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INDUSTRIAL ODOR SOURCES AND AIR POLLUTANT CONCENTRATIONS IN GLOBEVILLE, A DENVER COLORADO NEIGHBORHOOD

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ABSTRACT

An odor of unknown origin described as a “tar” or “asphalt” smell has become unbearable for many of Globeville, Colorado residents over the past few years. Residents report during odor events burning eyes and throat, headaches, skin irritation, and problems sleeping. This study was undertaken to identify the potential sources of the odor and the concentrations of air pollutants making up the odor by conducting meteorological correlations and sampling for a panel of volatile organic compounds (VOCs), sulfur gases, and polycyclic aromatic hydrocarbons (PAHs) in the neighborhood and near suspected sources. Wind speed and direction data collected every one minute in the neighborhood indicate that, when the odor is noticed, the community is directly downwind of a wood preservation facility and an asphalt roofing facility. Air samples collected during high intensity odor events have shown concentrations of methylene chloride, hexane, toluene, naphthalene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene each at least two times higher than background concentrations. Naphthalene and the other PAHs are known pollutants emitted from wood treatment processes, and are known to have

a coal tar odor. Naphthalene was present in a sample collected directly adjacent to the Koppers facility and was not present in any background samples. Single compound odor and health thresholds, however, were never surpassed. Given the technical and regulatory challenges of sampling odors and controlling emissions, it is recommended that Globeville residents and neighboring industry pursue a "good neighbor policy" to solve the odor issue. Specific offending industrial processes could be identified for which there exist cost-effective control technologies that would reduce exposure to odors and air toxics in Globeville.

Implications

Meteorological correlations and samples of volatile organic compounds (VOCs), sulfur gases, and polycyclic aromatic hydrocarbons (PAHs) in the Globeville Colorado neighborhood and near suspected sources during odor events indicate potential industrial sources of a transient and noxious odor. Legislative approaches have proven unfruitful and no health or odor thresholds were typically violated. New approaches are warranted to address odor mixture effects in neighborhoods near industrial facilities.

INTRODUCTION

Globeville is a mixed residential-industrial neighborhood of Denver that is bisected in two directions by major highways. The residential community is an island surrounded by numerous industries, including asphalt manufacturers, a wood treatment facility, a pet food manufacturer, a stock complex, animal rendering facilities, a coal-fired power plant, two smelters, and a wastewater treatment facility. Globeville residents have faced environmental pollution for decades, beginning in 1974 when metal contamination was found in the groundwater and soil sediment caused by the Asarco Globe Plant, now a Superfund site, after which Globeville was named (CDPHE, 2013; EPA, 2013a).

Since 1980 residents have been reporting strong industrial odors. In the past few years, there has been an increase in reports of a sporadic tar or asphalt odor that is strong enough to cause eye, nose, and throat irritation and headaches. Residents are often forced to leave their patios and yards, shut windows, and turn off swamp coolers to keep the smell out of their homes. Initial conversations with elected officials, state health department staff, and others in a regulatory capacity were ineffective due to regulators' unwillingness to assist residents as well as a lack of data conclusively identifying the odor source.

Odor exposure is a particularly difficult issue to address given that many pollutants cause strong odors at extremely low concentrations. Nicell notes, "the more frequently an odour intrudes into a person's life, the more annoying each odour episode experience becomes" (Nicell, 2009). This annoyance can trigger physiological mechanisms such as an instinctive odor aversion and stress-induced illness, and exacerbate underlying health conditions (Shusterman, 1992).

During several odor events studied in California (and also those reported here), pollutant concentrations were measured well below toxicological thresholds, despite reporting of acute health symptoms experienced by residents exposed to odors (Shusterman, 1992). Therefore, reported health symptoms in these cases most likely involve odor-related mechanisms that are unrelated to toxicological health impacts (Shusterman, 1992). Furthermore, the pollutants causing the odors are often present in concentrations well below chemical detection limits.

Despite this limitation, studies continue to be conducted in response to odor complaints by citizens, usually with inconclusive results about the source and the odor. Nicolas et al. (2010) emphasizes that it is important to make an assessment of the odor annoyance using the residents themselves as measuring tools, as they are experiencing the impacts firsthand. Social participation and strong community involvement are needed to identify odor sources.

Odor studies that consider input from the impacted community are not all that common. In the Bruvold et al. (1983) study of odors from wastewater treatment plants in California, affected communities had a higher percentage of respondents say that they noticed odors, and did so more often and for longer periods of time, as compared to control communities. Also, ambient H_2S measurements confirmed higher concentrations in affected neighborhoods. This study confirmed that chemical data correlate with social data when compared with a control community.

Blood samples from residents, as well as soil sediment and dust samples collected from homes in a neighborhood adjacent to a wood processing plant (which used creosote and pentachlorophenol) showed elevated levels of dioxins and polycyclic aromatic hydrocarbons. Air dispersion modeling indicated possible elevated air exposure to benzo(a)pyrene and tetrachlorodibenzodioxin due to the wood processing plant. These data suggested contamination of a neighborhood by the plant and the need for more stringent regulations on waste discharged from wood treatment plants (Dahlgren et al., 2003).

In response to citizen complaints, the City of Edmonton in Alberta, Canada developed an ambient odor-monitoring program near the Edmonton Waste Management Centre (Bowker et al., 2004). Odor inspectors documented odor intensity over three years, and volunteer citizen odor observers maintained logs of episodes for one year. This program provided an inventory of odor sources with the highest frequency of detection from biosolids lagoons, composting, a chemical plant, feed mills, and a mushroom farm.

