact with the chemical, there is no exposure or public health risk from that chemical.

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Exposure assessment is a critical component of the risk assessment. An exposure assessment includes the identification of the appropriate sources, microenvironments with potentially high concentrations, and factors that when combined with the emissions products result in increased risks to the exposed human populations and ecosystems. The major elements of an exposure assessment are: *a*) identifying and quantifying source emissions and transformation products (source characterization and fate); *b*) understanding the movement of pollutants to exposed populations (both humans and ecosystems) and identifying exposure route(s); *c*) determining the concentration of the substance in various media and microenvironments; *d*) assessing exposure from all sources; *e*) determining the magnitude, duration, frequency, and probability of exposure and the percentage of a population exposed above specified levels of health or ecosystem concern; and *f*) determining the amount of a pollutant to which the subject is exposed actually enters the subject.

In the absence of exposure information, the typical exposure assessment has relied on standard assumptions, such as a 70-kg man who spends 24 hr each day of his life on his porch being exposed to the ambient air (commonly referred to as the "porch potato"). Air exposure is estimated by "exposure models," which are generally air pollution dispersion models designed to provide a reasonable estimate of a pollutant concentration at a fixed point in space. In general, this is the state of exposure science today for most pollutants under regulatory consideration. Within this list of pollutants is the complex, constantly changing mixture we call gasoline. The available information on gasoline exposures is summarized in the following sections.

## Gasoline Exposures

As highlighted by the Workshop on Gasoline Exposures, little is known about personal exposures for even the inhalation pathway. What we have learned is primarily the result of TEAM studies (6) using benzene as the surrogate chemical for automotive emissions. Unfortunately, TEAM studies do not provide much information needed to understand exposures to gasoline. For example, Table 1 lists nine microenvironments or activities identified at the workshop as needing additional exposure data. TEAM studies provide us with some information about exposures at home, at work (nonoccupational), and outside ambient exposures. Other microenvironments (worker exposures, underground leaks, fence-line community exposures, and parking

garages) are not specifically addressed in the TEAM study design, or the data are severely limited by time integration of the sampling methodology (e.g., 12-hr sample integration [exposures at service stations and exposures in transit]).

In contrast, we know a lot about the chemistry and automotive emissions of gasoline. For example, liquid gasoline is a complex mixture that consists of many constituents that vary from company to company, region to region, season to season, and year to year. The use of aromatic compounds in gasoline has increased over the past decade to boost automobile performance. In 1980, U.S. unleaded gasoline contained approximately 22% aromatic hydrocarbons. Typical blends of unleaded gasoline today contain about 33% (7). One aromatic compound in gasoline, benzene, is generally present in small amounts (<5% by volume, typically about 1.5%).

Gasoline vapor has significantly lower amounts of aromatic compounds than the liquid phase of gasoline. For example, at 25°C under equilibrium conditions, gasoline vapor contains approximately 2% aromatic compounds (8). Benzene typically averages less than 1% (0.7%). Benzene will be the primary compound characterized in this paper because it is the compound that has the most information by which to judge human exposures to gasoline-related emissions.

Motor vehicles emit organic compounds from a variety of sources, generally categorized according to tailpipe, parking (diurnal and hot soak), and running loss (evaporative and refueling emissions). The relative contribution of each depends on fuel characteristics and vehicle operating conditions (e.g., speed and temperature). Light-duty gasoline vehicles are responsible for more than 90% of the motor vehicle nonmethane hydrocarbon (NMHC) emissions. Approximately 50% of the emissions occur from the tailpipe during routine operations, 45% is due to evaporative losses, and 5% while refueling. Between 1975 and 1990, fleet average NMHC emissions decreased more than 70%, of which 4% or less is benzene.

Mobile sources account for 85% of the total benzene emissions in the United States. Of this amount, 70% comes from exhaust, 14% from evaporative emissions, and 1% from motor vehicle refueling (9). Opportunities for human exposure to gasoline and gasoline combustion byproducts are abundant. Whereas relatively few people are occupationally engaged in the production, distribution, and storage of gasoline where there may be greater opportunities for high exposure (both in time and concentration levels), virtually the entire population is exposed nonoccupationally through exposures to gasoline engine emission products found in the ambient air or while driving their vehicles. In addition, a large portion of the U.S. population (about 110 million) engages in refueling their vehicles, others live downwind of refineries and major storage and transfer facilities, have homes with attached garages where evaporation of gasoline vapors may seep into the homes, and may find their source of drinking water has been contaminated from leakage of gasoline into the water supply. These nonoccupational exposures to gasoline generally occur through inhalation (air), with the exception of

**Table 1. Ranking of exposure microenvironments/activities based on data need and potential for maximum exposure.**

Occupational exposures
Homes with contaminated water source
Fence-line community exposures
Home exposures
General population at work
In-transit exposure
Parking garages
Urban air (ambient exposures)

exposures caused by underground leaks, which may lead to multimedia exposures. The exposures measured in each of the above-mentioned microenvironments (ambient air, refueling, fenceline, parking garages, etc.) will be described based on the available information.

## Inhalation Exposures

### Ambient (Outdoor) Concentrations

Ambient levels become the reference to which additional concentration levels are added. For example, concentration levels within the indoor microenvironment (described below) are some function of the outdoor levels plus the contribution from the indoor sources and activities. Accordingly, the ambient concentration levels are the first microenvironment of concern in this paper.

Several investigators have measured benzene over the past 20 years. Shah (10) summarized a database consisting of over 5400 measurements he had compiled wherein the average value was 3.3 ppb, which is 1.3 ppb larger than the average reported by Wallace (6). Wallace (11) offers an explanation for these differences as a result of differences in sampling locations (TEAM outdoor measurements were primarily in residential areas instead of the commercial center city data reported by Shah). A more recent EPA investigation of 6 A.M.–9 A.M. average concentrations in U.S. cities showed the median of the median values of the 39 cities to be 2 ppb in 1984–1986, with median values by city ranging from less than 1 ppb to 5.7 ppb (12). Sexton and Westberg (13) reported 6 A.M.–9 A.M. geometric mean values ranging in seven cities from 6 ppb in Houston, Texas, to 2.7 ppb in Washington, DC. In contrast, rural areas have geometric values of less than 0.5 ppb. These results clearly establish the importance of the automobile as a source of benzene values. Furthermore, a factor of three about the average benzene concentration might be expected from urban area to urban area depending on the sample location and time of sample collection and/or the availability of additional stationary source emissions (e.g., concentrated oil refinery and petrochemical operations as in Houston, Texas).