Dincer and Muezzinoglu (2006) studied the composition of odorous gases generated by a municipal landfill in the city of Izmir, Turkey. They estimated odor concentrations by olfactometry and quantified volatile organic compound (VOC) concentrations by thermal desorption gas-chromatography-mass spectrometry (GC-MS). Results showed a statistically significant linear relationship between odor concentrations determined by olfactometry and total VOC concentrations. Measured VOCs were important in the odor formation and composition in selected sites that had documented odor complaints, with aldehydes, ketones, and esters as the best estimators of odor. Only one compound, however, exceeded odor thresholds (propanal).

Colorado is one of a few states that have attempted to regulate odors. Regulation 2 identifies odor as a nuisance and was adopted in 1979 to address odor emissions (CAQCC, 2008). Regulation 2 states: “no person, wherever located, shall cause or allow the emission of odorous air contaminants from any single source such as to result in detectable odors which are measured in excess of one part odorous air diluted with seven units of odor free air in areas used predominantly for residential and commercial purposes” (CAQCC, 2008).

The rubric for odor violations uses a measurement system involving Dilutions/Threshold (D/T). Odor-free air is mixed with odor-filled air in a device called a scentometer. If an odor is detectable at a D/T of 7:1, and the origin of the odor can be determined, a written violation is permissible only if Colorado Department of Public Health and Environment (CDPHE) can prove the industry is not using best available control technology (CLCS, 2012).

In response to odor and health symptom complaints from residents in Globeville, the nonprofit organization Groundwork Denver (GWD), Globeville residents, Globeville Civic Association #1 (GCA#1), and the University of Colorado Boulder Mechanical Engineering Department (CU-ME) collaborated to collect data through air sampling, and meteorology measurements. Objectives of the project were: to better understand the odor and health concerns of the residents, to identify compounds present in Globeville air during odor events, to determine the likely sources of odors using wind direction, to investigate industrial processes likely to emit compounds related to detected odors, and to determine the range and frequency of impacts associated with odors. Ultimately the hope of the community was to inform next steps in addressing odor exposure in Globeville.

EXPERIMENTAL METHODS

Residents in a 24 square block (0.41 square km) area in Globeville reported smelling a tar/asphalt odor. Air sampling was conducted only in this region. Figure 1 depicts the boundary of Globeville, the location of the homes that reported smelling the tar/asphalt odor, and the air quality sampling locations.

Air Quality Sampling

Air quality sampling was conducted to identify compounds present in the air when tar/asphalt odors were present, with the goal of detecting odorous and/or unique compounds that could be linked to specific industrial processes and facilities near Globeville. Three classes of compounds – volatile organic compounds (VOCs), sulfur compounds, and polycyclic aromatic hydrocarbons (PAHs) – were chosen based on their association with tar and asphalt industries as well as the odor properties of many compounds in these classes. In total, samples were analyzed for 92 compounds, including 62 VOCs, 14 sulfur compounds, and 16 PAHs. Table 1 below provides the full list of analytes.

Evacuated six-liter SUMMA canisters were used to collect grab samples to be analyzed for VOCs and sulfur compounds. Each canister was equipped with a two-micrometer glass fiber filter to prevent large particles from being drawn in with the sample. Flow restrictors were not used, so each SUMMA canister sample was collected over a period of approximately 30 seconds.

PAH samples were collected by pulling 15-30 liters of air at 1 lpm ± 5% through XAD-7 OVS sorbent tubes (SKC 226-57, SKC Inc., Eighty Four, PA) using universal sample pumps (SKC 224-PCXR8). Sample pumps were calibrated with a representative sampler in line before and after collection of each sample using a Gilian Gilibrator 2 (Sensidyne. St Petersburg, FL).

SUMMA canister and sorbent tube samples were taken concurrently, but do not perfectly represent the same time due to the large difference in sample run time for SUMMA canister samples (30 seconds) compared to sorbent tube samples (15 to 30 minutes). A total of ten

SUMMA canister and ten sorbent tube samples were collected, consisting of two background sets, two industrial sets at suspected source locations, and six odor sets. Background samples were collected at a vacant lot and a residential yard in Globeville at times when industrial odors were not observed. Industrial samples were collected directly adjacent to a wood treatment facility, Koppers Inc., and on the fence line between two asphalt plants, Owens Corning Trumbull Asphalt and Cobitco Inc., when tar/asphalt odors were present. These three facilities were identified as probable odor sources from the Industry Assessment (discussed below). Odor samples were collected in a residential yard in Globeville when industrial odors were observed. The sample size was limited by budget constraints.

All samples were shipped to ALS Environmental (Salt Lake City, UT laboratory) for analysis. Samples were shipped immediately after collection and analyzed within 72 hours to minimize decay of compounds prior to analysis (Brymer et al., 1996). The SUMMA canisters were provided by ALS Environmental. ALS provided chain of custody forms that were used to ensure proper handling of the samples. SUMMA canister samples were analyzed for VOCs using gas chromatography-mass spectrometry following method EPA TO-15 and for sulfur compounds using gas chromatography with a sulfur chemiluminescence detector. Sorbent tube samples were analyzed according to method NIOSH 5528.

CU-ME collected background and industrial samples, and trained Globeville residents to collect air samples during tar/asphalt odor events. Training of residents included an introduction to the equipment, discussion of the classes of compounds that would be analyzed, instructions on filling out sampling data sheets, a demonstration of the sampling procedure, and hands-on practice with extra samplers.

Residential samples were collected over a seven-month period from September 2012 to March 2013. The timing of sample collection depended on resident availability, concurrent observation of odors, and availability of equipment. Odor samples were collected on 9/11/12, 11/13/12, 11/19/12, 11/28/12, 12/30/12, and 3/3/13. As winter set in, the tar/asphalt odor was noticed less frequently, most likely due to more time spent indoors with closed windows.

Wind Monitoring

A RainWise WindLog Data Logger (RainWise Inc., Bar Harbor, ME) was used to monitor wind velocity and direction so that detected compounds could be linked to emissions from specific facilities. The WindLog had a minimum wind speed threshold of 0.45 m/s and ± 2% wind speed accuracy. The wind direction range was 360° with no deadband; the resolution was 22.5°, averaged; and the accuracy was ± 22.5°. Wind speed and direction data were logged at one-minute intervals during the sampling period.

Industry Assessment

An assessment of nearby industry was conducted to identify potential sources of the tar/asphalt odor. This assessment consisted of mapping and air pollutant emissions profiling. Wind data provided the basis for focusing the industry assessment on the facilities to the northwest of Globeville. Air pollutant emissions data were obtained from the Air Pollution Control Division

(APCD) of the Colorado Department of Public Health and Environment (CDPHE) as well as the United States Environmental Protection Agency's (EPA) Toxic Release Inventory (TRI).

RESULTS AND DISCUSSION

Odor Event Samples Show High Concentrations of Hazardous Air Pollutants

All SUMMA canister and sorbent tube samples were analyzed by ALS Environmental for VOCs, sulfur compounds, and PAHs. The analytical reports provided by ALS included a qualifier for each compound indicating whether the detected concentration was below the Method Detection Limit (MDL) or between the MDL and Reporting Limit (RL). The MDL is a statistical estimate of method/media/instrument sensitivity, and the RL is a verified value of sensitivity. For the purposes of this study, only compounds that were detected at concentrations greater than the RL in at least one sample were considered.

A summary of compounds found above the RL in at least one sample is provided in Table 2. Concentrations of PAHs assume a pump flow rate of 1 liter per minute. Due to a +/- 5% accuracy on pump flow rate, the reported PAH concentrations also have a +/- 5% accuracy.

Of the 92 compounds analyzed, acetone, methylene chloride, hexane, benzene, heptane, toluene, *m,p*-xylene, and naphthalene were all present above the RL in at least half of the odor samples. Of these compounds, hexane, heptane, benzene, toluene, *m,p*-xylene, and naphthalene were present in odor samples in concentrations at least three times those found in background samples on average. These six compounds were therefore considered to be the prevalent compounds detected in the odor samples. Table 3 displays average odor sample concentrations alongside average background sample concentrations, while Table 4 lists common uses of these compounds.

Figure 2 displays the concentrations for all ten samples of each of the six compounds that were detected above the RL in at least half of the odor samples and which had average odor sample concentrations at least three times greater than average background concentrations.

Sulfur compounds were not detected in any odor sample. Carbon disulfide, however, was detected at 5.9 ppb in one background sample and 6 ppb in the sample collected on the Owens Corning Trumbull Asphalt Plant and Cobitco Inc. fence line.

The odor sample collected on 9-11-12 showed a high concentration of naphthalene, 25 ppb, along with detectable concentrations of three other PAHs: dibenz(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. In addition to its presence in this first odor sample, naphthalene was detected in two other odor samples and in the Koppers Inc. industrial sample (Figure 2).

Of the compounds listed in Table 3, all except heptane are listed as hazardous air pollutants (HAPs) by the EPA. HAPs, also known as air toxics, are “pollutants that cause or may cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental and ecological effects” (EPA, 2012). HAPs are regulated by establishing control technology requirements on major sources, i.e., sources which emit more than ten tons per year of a single HAP or more than 25 tons per year of a mixture of HAPs.

Wind in Globeville is Typically Light

Minute wind speed and direction data were collected from September 2012 through March 3, 2013, with one two week period from October 3 to October 16 lost due to dead batteries. These data were used to develop an understanding of general wind patterns in Globeville, as well as an understanding of wind activity during air quality sampling.

As shown in Figure 3, Globeville experienced calm conditions and low wind speeds less than three meters per second for the majority of the sample period. There was no wind (< 0.1 m/s) nearly 25% of the time, and wind below two meters per second (approximately the lower threshold of a “light breeze” on the Beaufort scale) another 68% of the time (Beaufort, 1805). The light breeze that did occur was a southwesterly wind approximately 18% of the time, and was spread somewhat equally around the compass the remaining 58% of the time.

All Observed Tar/Asphalt Odor Events Occurred During NNW Winds

Wind plots displaying direction and time of day were generated for each odor sample. Figure 4 shows a 3.5-hour period encompassing the odor sample taken on 11-13-12.

The odor sample dated 11-13-12 was collected from 4:05 p.m. to 4:20 p.m., as indicated by the dashed box in Figure 4. A light 2-4 m/s north by northwest breeze held for at least one hour leading up to the odor sample and throughout sample collection. Wind blowing from the NNW corresponds to wind blowing into Globeville from the industrial area that contains that most likely odor sources. This observation – a NNW breeze leading up to and lasting throughout odor samples – was consistent for all six-odor event samples.

The wind speed during odor samples varied. There was essentially no wind during odor sample collection on 11-19-12, 11-28-12, and 12-30-12, but a slight NNW breeze preceded each of these samples. Wind speeds during samples collected on 9-11-12, 11-13-12, and 3-3-13 ranged from 1.5 to 4.5 m/s.

Upwind Industrial Facilities are Permitted to Emit Hazardous Air Pollutants

Globeville is surrounded by a multitude of potential industrial odor sources, including: Nestle Purina Pet Care, National Western Stock Show, Suncor Energy, Darling International, Metro Wastewater Reclamation, Koppers Inc., Altogether Recycling, Owens Corning Denver Trumbull Asphalt Plant and Owens Corning Roofing Plant (Figure 5).