### Concentration Levels Near Service Stations, Bulk Terminals, and Refineries

Benzene exposures to people living in the vicinity of service stations, bulk plants, bulk terminals, and refineries may be increased above average ambient levels when the wind direction distributes emissions that may occur from these facilities to the nearby residences. However, in the TEAM studies conducted in Bayonne and Elizabeth, New Jersey, people living within 1 km of chemical and petroleum refineries did not have elevated exposures as compared to those people living more than 1 km from these sources (14). In contrast, a number of microenvironmental studies have been conducted that characterize gasoline vapor exposures at service stations. In particular, the Petroleum Association for Conservation of the Canadian Environment (15,16) collected and analyzed samples at the

boundaries of service stations. They reported mean concentration levels of 146 ppb in the summer and 461 ppb in the winter, with corresponding maxima of 2277 and 5417 ppb, respectively. These results should be considered as of very short-term duration and are likely to be higher than those observed at residences located adjacent to the service station properties.

To obtain a more realistic estimate of actual concentrations at the residence, the data were adjusted based on findings by Bond et al. (17) that concentrations away from the pump were typically 2% of the concentrations at the pump, with a maximum of about 10%. This would result in indoor levels of about 6 ppb and outdoor levels of 540 ppb for people living right at the boundary of the service station property. However, these values are probably extremely high when viewed by data published by the Northeast States for Coordinated Use Management (NESCAUM) (18), which estimated annual benzene levels to average 0.04 ppb with an upper limit of 0.16 ppb for residents in neighborhoods near (within 30–200 m downwind) service stations. Because these values are below typical outdoor values in the United States, it is clear that we have great uncertainty in our exposure estimates.

There is little information available in the literature about gasoline vapors in the vicinity of bulk plants (there are some 15,000 in the United States). Exxon (19) published fenceline measurements of benzene vapor concentrations at four refinery plant complexes located in the United States, showing that the concentrations were 1 to 4 ppb. Westberg and Lamb (8) reported 24-hr ambient benzene concentrations at distances greater than 1 km from the refinery perimeter to range from 1 to 4.3 ppb, the typical urban monitoring average concentration. This confirms Wallace's conclusion that refineries and chemical manufacturing plants do not contribute to one's total exposure in any discernible way (14).

### Indoor Residential Concentrations

Several indoor air studies of volatile organic compounds, including benzene, have been carried out. In the United States, Wallace and Pellizzari (20) reported indoor air concentrations in homes without smokers averaged 3.1 and 1.5 ppb during the fall and winter and spring and summer, respectively. In contrast, homes with smokers averaged 5.3 and 1.6 ppb, over the same time periods, respectively, with an average increase of approximately 1.2 ppb benzene in homes with smokers. These findings are similar to those obtained in homes in Holland (21) and West Germany (22). The few measurements of benzene in office buildings generally have shown no increase in indoor air levels above those found in the outdoor air.

There are a number of consumer products, surface coatings, and materials found indoors that emit benzene vapors, such as latex paints, adhesives, marking pens, and rubber products. Even though each of these materials and products emit small amounts, when combined they account for about 20% of the total population exposure to benzene (10) because of the amount of time spent near these sources.

## Residential Garages

There is little information in the literature that documents the levels of benzene concentrations inside garages. One study (23) indicated that garage levels were 16 times higher in the summer than outdoor levels and three times higher in the winter. The concentrations reported were 24 ppb in the summer and 8 ppb in the winter. The authors conclude that evaporative emissions from automobiles and the storage of fuels and solvents in the garage were the likely sources for the higher levels (23). There also may be evaporative contributions from other mechanical devices often found in the garages, such as power lawn mowers and chain saws. The extent to which these may add to the total concentrations measured was not quantified.

## Other Routes of Exposure

### Drinking Water

Surveys of the U.S. drinking water supplies have rarely found benzene levels above the detection limit. Letkiewicz et al. (24) estimated that 99.8% of all the groundwater systems contain either no benzene or levels below 0.5  $\mu\text{g/L}$ ; an additional 118 systems were estimated to have levels between 0.5 and 5  $\mu\text{g/L}$ , and no systems were expected to exceed 5  $\mu\text{g/L}$ . Of the 11,202 surface water systems, all were expected to have benzene levels below 0.5  $\mu\text{g/L}$ . However, discharges into the soil or groundwater have become an important concern for many state and local health officials. Because there are approximately 1.4 million underground storage tanks, with some 20 to 35% leaking (25), the potential for contamination of the water supply can be a significant concern for exposures. The affected water can enter a house through the plumbing (faucets, commodes, showers/baths, washing machines, and dishwashers), which can lead to exposures through ingestion of water or food, inhalation of vapors released from sources of water in the house, and dermal contact via bathing/showering or in other uses of water such as washing dishes. Benzene levels in homes where there has been a contaminated water source have been measured, but the levels are generally less than 1 ppb (18). However, severely contaminated homes may have levels in excess of 20 ppb, with peak concentrations in the bathroom while showering in excess of 160 ppb. Peak concentrations while showering represent a 6-fold increase over the drinking water concentration (18).

### Auto-related Activities

Exposure to automobile exhaust while in an automobile and pumping gas results in increased personal exposure to benzene. (In addition, benzene vapors are emitted from parked cars after being driven, which has an impact on concentrations in garages, as noted above.) Available information about each of these microenvironments/activities is described below.

**Self-serve Automobile Refueling.** Exposures to gasoline and its vapors at self-serve stations result from: a) vapors displaced from the filler tubes and gas tanks

during refueling, b) fuel spills during refueling, c) loss of vapors from vented underground storage tanks, and d) evaporative and tailpipe emissions from other automobiles present. Exposures can occur during refueling and during nonfueling time spent at the service station. Based on studies summarized by NESCAUM (18), the range of average benzene levels was 164 to 1100 ppb, with upper limits of 4200 ppb. The Petroleum Association for Conservation of the Canadian Environment (15,16) conducted a study in five Canadian cities (Halifax, Montreal, Toronto, Calgary, and Vancouver) in the summer of 1985 and the winter of 1986. Benzene concentrations ranged up to 7070 ppb with an average of 1130 ppb for the summer, and in excess of 10,000 ppb with an average of 1250 ppb for the winter.