Observations of wind direction during tar/asphalt odor episodes were used to target the most relevant facilities. Given that the wind always came from NNW when the tar/asphalt odor was observed, all of the facilities to the east of I-25 in Figure 5 were eliminated from consideration. The industrial area NNW of Globeville was then mapped more thoroughly. Six facilities were located close to Globeville and west of I-25: Koppers Inc. (wood treatment), Altogether Recycling, Owens Corning Roofing Plant, Owens Corning Trumbull Asphalt Plant, Cobitco Inc.

(Asphalt), and Metech Recyling. Of these six facilities, only Koppers Inc., Cobitco Inc., and the Owens Corning facilities were considered likely to produce a tar/asphalt odor.

The Denver Koppers Inc. facility (Figure 5) is a wood treatment plant that applies a proprietary blend of coal tar creosote – referred to as Creosote Petroleum Solution, or CPS – to railroad ties as a preservative. The Material Safety Data Sheet (MSDS) for CPS lists numerous PAHs as constituents, including the following pollutants detected in odor samples: naphthalene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. Furthermore, the MSDS lists the potential short-term health effects of inhalation as: "irritation, nausea, vomiting, headache, drowsiness, dizziness, loss of coordination" (Koppers Inc., 2012).

The three primary sources of air emissions at wood treatment facilities are off-gassing of treated wood immediately after removal from the treating cylinder, venting of the vacuum pump system, and venting of displaced air when creosote is returned to the work tanks (EPA, 1999).

Cobitco Inc. (Figure 5) creates asphalt emulsions for use in road paving. Asphalt emulsions combine asphalt, water, and an emulsifying agent to produce a liquid product suitable for road construction and maintenance (AEMA, n.d.). The only compound listed on any Cobitco Inc. MSDS that was covered in the air quality sampling program is a styrene/butadiene copolymer (Chemical Safety Associates, Inc., 2004). Exposure to asphalt via inhalation is not expected under normal operating conditions at Cobitco Inc., but asphalt inhalation can cause "difficulty breathing, wheezing, headache, dizziness, indigestion, and nausea" if it occurs (Chemical Safety Associates, Inc., 2004).

There are two Owens Corning facilities near Globeville (Figure 5): Denver Trumbull Asphalt Plant at 5201 Bannock Street and Owens Corning Roofing Plant at 5201 Fox Street. Trumbull asphalt products are used for roofing shingles, built-up roofing systems, and roadway paving (Owens Corning, 2010). The roofing facility produces four types of shingles. The MSDS for the primary asphalt product at this facility states that “fumes from hot materials can be unpleasant and produce nausea, headaches and irritation of the upper respiratory tract” (Owens Corning, 2012). The only pollutant specifically mentioned in this MSDS is hydrogen sulfide (H_2S).

The EPA’s TRI reports and the APCD construction permits were reviewed for these facilities to develop an understanding of the relative quantities of air pollutant emissions from each.

Cobitco Inc. only lists hydrochloric acid on its TRI reports, and it has reported zero pounds released every year since 1995 (EPA, 2013b). Both Owens Corning facilities list benzo(g,h,i)perylene and PAHs, but the Trumbull Asphalt Plant has always reported zero pounds released (EPA, 2013c). The Roofing Plant listed one kilogram of PAHs released for the years 2006 to 2011 (EPA, 2013d).

Koppers Inc. reported creosote air emissions for 2006 to 2011 as shown in Table 5 (EPA, 2013e).

The only specific component of creosote air emissions regulated by the APCD is naphthalene. Koppers Inc. is permitted to emit up to 8,160 kilograms per year of naphthalene from its wastewater treatment (WWT) system and up to 59 kilograms per year of naphthalene from its creosote storage tank, as shown in Table 6 (APCD, 2009a, 2010).

Facility-wide APCD construction permits were obtained for both Owens Corning facilities (APCD, 2003, 2007, 2009b); permits for two specific pieces of equipment were obtained for Koppers Inc. (APCD, 2009a, 2010); and no permit was obtained for Cobitco Inc. Emissions limits for non-criteria reportable air pollutants based on current construction permits are listed for both Owens Corning facilities (Table 7) and for a portion of the Koppers Inc. facility (Table 6).

A literature search was conducted for odor complaints about other Koppers Inc. and Owens Corning facilities. There are no other Cobitco Inc. facilities. The Agency for Toxic Substances and Disease Registry (ATSDR) conducted a public health assessment of the Koppers wood treatment facility in Little Rock, AR in response to community concerns over groundwater contamination and odors (Arkansas Department of Health, 2005). In response to odor complaints, ATSDR collected data on airborne concentrations of PAHs and other VOCs. Canister samples yielded naphthalene concentrations ranging from 5.5 to 44.5 ppb. In comparison, naphthalene concentrations detected in Globeville odor samples ranged from ND to 25 ppb (Table 2). No complaints or health assessments were found in published studies for Owens Corning facilities.

Health and Odor Thresholds Not Met for Prevalent Compounds in Odor Event Samples

Odor and health effect thresholds have been established for each of these compounds. Table 8 presents the maximum concentrations found in Globeville odor samples alongside typical urban concentrations, odor thresholds, and health effect thresholds.