The U.S. EPA (26) estimated in 1984 that approximately 70% of the gasoline was dispensed by self-service pumps (a percentage that is likely low compared to today). With at least 158 million U.S. automobile drivers, this translates into more than 110 million people being exposed while engaged in self-serve automobile refueling, which usually lasts 2 min or less. NESCAUM (18) has estimated that the annual number of station visits is 70, with the average time at a station lasting 5 min. This results in an average yearly time of 350 min (about 6 hr) at a service station. NESCAUM provides an extreme case of 262 min per year (18), which is likely to be low for multicar families with one individual performing the fueling activity.

**Auto Travel.** Benzene exposures increase in proportion to the time spent in the car. Wallace (11) calculated that while in the car, exposures increased by a factor of 3–4 over normal exposures (15–20 ppb). The average commute time one way is about 40 min, which results in about 30 ppb during each commute. In-vehicle concentrations of benzene were also recorded in a study conducted in the South Coast Air Basin of California (27). During the trips that averaged 33 min in duration (typical of local commuters), in-vehicle levels averaged 13 ppb, 2–4 times the ambient levels measured at fixed sites. These levels were higher in the winter (16 ppb) than in summer (10 ppb), with maximum levels recorded over 80 ppb during the study. It was noted that when average speeds were below 25 mph, the concentrations were significantly higher (by 4 ppb). In another study of in-transit exposures, Chan et al. (28) observed lower benzene levels in their simulated study of travel around the EPA facility in Research Triangle Park, North Carolina (3–4 ppb average, with maximum levels of 15 ppb), which were about six times the value measured at fixed sites throughout the area.

**Other Activities.** Exposure to gasoline and gasoline vapors can occur through other activities, although actual concentrations are generally not known. For example, it is known that people receive relatively higher exposures to carbon monoxide while using chain saws and other gasoline-powered appliances in and around the home. Therefore, it is reasonable to assume that exposures to the other gasoline emissions, including benzene, are likely. The actual exposure levels are not known; however, a doubling of the ambient levels would be a first approximation to the exposure levels experienced while operating the equipment.

Table 2. Estimated daily benzene exposures based on microenvironmental concentrations (ppb).

		Indoor, 1320 min		Attached garage, 5 min	Outdoor	In transit, 80 min	Refueling, 5 min	Time-weighted exposure, 1440 min
		Home	Showering <sup>a</sup>					
Urban environments	Average	4		16.0	3	13	630	6.7
	Maximum	27		48	6	80	1000	33.0
Near gas station (fenceline)	Average	6		16.0	300	13	630	14.7
	Maximum	540		588	5400	80	1000	617
Contaminated groundwater	Average	20	1500	16.0	3	13	630	42.0
	Maximum	200	6000	48	6	80	1000	272

<sup>a</sup>While showering (5 min).

## Synthesizing Exposure Information

Driven by the fact that health officials must use data whether it is good or bad, I will calculate what Wallace (11) describes as an "exposure budget" for the average non-occupationally exposed individual and the maximally exposed individual. This budget will be estimated based on the data available for each of the previously discussed microenvironments and activities that are influenced by gasoline sources. This calculation does not include the influence of other sources of benzene, most notably the effect of smoking. For the individuals who smoke or who spend time in microenvironments that are occupied or have been occupied in the recent past by active smokers, there would be an increased total benzene exposure. Other activities such as painting, working with solvents, etc., would likewise increase these exposure levels.

Table 2 summarizes the results of this analysis, which is the calculation of concentrations in the microenvironments listed across the top of the table multiplied by the estimate of time people spend in these microenvironments. It can be seen that the average person is likely to have an average exposure of no more than 6.7 ppb, but if the residence has a contaminated water supply from a leaking gasoline source, then the average exposure could be about six times greater, to 42 ppb. In the extreme, the highest exposure might exceed 270 ppb if there were the underground water source, or 600 ppb for an individual who might live within the immediate property of a very large gasoline station.

Estimates such as these are imprecise and especially vulnerable to errors in the measurements (or mathematical estimates) that were used to calculate the exposures. However, within the constraints and assumptions given, it provides a ballpark upper exposure limit, and it also serves to emphasize just how important some microenvironments potentially can be for the total contribution to one's exposure. In the benzene example, if only the outdoor concentrations were increased by a factor of 10, the resulting impact on total exposure would be less than 10%. However, changes in the indoor concentrations would result in a more comparable change in total exposure because the general population spends over 90% of its time indoors.

Participants at the Workshop on Gasoline Exposures recognized these difficulties and came up with a list of recommendations for future research to address many of the noted deficiencies. In particular, they recommended

Table 3. Recommendations for future research.

Develop a critically reviewed database
Refine exposure pathway analyses to include total exposure measurements and source contributions
Improve the understanding of sources contributing to the short- and long-term variation in ambient levels
Validate and define the limitations of models for both short- and long-term exposures
Standardize methods for sampling and analysis
Enhance our information about how people spend their time in microenvironments that would receive higher exposures
Improve the scientific understanding of the exposure impacts of additives and reformulations
Develop the scientific understanding that would relate exposure to biological indicators
Refine exposure measures used in epidemiological studies and health assessments
Evaluate the effectiveness of public policies to reduce exposures

that a critically reviewed database and a compendium of methods for sampling and laboratory analysis for measuring gasoline exposures should be developed. The complete list of recommendations is provided in Table 3.

## Summary and Conclusions

There is a direct relationship between the fuel consumed for transportation and the resulting emissions. Because gasoline is the major fuel used currently and in the foreseeable future, it is necessary to understand the potential exposures to the general population from the use of gasoline. This is especially important to us as we consider the potential impact on exposures that could develop from the United States switching from this fuel to alternative forms of energy, such as methanol- or ethanol-based fuels. In addition, this understanding is important on a global basis, because the United States alone consumes about 35% of the world's transport energy (29).

There is a nearly complete database on the chemical composition of gasoline and the resulting automotive emissions. Likewise, there is a database that contains some information about the magnitude and extent of occupational exposures for those engaged in the refining and distribution of gasoline. Unfortunately, the information about general population exposures is incomplete, nonexistent, and often what is available is inconsistent with other data. However, the limited information on benzene, which

is one of the constituents of gasoline, is presented as an example by which to judge the relative importance of several of the identified major microenvironments and activities that increase exposures to gasoline emissions. The analysis showed, for example, that average benzene exposures should be about 7 ppbv. If the individuals happen to have a contaminated groundwater supply, their exposures could average over 40 ppb. The extreme portion of the distribution (the most uncertain part of the distribution) indicates that individuals who live near a gas station under the worst measured concentrations could experience maximum exposures over 600 ppb, which is about a factor of 100 greater than the average benzene exposures.

The uncertainty of these estimates cannot be over-emphasized. The concluding message is to appreciate the need for complete, accurate exposure information in the process of determining risks related to any pollution source. It would be extremely unfortunate and costly to the consumer if we should develop a national policy for mitigating gasoline exposures based entirely on our understanding of outdoor ambient exposures. Or, similarly, it would be most unfortunate if we attempt to regulate based on our exposures while at a service station. Clearly, the activities, locations, the amount of time spent while engaging in these activities, and the concentrations within these microenvironments are needed before a scientifically defensible exposure assessment for gasoline can be undertaken. Fortunately, this workshop can help spread this message to all the scientists engaged in risk assessment, so that we can encourage the gathering of appropriate exposure data in the future.

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# Exposure to Methyl Tertiary Butyl Ether and Benzene in Close Proximity to Service Stations

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## ABSTRACT

Exposure estimates based solely on proximity to air pollution sources are not sound and require confirmation. Accordingly, since a very limited amount of actual data for this type of exposure estimate is currently available, this study was conducted to provide actual data on residents' exposure to two important gasoline constituents [methyl tertiary butyl ether (MTBE) and benzene] relative to their proximity to roadside service stations. The results confirmed that residents in neighborhoods near service stations are exposed to elevated ambient MTBE and benzene levels compared with those living farther from such a source. However, it was also found that the presumed elevated outdoor benzene levels (a mean of 1.7 ppb) even in close proximity to service stations did not exceed the indoor levels (a mean of 2.2 ppb) of exposure for those living nearby. Regardless of residents' distance from service stations, an indoor source (cigarette smoking) appeared to be the major contributor to their benzene exposure.

Conversely, for MTBE, roadside service stations were found to be the major contributor to residents' exposure. In addition, the residents close to the stations were exposed to elevated indoor and outdoor MTBE levels. The sampling period (daytime and nighttime) and season (winter and summer) were additional parameters for the

outdoor MTBE and benzene levels and the indoor MTBE levels. Meanwhile, the breathing zone air concentrations of service station attendants for both MTBE and benzene were significantly higher than those of drivers ( $p < 0.05$ ). In addition, the breathing zone concentrations were significantly higher during summer than during winter for both drivers and attendants ( $p < 0.05$ ).

## INTRODUCTION

Proximity to air pollution sources has long been used to indicate environmental exposure in many epidemiologic studies because it is intuitive and easy to establish, and needs minimal exposure or monitoring data. However, exposure estimates based solely on this indicator are not sound and require confirmation.<sup>1</sup> For example, it has been assumed that residents in neighborhoods near service stations or major roads are exposed to elevated levels of certain gasoline constituents compared with those living farther from such sources. As regards exposure to ambient air levels, this assumption may be true. The Petroleum Association for Conservation of the Canadian Environment (PACE) measured gasoline vapor exposure at the property boundaries of service stations in five Canadian cities.<sup>2</sup> The mean values of the major aromatic volatile organic compounds (VOCs) were much higher than the means measured in various U.S. urban air studies, as reported by Edgerton et al.<sup>3</sup> Gelencser et al.<sup>4</sup> reported that benzene and toluene concentrations decreased by more than 1 order of magnitude from heavily polluted urban roadsides to unpolluted background areas. However, for indoor levels of some gasoline constituents such as benzene and toluene, the same assumption is unsubstantiated because there are other indoor benzene sources, including cigarette smoke, paint, solvents, paint thinners, and combustion sources.<sup>5,6</sup>

Furthermore, it is also questionable whether the presumed higher outdoor levels near service stations actually exceed the indoor levels as regards exposure for people who live nearby. Very limited actual data for this question are

## IMPLICATIONS

This study found that, regardless of residents' distance from roadside service stations, service stations and major roads are the major contributors to residents' exposure to indoor and outdoor MTBE, and nearby residents are exposed to elevated indoor and outdoor MTBE levels. However, in the case of benzene, an indoor source (smoking) appears to be the major contributor to residents' exposure, regardless of their distance from service stations. These results can assist epidemiologists in exploring the associations between health effects and the exposure of residents who live near service stations to gasoline constituents.

available.<sup>7</sup> In contrast to benzene, no previous literature has reported on any significant indoor methyl tertiary butyl ether (MTBE) sources other than gasoline in typical homes. Accordingly, in the absence of gasoline in homes, outdoor MTBE is presumed to be the major contributor to indoor MTBE in homes near service stations. However, this presumption has not been confirmed.

This study was conducted to (1) confirm whether residents of neighborhoods near a service station are exposed to elevated ambient levels of two important gasoline constituents (MTBE and benzene) compared with those living farther from such a source, (2) examine whether the presumed elevated outdoor benzene levels near service stations actually exceed the indoor levels as regards exposure for those living nearby, and (3) examine whether the presumed elevated outdoor MTBE levels near service stations are the major contributor to indoor MTBE levels. These goals were achieved by evaluating the exposure of residents to MTBE and benzene relative to the proximity to service stations, based on the concurrent measurement of indoor and outdoor air concentrations. Since gasoline refueling is an important activity associated with potential exposure to gasoline constituents for those who live close to service stations,<sup>2,8,9</sup> this study also measured the MTBE and benzene air concentrations in the breathing zones of drivers and service station attendants during refueling.

According to the Korean Petroleum Corporation (KPC), the gasoline manufactured by all five Korean petroleum companies contains 6.0–8.0% MTBE and 1–3% benzene by volume. MTBE has been added to gasoline in Korea for almost a decade to enhance the octane ratings. Exposure to these compounds is of particular concern because of their toxicity. Benzene is a known carcinogen, and MTBE, although its toxicity is still somewhat controversial, is apparently acutely toxic,<sup>10</sup> chronic noncancer toxic,<sup>11</sup> and carcinogenic.<sup>12</sup>

The current study was conducted in Taegu, the third largest city in Korea, with a population of 2.49 million and a population density of 2812/km<sup>2</sup>. Many residences in Korea front onto trunk roads with heavy traffic volumes. The Taegu Regional Environmental Management Agency estimates that more than 1 million people live within 200 m of major roads in Taegu. Many service stations in the city are located alongside major roads. According to the statistical yearbook for Taegu published in February 1999, the number of vehicles registered in this area was as follows: 447,296 passenger cars, 18,142 taxicabs, 50,059 buses (2813 public buses), 131,147 trucks, 120,125 motorcycles, and 832 special cars. Most of these passenger cars and motorcycles consume gasoline, while the buses and taxis primarily use diesel fuel and liquid petroleum gas (LPG), respectively.