Odor thresholds are established by exposing a panel of individuals to known concentrations of a compound to determine the minimum concentration required for the panelists to observe the odor. Odor thresholds reported in the literature vary substantially due to the variety of definitions and methods followed. An odor threshold can be defined as the “minimum concentration of an odorant which produces a noticeable change in the odor of the system” or as “the minimum concentration at which the odor quality (description of smell) of the compound can be described” (Ruth, 1986). The odor panel can consist of trained or untrained individuals. Furthermore, the threshold can be set based on the concentration at which one panelist, half the panelists, or all of the panelists detect the odor. Odor thresholds are established based on exposure to pure compounds and not compounds in mixtures. It is not known how mixtures affect odor thresholds (Ruth, 1986). This is a significant gap in the literature given that ambient air in industrial areas will always contain a mixture of compounds.

The odor thresholds reported in Table 8 are based on literature reviews by the EPA (EPA, 1992) and by the ATSDR (ATSDR, 1999, 2000, 2005, 2007a, 2007b). Heptane was not referenced in either of these compilations as it is not a HAP; therefore an independent study of odor thresholds was used for heptane (Amoore & Hautala, 1983).

The single compound odor thresholds for hexane, heptane, benzene, and toluene are three to five orders of magnitude greater than the maximum concentrations detected in the odor samples. Therefore, these compounds likely did not contribute to observed tar/asphalt odors during the sample period. The maximum detected concentration of *m,p*-xylene came within one to two orders of magnitude of the odor threshold; and the maximum detected concentration of naphthalene (25 ppb) was on the same order of magnitude as the odor threshold (38 ppb).

Although naphthalene was never detected at concentrations greater than the published odor threshold, it is likely that naphthalene, which is known to have a coal tar odor, contributed to tar/asphalt odor observations during the sample period. It is possible that naphthalene concentrations in the samples partially degraded before analysis, or that odor thresholds established based on exposure to pure naphthalene do not accurately represent scenarios in which residents are exposed to naphthalene in mixture with other PAHs. For example, the Koppers Inc. APCD permit lists quinoline (also known as benzo[b]pyridine) emissions of nearly 600 pounds per year. Quinoline was not included in the air quality sampling program, but it is a compound derived from coal tar that is known to have an unpleasant odor above an odor threshold of 5.3 parts per million (EPA, 1992). While it is unknown whether quinoline concentrations exceeded 5.3 parts per million in Globeville, it is possible that the interaction of multiple odorous compounds creates a noticeable tar/asphalt odor.

Health thresholds reported in Table 8 include the threshold limit value (TLV); the short-term exposure limit (STEL); acute, intermediate, and chronic minimal risk levels (MRLs); and the per million (E-6) Cancer Risk Level. The TLV and STEL are exposure limits for workers set by the American Conference of Governmental and Industrial Hygienists (ACGIH). The TLV is an eight-hour time-weighted average concentration to which workers can be exposed without adverse health effects (EPA, 2009). The STEL is a 15-min time-weighted average acute exposure threshold that should not be exceeded at any time during a workday (EPA, 2009). An MRL, established by ATSDR, is "an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure" (ATSDR, 2013). Durations of exposure include acute (14 days or less), intermediate (15 to 364 days), and chronic (365 days or more). Finally, the per million Cancer Risk Level, reported in the EPA's Integrated Risk Information System (IRIS), is the concentration to which a lifetime (seventy years) of exposure will cause no more than a one-in-a-million increased chance of developing cancer (EPA, 2013f). Compounds are assigned a letter A through E corresponding to their likelihood of causing cancer as follows: A - known human carcinogen, B - probable human carcinogen, C - possible human carcinogen, D - not classifiable as a human carcinogen, and E - evidence of non-carcinogenicity.

All health thresholds for hexane, heptane, toluene, and *m,p*-xylene are at least one order of magnitude greater than the maximum detected concentrations of these compounds.

Both the maximum detected concentration of naphthalene (25 ppb) and the odor sample average concentration (4.47 ppb) exceed the chronic MRL (0.7 ppb). The maximum detected concentration of benzene (1.60 ppb) was just below the chronic MRL (3 ppb); and both the maximum and the odor sample average benzene concentration (0.56 ppb) far exceeded the per million Cancer Risk Level (0.04 ppb). Although short-term exposure to hexane, heptane, benzene, toluene, *m,p*-xylene, and naphthalene is not expected to cause adverse health effects at the concentrations detected in the odor samples, uncertainty about duration of exposure in Globeville and exposure from other sources near Globeville provide grounds for further studies.

The following HAPs were detected in one or two odor samples: chloromethane, 1,3-butadiene, 2-butanone (methyl ethyl ketone, or MEK), ethyl benzene, and *o*-xylene. As these compounds were present in less than half of the odor samples, it is unlikely that their presence was related to the tar/asphalt odor.

Odor Sample Pollutants Linked to Facilities

Some pollutants that were detected in odor samples can be linked to specific facilities based on the emissions reported in APCD permits and in the TRI.

The presence of naphthalene and other PAHs in the odor event samples indicate emissions from Koppers Inc. Although these compounds are often listed as common pollutants from asphalt plants (ATSDR, 1995), they are not listed in the TRI reports for Cobitco Inc. (EPA, 2013b) nor Owens Corning Trumbull Asphalt Plant (EPA, 2013c). The Owens Corning Roofing Plant reported only one kilogram of PAHs released to the air in 2011 (EPA, 2013d), as compared to 1,057 kilograms reported by Koppers Inc. (EPA, 2013e). Furthermore, the Koppers Inc. APCD permit lists emissions of more than 8,000 kilograms per year of naphthalene for the wastewater treatment system alone (APCD, 2010), whereas naphthalene is not listed in any Owens Corning permit (APCD, 2003, 2007, 2009b). The Cobitco permit could not be obtained from the APCD, but the MSDS available on Cobitco Inc.'s website does not list naphthalene or any other PAH (Chemical Safety Associates, Inc., 2004). Given that naphthalene is not typically found in urban air at concentrations as high as those found in the Globeville odor samples (ATSDR, 2005), and that naphthalene was not detected in background samples in Globeville, it can be assumed that naphthalene in the samples originated from Koppers Inc.