## EXPERIMENTAL METHODS

### Survey Protocol

Two experimental designs were developed to evaluate exposure to MTBE and benzene in close proximity to roadside service stations. Both designs were conducted for two seasonal temperature extremes: winter, between January 4, 2000, and February 28, 2000, and summer, between June 21 and August 14, 2000. The first experiment was designed to measure indoor and outdoor air MTBE and benzene concentrations in houses both close to and some distance away from roadside service stations. In the second experiment, MTBE and benzene air samples were collected from the breathing zone of the driver and the gas station attendant during refueling.

Two residential areas with different relative proximities to roadside service stations were determined for the first experiment as follows: Area A was within 50 m of a service station located on a major road, and area B was at least 100 m away from any service station or major road. Twenty-five houses were then selected from each area and concurrently surveyed during both the summer and winter studies. The service stations were all located on the nearest main road to the area B houses to avoid any significant influence from other main roads. In addition, the houses were all similar distances from and perpendicular to the main roads where the service stations were located. The houses were all semi-Western with external structures similar to those of Western houses; however, other characteristics, such as the construction materials and home furnishings, were different from Western homes. All the houses used kerosene boilers as their primary heating system, and LPG, butane gas, or electric heaters served as subsidiary heating systems. The primary heating systems were all installed outside, while the subsidiary heating systems were utilized inside the houses. LPG and electricity were used for cooking.

In the first experiment, two consecutive 12-hr indoor air samples were collected (nominally 8:00 a.m.–8:00 p.m. and 8:00 p.m.–8:00 a.m.). The daytime samples were collected in the main living area, where the participants spent most of their time when awake, and the nighttime samples were taken from the bedroom or living room. Concurrently, two consecutive 12-hr outdoor air samples were collected in the yards of all the homes. The residents were interviewed at the end of the 24-hr measurement period about the presence of smokers in the house and other potential exposure to the target compounds during the sampling hours. The number of households with smokers was 20 and 19 out of 25 for areas A and B, respectively. No residents reported any other potential residential exposure to the target compounds during the sampling hours.

Ten service stations were selected for the second



experiment, and four different four-cylinder sedans, all equipped with electronic fuel-injected engines, were selected as the cars. During refueling, the window on the driver's side was open, the window on the passenger side was closed, and the engine was turned off. One refueling visit was made to each service station, during which air samples were collected from the breathing zones of the driver and the pump attendant. Refueling time ranged from 1.4 to 2.9 min. Neither drivers nor attendants were allowed to smoke during refueling.

#### Sampling and Analysis

**Sampling.** MTBE and benzene were simultaneously collected by pulling air through a 0.64-cm-o.d. and 18-cm-long stainless steel trap containing 0.3 g of Tenax TA and 0.4 g of carboxen 569 using a constant flow sampling pump (A.P. Buck Inc., Model I.H.). The sampling pump was calibrated by a digital flow meter before and after collecting each sample. The average of these two rates was used as the sample flow rate in all volume calculations. No samples departed more than 10% from the initial flow rate during this study. All the outdoor air samples were collected 1.8 m from the ground, and the indoor air samples were taken at a height of 1.5 m in the center of the room. A nominal flow rate of ~20 mL/min was set for both the house and service station sampling. The air volumes collected were sufficiently large as regards the sensitivity of the analytical system and sufficiently small to remain below the breakthrough volumes of the target chemicals.

**Analysis.** The MTBE and benzene collected on the Tenax/carboxen 569 trap were analyzed by coupling a thermal desorption system (TDS, Tekmar Model Aerotrap 6000) to a gas chromatograph (GC, Varian 3400CX) with a flame ionization detector. The trap was thermally desorbed at 250 °C for 10 min, and the target compounds were cryofocused at -120 °C on a cryo trap (15.2-cm-long, 0.32-cm-o.d. tube packed with glass beads). The cold trap was rapidly heated to 250 °C, flushed through the cryofocusing module (CM) of the TDS, and cooled to -120 °C to refocus the target compounds. The CM was then heated to 225 °C and flushed to transfer the target compounds to a GC. The initial oven temperature was set at 35 °C for 5 min and ramped at 4 °C/min to 200 °C for 5 min. The calibration standard concentrations were prepared by injecting 11.1–1110 ng of MTBE prepared in water and 10.5–1050 ng of benzene prepared in methanol into a flash evaporation system (FES) to transfer the target compounds to a trap. The injected amounts were within the operational range for analysis.

**Quality Control/Quality Assurance.** The quality control/quality assurance program included laboratory and field

blank traps, spiked samples, and duplicate measurements of integrated samples. At the beginning of the day, the laboratory and field blank traps were analyzed to check for trap contamination. No trap contamination was identified in any trap. To check the quantitative response, known standards of MTBE prepared in water and of benzene prepared in methanol were directly injected into a trap to transfer the target compounds to the GC through the TDS. When the quantitative response differed by more than  $\pm 25\%$  from that predicted by a specified calibration equation, a new calibration equation was determined. Using an FES, seven sampling traps were spiked with MTBE and benzene standards of 11.1 ng and 10.5 ng, respectively, to identify the method detection limits of the system, which were determined at 5 ng for MTBE and 3 ng for benzene. Twenty duplicate samples were collected to test the precision of the sampling and analytical techniques. The mean relative standard deviations were 14 and 13% for MTBE and benzene, respectively.

**Statistical Analyses.** Statistical analyses were performed using the SAS program (Version 6.1). A statistical model (three-way general linear model) tested the interactions between three effects (area, sampling period, and season) on the MTBE and benzene air levels. The test showed no significant interactions between the three effects. Accordingly, each effect was separately analyzed with paired-sample *t* tests and a nonparametric test (Wilcoxon test). The criterion for significance in the procedures was  $p < 0.05$ .

## RESULTS

### Concentration Difference Based on Residential Area

The indoor and outdoor air concentrations of MTBE and benzene measured in the two residential areas relative to their proximity to roadside service stations are summarized in Table 1. Since the distributions of all the results for the indoor and outdoor air concentrations were right-skewed with higher arithmetic means than median values, it would seem that the data were log-normally distributed. However, a statistical test of normality (Shapiro-Wilk statistics) did not indicate whether the data were normally or log-normally distributed. A Wilcoxon test showed that outdoor air concentrations of both MTBE and benzene were significantly higher in area A than in area B ( $p < 0.05$ ). However, the outdoor concentrations were not always higher in area A; for some periods, the results were reversed. The median values for the outdoor samples of MTBE and benzene in area A were 2.6 and 1.5 ppb, respectively, while they were consistently 1.9 and 1.0 ppb in area B.