As mentioned previously, off-gassing of treated wood is a primary source of emissions from Koppers Inc. In a successful effort to remove wood treatment facilities from the EPA's list of industries that must apply best available control technology (BACT) in order to control HAP emissions, the American Wood Preservers Institute (AWPI) conducted a study proving that naphthalene emissions from treated wood storage at Koppers Inc. total less than ten tons per year (Wikstrom, et al., n.d.). This very study, however, demonstrated elevated naphthalene emissions during the first ten to 20 hours immediately following wood treatment (Figure 6).

The daily operating schedule of Koppers Inc. was not determined, but it is possible that tar/asphalt odors are observed in Globeville when north by northwesterly winds occur within one day of wood treatment at Koppers Inc.

Hexane, heptane, benzene, toluene, and *m,p*-xylene are all common industrial pollutants that cannot be linked to any one facility. Benzene, toluene, and *m,p*-xylene are also found in automotive exhaust due to the use of BTEX as a gasoline additive (ATSDR, 2000, 2007a, 2007b). Therefore, the major highways bisecting Globeville likely contribute to the presence of these pollutants in the samples. However, the Owens Corning Asphalt Plant permit does list benzene emissions of 2,972 kilograms per year, as compared to 169 kilograms per year for Owens Corning Roofing Plant and no benzene emissions from Koppers Inc. Therefore, the Owens Corning Asphalt Plant is more likely to have contributed to the benzene concentrations found in odor samples than the other facilities in the area.

CONCLUSIONS

Residents of Globeville have been complaining for years of transient and noxious odors in their neighborhood. An independent investigation of specific complaints related to asphalt/tar odors was conducted for the neighborhood through air quality sampling of odor events, and background and source location samples. Detailed wind monitoring and an industry assessment were also conducted. Results showed naphthalene to be the predominant and elevated pollutant, and that odor events occur when the wind comes from the north northwest. Naphthalene is reported in permits to be emitted from Koppers Inc., a wood treatment facility.

Regulation 2 (Reg 2) is Colorado's current approach to addressing and regulating odors. It has proven ineffective for addressing Globeville's odor events. Despite residents calling and asking for Reg 2 assessments, no violation has been recorded. For example, one odor event that occurred in September 2011 was reported to CDPHE and investigated by an odor inspector. The wind was out of the WNW at 1-3 mph, but odor could not be detected at a dilution of 2:1. The odor dissipated as rain began to fall and the investigation was concluded (CDPHE 2011). Current strategies for investigating odor do not sufficiently take into account rapidly changing climatic conditions (i.e. wind direction shifts), nor the time and staff required to properly address odor concerns. Reg 2 is not necessarily protective of public health for these reasons, among others. Numerous variables influence odor detection and therefore determine odor violations: rapidly changing and unpredictable meteorological conditions, individual sensitivity to odors, and odors mixing in ambient air.

What can be done about the odor related to asphalt/tar in Globeville? Some residents have taken matters into their own hands and moved out of the neighborhood (Escamilla, 2013). Research is needed to understand odor mixtures compared to single compound toxicity. A more detailed study should be undertaken to elucidate the impacts of odor in communities such as Globeville, including assessing acute and long-term health effects as well as stress and wellbeing issues.

Legislative approaches have proven unfruitful and no health or odor thresholds were typically violated. A new regulation that is focused on neighborhood odors could use a panel of residents in various land use types to address specific odors, as well as rates of sensitivity based on residence in certain neighborhoods. New approaches are warranted to address odor mixture effects in neighborhoods near industrial facilities. Given the technical and regulatory challenges of sampling odors and controlling emissions, it is recommended that Globeville residents and neighboring industry pursue a “good neighbor policy” to solve the odor issue. Specific offending industrial processes could be identified for which there exist cost-effective control technologies which would reduce exposure to odors and air toxics in Globeville.

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Table 1. List of air quality sample analytes

Volatile Organic Compounds		Sulfur Compounds
Dichlorodifluoromethane	Heptane	Hydrogen sulfide
Chloromethane	cis-1,3-Dichloropropene	Carbonyl sulfide
Freon 114	4-Methyl-2-pentanone	Methyl mercaptan
Vinyl chloride	trans-1,3-Dichloropropene	Ethyl mercaptan
1,3-Butadiene	1,1,2-Trichloroethane	Dimethyl sulfide
Bromomethane	Toluene	Carbon disulfide

Chloroethane	2-Hexanone	Isopropyl mercaptan
Freon 11	Tetrachloroethene	t-Butyl mercaptan
Freon 113	Dibromochloromethane	n-Propyl mercaptan
1,1-Dichloroethene	1,2-Dibromoethane	Thiophene
Acetone	Chlorobenzene	Diethyl sulfide
Carbon disulfide	Ethyl benzene	n-Butyl mercaptan
Methylene chloride	*m,p*-Xylene	Dimethyl disulfide
trans-1,2-Dichloroethene	*o*-Xylene	Tetrahydrothiophene
Methyl t-butyl ether	Styrene	**Polycyclic Aromatic**

		Hydrocarbons
Vinyl acetate	Bromoform	Acenaphthylene
2-Butanone (MEK)	1,1,2,2-Tetrachloroethane	Chrysene
cis-1,2-Dichloroethene	4-Ethyl toluene	Benzo(a)pyrene
1,1-Dichloroethane	1,3,5-Trymethylbenzene	Dibenz(a,h)anthracene
Ethyl acetate	1,2,4-Trymethylbenzene	Benzo(a)anthracene
Hexane	1,3-Dichlorobenzene	Acenaphthene
Chloroform	1,4-Dichlorobenzene	Phenanthrene