Indoor air concentrations were also compared. A

**Table 1.** Twelve-hour indoor and outdoor air concentrations (ppb) measured in two residential areas.<sup>a</sup>

Area:	Compound	Indoor							Outdoor							I/O <sup>b</sup>
		Min	25%	Median	75%	Max	Mean	S.D.	Min	25%	Median	75%	Max	Mean	S.D.	
MTBE	A	0.6	1.6	2.4	3.4	7.4	2.6 <sup>c</sup>	1.3	0.6	1.8	2.6	3.4	6.6	2.8 <sup>c</sup>	1.3	0.92
	B	0.4	1.3	1.8	2.3	5.1	1.9 <sup>c</sup>	0.9	0.3	1.1	1.9	2.5	5.1	2.0 <sup>c</sup>	1.1	0.95
Benzene	A	0.7	1.4	1.9	2.8	5.7	2.2 <sup>d</sup>	1.2	0.6	1.3	1.5	1.9	4.6	1.7 <sup>c,d</sup>	0.8	1.27
	B	0.6	1.5	1.9	2.3	5.3	2.1 <sup>d</sup>	0.9	0.3	0.8	1.0	1.4	3.9	1.2 <sup>c,d</sup>	0.7	1.90

<sup>a</sup>Number of samples:  $N = 98$  for indoor-area A,  $N = 97$  for indoor-area B,  $N = 97$  for outdoor-area A,  $N = 93$  for outdoor-area B; <sup>b</sup>Median concentration ratios of indoor air to outdoor air; <sup>c</sup>Indicates that area A and B data sets are significantly different at  $p < 0.05$ ; <sup>d</sup>Indicates that indoor and outdoor air data sets are significantly different at  $p < 0.05$ . Area A includes the area within 50 m of service station, whereas area B is at least 100 m away. Concentrations measured below the detection limit were set as equal to half of the detection limit for the calculations.

Wilcoxon test showed that indoor air MTBE concentrations were significantly higher in area A than in area B ( $p < 0.05$ ). The median indoor MTBE concentration was 2.4 ppb in area A and 1.8 ppb in area B. However, for benzene, the indoor air concentration difference between the two areas was not significant.

The indoor air levels of MTBE and benzene were compared to the matched concurrent outdoor air levels in the two residential areas using a Wilcoxon test. Benzene showed significantly higher indoor levels in both areas ( $p < 0.05$ ). The median concentration ratios of indoor to outdoor air were 1.27 and 1.90 for areas A and B, respectively. However, for MTBE, the concentration difference between the indoor and outdoor air samples was not significant.

#### Concentration Difference Based on Sampling Period

The daytime and nighttime air concentrations measured in the two residential areas are shown in Figure 1. A Wilcoxon test showed that outdoor levels of both MTBE and benzene in the two areas were significantly different between the daytime and nighttime periods ( $p < 0.05$ ). The daytime-to-nighttime ratios for median outdoor MTBE concentrations were 1.19 and 1.23 for areas A and B, respectively, and those for outdoor benzene concentrations were 1.23 and 1.19. As with outdoor MTBE levels, indoor MTBE levels were significantly higher during the day than at night in both areas. The daytime-to-nighttime ratios for median indoor MTBE concentrations were 1.21 and 1.28 for areas A and B, respectively. By contrast, indoor benzene levels were not significantly different between the two periods for either area.

#### Concentration Difference Based on Season

Figure 2 shows the air concentrations measured in the two residential areas during the two seasonal temperature extremes, winter and summer. The outdoor concentrations of both MTBE and benzene in the two areas were

significantly higher in summer than in winter. The summer-to-winter ratios for median outdoor MTBE concentrations were 1.24 and 1.40 for areas A and B, respectively, and those for the outdoor benzene concentrations were 1.28 and 1.36. As with the outdoor MTBE concentrations, the indoor MTBE concentrations in the two areas were significantly higher in summer than in winter. The summer-to-winter ratios for the median indoor MTBE concentrations were 1.25 and 1.18 for areas A and B, respectively. By contrast, indoor benzene concentrations in the two areas did not differ between the two seasons.

#### Refueling Study

A summary of the results from the refueling experiments is shown in Figure 3. Two air samples were collected using personal sampling pumps and adsorbent traps worn in both the driver's and the attendant's breathing zone during refueling at service stations in the Taegu area. All of the service stations had attendant-assisted refueling. The breathing zone air concentrations of the attendants were significantly higher than those of the drivers. In winter, the median concentration ratios of the attendants to the drivers were 8.8 and 3.0 for MTBE and benzene, respectively. In summer, the median concentration ratios of the attendants to the drivers were 3.3 and 2.5 for MTBE and benzene, respectively. Meanwhile, the breathing zone concentrations of MTBE and benzene were significantly higher in the summer than in the winter for both drivers and attendants.

#### DISCUSSION

##### Residential Indoor and Outdoor Air Concentrations

As expected, residential outdoor levels of both MTBE and benzene were higher when in close proximity to service stations. Since all the service stations were located on major roads and there were no other significant sources in the residential areas, service stations and motor vehicles were

apparently the major sources of these concentrations in both residential areas. Further information on the relative contribution of these two emission sources to the outdoor levels was unavailable. The most probable cause for the difference in the outdoor levels would appear to be the dilution of the target compounds relative to the distance from the emission sources.<sup>4</sup> These results support previous studies<sup>2</sup> that predict that outdoor VOC levels will be lower at residences located a short distance away from service stations compared with levels at the property boundaries of service stations. Furthermore, the current results confirm the assumption that residents in neighborhoods near service stations or major roads are exposed to elevated outdoor levels of certain gasoline constituents compared with those living farther from such sources.

Unlike outdoor benzene concentrations, indoor benzene concentrations did not differ significantly between the two residential areas. In addition, elevated outdoor benzene concentrations, even in area A, did not exceed indoor benzene concentrations. Instead, indoor concentrations were significantly higher than the outdoor concentrations in both areas (Table 1), regardless of the distance from service stations. These results were consistent with those from a previous study<sup>12</sup> that reported on

benzene and other aromatic compounds.