Tetrahydrofuran	Benzyl chloride	Fluorene
1,2-Dichloroethane	1,2-Dichlorobenzene	Naphthalene
1,1,1-Trichloroethane	1,2,4-Trichlorobenzene	Anthracene
Carbon tetrachloride	Hexachlorobutadiene	Pyrene
Benzene	Isobutane	Benzo(g,h,i)perylene
Cyclohexane	Ethanol	Indendo(1,2,3-cd)pyrene
Trichloroethene	Isopropyl alcohol	Benzo(b)fluoranthene
1,2-Dichloropropane	Butane, 2-methyl-	Fluoranthene

Table 2. Air quality sampling results for all compounds that were detected above the RL in at least one sample (all values in ppb)*

	Odor Event Samples						Background Samples		Source Samples	
Compound	**9-11-12**	**11-13-12**	**11-19-12**	**11-28-12**	**12-30-12**	**3-3-13**	**7-13-12**	**11-20-12**	**Koppers 8-21-12**	**Owens Asphalt/Cobitco 8-21-12**
VOCs (ppb)**										
Dichlorodifluoromethane	**0.69**	0.36	0.40	**0.74**	0.45	**0.58**	0.49	0.37	**0.52**	0.45
Chloromethane	0.35	0.38	0.44	**0.50**	0.46	**0.52**	**0.64**	0.41	**0.50**	0.46
1,3-Butadiene	ND	ND	**0.54**	0.28	ND	ND	ND	ND	ND	ND

Acetone	**5.90**	**1.40**	**5.90**	**7.10**	**3.60**	**5.90**	**7.10**	**1.70**	**6.00**	**11.00**
Methylene chloride	**2.20**	ND	**0.57**	**0.57**	**0.79**	0.29	**0.99**	**0.54**	**3.30**	**1.10**
2-butanone	ND	ND	**1.20**	**1.20**	ND	ND	**0.73**	**0.58**	ND	**0.69**
Ethyl acetate	ND	ND	ND	ND	ND	ND	**0.64**	ND	ND	ND
Hexane	0.30	0.28	**2.60**	**1.40**	**1.90**	ND	0.33	0.29	**0.67**	**0.57**
Tetrahydrofuran	ND	ND	ND	0.24	ND	ND	ND	**0.63**	ND	ND
Benzene	ND	0.15	**1.60**	**0.87**	**0.72**	ND	ND	0.17	0.38	0.37
Cyclohexane	ND	ND	**0.71**	0.40	**0.56**	0.24	ND	ND	ND	**0.56**

Heptane	ND	0.15	**1.10**	**0.61**	**0.50**	0.15	ND	ND	ND	0.19
Toluene	0.43	**0.90**	**6.30**	**3.70**	**1.80**	0.42	0.47	**0.73**	**1.30**	**1.70**
Tetrachloroethene	ND	ND	0.16	**1.80**	ND	ND	0.22	ND	0.35	ND
Ethyl benzene	ND	ND	**1.00**	0.44	ND	0.30	ND	ND	ND	ND
m,*p*-Xylene	0.24	ND	**2.90**	**1.40**	**0.68**	**0.82**	ND	0.24	0.44	0.30
o-Xylene	ND	ND	**0.91**	0.42	0.19	0.43	ND	ND	ND	ND
1,2,4-Trimethylbenzene	ND	ND	**0.86**	0.44	ND	**1.20**	ND	ND	ND	ND
Sulfur Compounds (ppb)										

Carbon disulfide	ND	ND	ND	ND	ND	ND	**5.90**	ND	ND	**6.00**
PAHs* (ppb)**										
Naphthalene	**25.00**	ND	ND	**1.50**	**0.33**	ND	ND	ND	**1.50**	ND
Dibenz(a,h)anthracene	**2.70**	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(g,h,i)perylene	**1.70**	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	**2.10**	ND	ND	ND	ND	ND	ND	ND	ND	ND

MDL = Method Detection Limit, a statistical estimate of method/media/instrument sensitivity. MDL for VOCs: 0.15 ppb

RL = Reporting Limit, a verified value of method/media/instrument sensitivity. RL for VOCs: 0.50 ppb; for sulfur compounds: 3.50 ppb; for PAHs: 0.10 µg/sample

ND = Not Detected, testing result not detected above the MDL or RL

Bold values are those greater than the RL

*Odor indicates samples that were collected during an odor episode in a residential yard in Globeville; background indicates samples that were collected when there was no odor episode in a in a vacant lot and residential yard. See Figure 1 for sampling locations.

**VOCs and sulfur compounds were collected using SUMMA canisters.

***PAHs were collected using sorbent tubes and sampling pumps; concentrations are +/- 5% due to pump flow rate accuracy limitations.