In addition, the indoor sources were also the major contributor to the benzene exposure of residents close to roadside service stations. The major benzene sources inside a home include cigarette smoke, paint, solvents, paint thinners, and combustion sources.<sup>5</sup> Cigarette smoking appeared to be the major source of indoor benzene because the number of houses with smokers was 20 and 19 out of 25 for areas A and B, respectively. And combustion systems did not appear to be significant sources of benzene because none of the fuels used in the kerosene, LPG, butane gas, or electric heaters and stoves contain benzene, according to the Korean Petroleum Association. None of the households had an attached garage or had been painted within 1 year of the current study. None of the participants reported any use of solvents in the home during the monitoring period. No other potential sources of benzene were observed in any of the homes.

In contrast to indoor benzene concentrations, indoor MTBE concentrations were significantly higher in area A than in area B. Furthermore, indoor MTBE levels were similar to the outdoor MTBE levels in both areas. Therefore, because no significant MTBE sources were identified inside the surveyed homes, indoor levels appeared to result

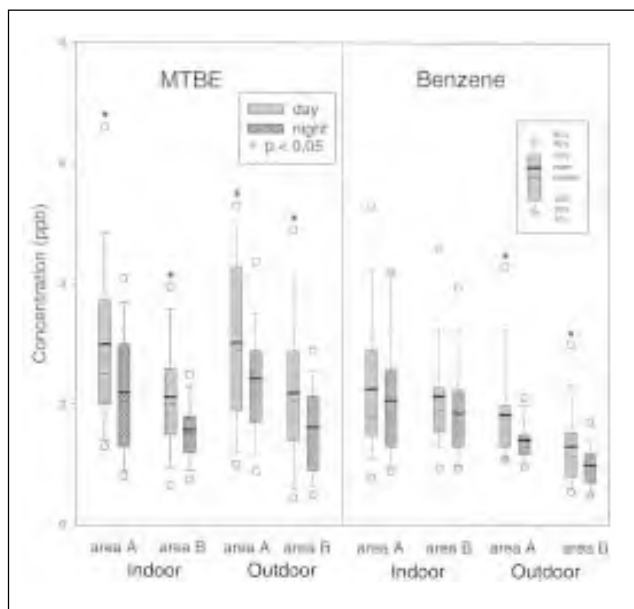


Figure 1. MTBE and benzene concentrations in indoor and outdoor air samples based on sampling period and residential area. Median concentration ratios of daytime samples to nighttime samples: 1.21 for MTBE-indoor-area A, 1.28 for MTBE-indoor-area B, 1.19 for MTBE-outdoor-area A, 1.23 for MTBE-outdoor-area B, 1.03 for benzene-indoor-area A, 1.11 for benzene-indoor-area B, 1.23 for benzene-outdoor-area A, and 1.19 for benzene-outdoor-area B. Number of MTBE and benzene samples: N = 49 for indoor-area A-day, N = 49 for indoor-area A-night, N = 48 for indoor-area B-day, N = 49 for indoor-area B-night, N = 49 for outdoor-area A-day, N = 48 for outdoor-area A-night, N = 45 for outdoor-area B-day, and N = 48 for outdoor-area B-night.

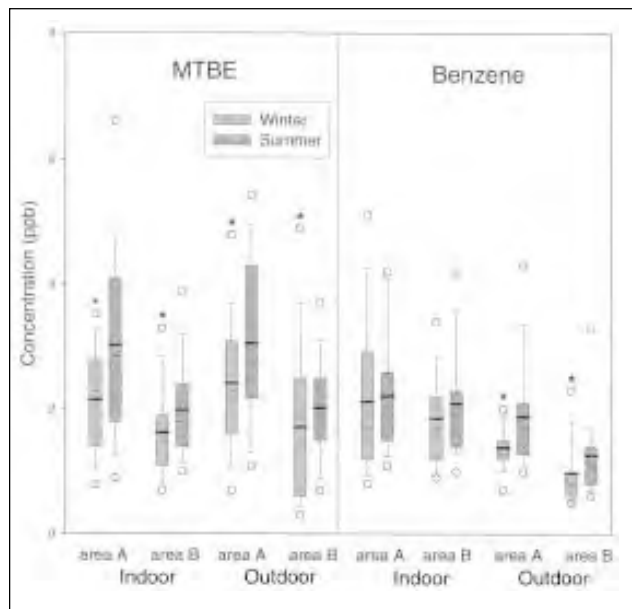


Figure 2. MTBE and benzene concentrations in indoor and outdoor air samples based on season and residential area. Median concentration ratios of summer samples to winter samples: 1.25 for MTBE-indoor-area A, 1.18 for MTBE-indoor-area B, 1.24 for MTBE-outdoor-area A, 1.40 for MTBE-outdoor-area B, 1.11 for benzene-indoor-area A, 1.09 for benzene-indoor-area B, 1.28 for benzene-outdoor-area A, and 1.36 for benzene-outdoor-area B. Number of MTBE and benzene samples: N = 49 for indoor-area A-winter, N = 49 for indoor-area A-summer, N = 49 for indoor-area B-winter, N = 48 for indoor-area B-summer, N = 49 for outdoor-area A-winter, N = 48 for outdoor-area A-summer, N = 46 for outdoor-area B-winter, and N = 47 for outdoor-area B-summer.

primarily from the penetration of gasoline-derived MTBE emitted from service stations and cars into the homes. Accordingly, service stations and roadways would seem to be the major contributors to residents' indoor and outdoor exposure to MTBE, regardless of their distance from service stations or major roads. In addition, residents living close to these sources were exposed to elevated indoor and outdoor MTBE levels.

The outdoor MTBE and benzene concentrations in areas A and B were significantly higher during the day than at night. This pattern is consistent with results previously reported by Jo and Moon<sup>7</sup> for benzene and other aromatic compounds. However, this pattern is not consistent with Wallace et al.,<sup>6</sup> who reported that overnight outdoor concentrations of VOCs exceeded daytime levels in Los Angeles in February 1987. Wallace et al.<sup>6</sup> assumed that the overnight inversions were attributable to higher nighttime levels. The pattern difference between our study and the Wallace et al. study<sup>6</sup> may be a reflection of the combined effects of emission strengths and meteorological conditions. By contrast, indoor benzene concentrations in the two areas did not differ between day and night in our study, and indoor MTBE concentrations were significantly higher during the day than at night.

The outdoor MTBE and benzene concentrations in the two areas were significantly higher during summer than during winter. This pattern is supported by Weisel et al.,<sup>13</sup> who measured in-vehicle VOC concentrations while idling in both winter and summer. However, indoor benzene concentrations in the two areas did not differ between the two seasons in our study, and indoor MTBE concentrations were significantly higher during summer than during winter.

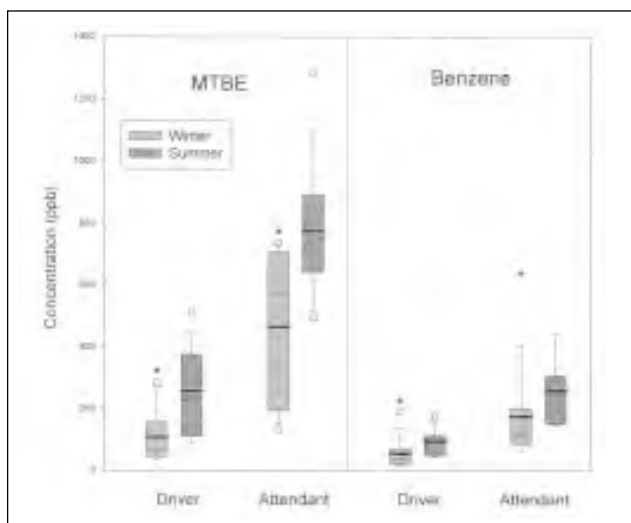


Figure 3. Breathing zone air MTBE and benzene concentrations of drivers and attendants during refueling based on season. Median concentration ratios of attendants to drivers: 8.8 for MTBE-winter, 3.0 for benzene-winter, 3.3 for MTBE-summer, and 2.5 for benzene-summer. Number of samples for each data set is 10.

#### Comparison of Residential Outdoor MTBE Concentrations with Other Studies

The ambient outdoor MTBE concentrations measured in the two residential areas were compared with those of earlier studies. The mean outdoor concentrations measured in areas A and B (2.8 and 2.0 ppb, respectively) (Table 1) were found to be lower than the average ambient concentrations previously measured in Porto Alegre, Brazil, and within the ranges measured in California.<sup>14-16</sup> Grosjean et al.<sup>14</sup> reported that ambient concentrations measured from March 20, 1996, to April 16, 1997, at a downtown location in Porto Alegre, Brazil, averaged 6.6 ppb. Zielinska et al.<sup>15</sup> reported that ambient levels measured from 1995 to 1996 at four southern California locations (sampling duration = 3 hr) averaged 0.6–7.2 ppb. Poore et al.<sup>16</sup> reported that ambient levels measured in 1996 at seven California locations (sampling duration = 24 hr) averaged 1.3–4.8 ppb. Unfortunately, certain information required to understand the differences between this study and earlier studies is unavailable.

#### Breathing Zone Concentrations of Drivers and Attendants

The service station attendants were found to be more exposed to elevated MTBE and benzene levels than were the drivers. Because only the driver's-side window was open during refueling, as is typical in most instances, this physical barrier could partly account for some of the difference. The results from the refueling experiments were compared with those of earlier studies. The mg/m<sup>3</sup> unit employed in certain previous studies was converted to ppb for this comparison. The mean breathing zone benzene concentrations of the attendants measured in this study (176 and 258 ppb for winter and summer, respectively) were found to be lower than those of attendants measured in previous studies.<sup>2,8,17</sup> The Northeast States for Coordinated Air Use Management<sup>8</sup> summarized data from nine studies on exposure to gasoline vapors at service stations and reported that benzene exposure averaged 900 ppb. PACE<sup>2</sup> reported that benzene exposure for full-service attendants and self-service stations averaged 944 ppb in summer and 1056 ppb in winter. Bond et al.<sup>17</sup> conducted a gasoline vapor exposure study on self-service refueling with unleaded regular gasoline in which the mean breathing zone benzene concentrations of the operators averaged 1400 ppb. By contrast, the mean breathing zone MTBE concentrations of the attendants measured in our study (465 and 774 ppb for winter and summer, respectively) were higher than those of the attendants measured by Liou et al. (300 ppb).<sup>9</sup> Similarly, the mean breathing zone MTBE concentrations of the drivers measured in our study (108 and 257 ppb for winter and

summer, respectively) were higher than those of drivers measured by Lioy et al. (87 ppb).<sup>9</sup>

The breathing zone concentrations of MTBE and benzene were significantly higher during summer than during winter. This seasonal difference can be partly attributed to temperature differences and the Reid Vapor Pressure (RVP), both of which affect the volatilization of gasoline components from a fuel tank.<sup>18</sup> According to the KPC, the average RVP in the Taegu area is 11.4 in winter and 7.1 in summer. The average ambient temperature was 2.8 and 25.2 °C in winter and summer, respectively, during the study period.

## CONCLUSIONS

This study evaluated residents' exposure to MTBE and benzene relative to their proximity to roadside service stations. For MTBE, regardless of residents' distance from service stations, service stations and major roads were the primary contributor to residents' exposure. In addition, residents close to major roads and service stations were exposed to elevated indoor and outdoor pollutant levels. Since no significant MTBE sources were identified inside the surveyed homes, indoor levels appeared to result primarily from the penetration of the gasoline-derived MTBE in nearby outdoor air into the homes. Therefore, these residents would experience an elevated health risk from MTBE exposure. In contrast to MTBE, an indoor benzene source (smoking) appeared to be the major contributor to residents' exposure to benzene, regardless of their distance from service stations. No other potential sources of benzene were observed in any of the homes. The sampling period (day and night) and season (winter and summer) were additional parameters for outdoor MTBE and benzene levels, as well as indoor MTBE levels. Finally, it was confirmed that service station attendants were exposed to higher levels of gasoline constituents than were drivers during refueling. In addition, attendants and drivers were exposed to higher levels of gasoline constituents during summer than during winter.

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# Housewives' exposure to volatile organic compounds relative to proximity to roadside service stations

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### Abstract

Residents in neighborhoods near a service station and/or major roadway would be expected to be exposed to elevated ambient volatile organic compound (VOC) levels compared to those further away from such source(s). We confirmed this and examined whether the anticipated high outdoor levels near a service station and/or major roadway outweighed the indoor levels as a factor for the exposure of nearby residents. Unlike the outdoor air concentrations, neither the indoor air nor breath concentrations were different for the two residential zones tested. The outdoor concentrations were higher during the daytime than at night, however, the indoor air and breath concentrations showed no difference between the two periods. The elevated outdoor levels nearby service stations were not identified as a major contributor to the exposure of housewives living in close proximity. Instead, it appeared that the indoor air levels were the major contributor to housewives' exposure in both residential zones. This was further supported by the finding that the indoor levels were actually higher than the outdoor levels, and that there was a significant correlation between the indoor and breath levels.

### Keywords

Breath sampling; Indoor air quality; Outdoor air quality; Residential air quality; VOC source