Table 3. Odor event and background sample average concentrations (values in ppb)*

Compound	Odor Event Samples Average (n = 6)	Background Samples Average (n = 2)	Ratio: Odor Average/ Background Average
VOCs (ppb)			
Dichlorodifluoromethane	0.54	0.43	1.3
Chloromethane	0.44	0.53	0.8
1,3-Butadiene	0.14	0.00	-
Acetone	4.97	4.40	1.1
Methylene chloride	0.74	0.77	1.0
2-butanone (MEK)	0.40	0.66	0.6
Ethyl acetate	0.00	0.32	0.0

Hexane	**1.08**	**0.31**	**3.5**
Tetrahydrofuran	0.04	0.32	0.1
Benzene	**0.56**	**0.09**	**6.2**
Cyclohexane	0.32	0.00	-
Heptane	**0.42**	**0.00**	**-**
Toluene	**2.26**	**0.60**	**3.8**
Tetrachloroethene	0.33	0.11	3.0
Ethyl benzene	0.29	0.00	-
***m,p*-Xylene**	**1.01**	**0.12**	**8.4**
o-Xylene	0.33	0.00	-
1,2,4-Trimethylbenzene	0.42	0.00	-

Sulfur Compounds (ppb)			
Carbon disulfide	0.00	2.95	0.00
PAHs (ppb)**			
Naphthalene	**4.47**	**0.00**	**-**
Dibenz(a,h)anthracene	0.45	0.00	-
Benzo(g,h,i)perylene	0.28	0.00	-
Indeno(1,2,3-cd)pyrene	0.35	0.00	-

Bold compounds are those that were detected above the RL in at least half of the odor samples and had an odor sample average concentration at least three times greater than average background concentrations.

*Odor event indicates samples that were collected during an odor episode in a residential yard in Globeville. Background indicates samples that were collected in a vacant lot and residential yard when there was no odor episode. See Figure 1 for sampling locations.

**PAH concentrations are +/- 5% due to pump flow rate accuracy limitations.

Table 4. Uses of industrial compounds detected in Globeville air quality samples

Compound	**Use**
Hexane[1]	Edible-oil extractant for seed crops; solvent and cleaning agent in the textile, shoe and leather, and furniture industries; various uses in printing; glues and adhesives
Heptane[2]	Standard for octane-rating determinations; anesthetic; solvent; organic synthesis; preparation of laboratory reagents
Benzene[3]	Solvent in chemical and drug industries; starting and intermediate material in chemical synthesis; gasoline additive
Toluene[4]	Starting material in benzene production; solvent in paints, coatings, adhesives, inks, and cleaning agents; gasoline additive
m,p-Xylene[5]	Starting material in ethyl benzene production; solvent in paints and coatings; gasoline additive
Naphthalene[6]	Intermediate in production of phthalic anhydride, insecticide carbaryl, synthetic leather-tanning agents, and surface active agents; moth repellent

[1](ATSDR, 1999), [2](Lewis R.J., 2001), [3](ATSDR, 2007a), [4](ATSDR, 2000), [5](ATSDR, 2007b), [6](ATSDR, 2005)

Table 5. Koppers Inc. creosote releases as reported to the TRI

Year	Fugitive Air Emissions (kg)	Stack Air Emissions (kg)	Total Air Emissions (kg)
2006	1,724	1,179	2,903
2007	1,451	454	1,905
2008	1,814	499	2,313
2009	1,542	680	2,223
2010	590	236	826
2011	726	331	1,057

Table 6. Koppers Inc. emissions of non-criteria reportable air pollutants as listed in APCD construction permits

CAS#	**Substance**	**Emissions (kg/yr)**	
		Koppers WWT* Effluent Tank[1]	Koppers Creosote Storage Tank[2]
92-52-4	Biphenyl	115	1
132-64-9	Dibenzofuran	9	0
86-73-7	Fluorene	245	2
91-20-3	Naphthalene	8,160	59
91-22-5	Quinoline	263	2

1 (APCD, 2010)

2 (APCD, 2009a)

* WWT – wastewater treatment

Table 7. Owens Corning emissions of non-criteria reportable air pollutants as listed in APCD construction permits

CAS#	**Substance**	**Emissions (kg/yr)**	
		Owens Roofing Plant[1,2]	Owens Asphalt Plant[3]
71-55-6	1,1,1 Trichloroethane	174	
	Arsenic Compounds	1	
71-43-2	Benzene	169	2,972
106-99-0	Butadiene		100
67-66-3	Chloroform		27
	Chromium Compounds	59	
	Cobalt Compounds	5	
100-41-4	Ethylbenzene	51	2,828

50-00-0	Formaldehyde	52	
7647-01-0	Hydrochloric acid	62	7,257
7439-92-1	Lead Compounds	6	
	Manganese compounds		55
74-87-3	Methyl chloride		181
78-93-3	Methyl ethyl ketone*	4,062	
75-09-2	Methylene chloride		308
	Nickel compounds		64
	Selenium Compounds	1	
100-42-5	Styrene		1,633
108-88-3	Toluene	291	

108-05-4	Vinyl acetate		4,694

*Methyl ethyl ketone was removed from the list of hazardous air pollutants in 2005, and therefore removed from the Owens Corning permit. The 2003 permit value is listed as a reference.

[1] (APCD, 2003)

[2] (APCD, 2009b)

[3] (APCD, 2007)

Table 8. Odor event sample concentrations of compounds detected in Globeville odor samples compared to odor and health effect thresholds

	Odor Sample Maximum (ppb)	Background Sample Average (ppb)	Typical Urban Conc. (ppb)	Odor Descriptors[2]	Odor Threshold (ppb)	Non-Carcinogenic Health Thresholds		Carcinogenicity	
						TLV (ppb)[3] STEL (ppb)[3]	Acute MRL (ppb) Intermediate MRL (ppb) Chronic MRL (ppb)	E-6 Cancer Risk Level (ppb)[4]	Category[4]
Hexane	2.60	0.31	2 - 25[1]	Faint, gasoline	130,000[1] 65,000[2]	50,000 -	- - 600[1]	-	-
Heptane	1.10	0	Median: 0.06[5]	Mild, gasoline-	150,000[7]	400,000	-	-	D

				like[6]		500,000			
Benzene	1.60	0.09	3.0 - 6.6 Median: 4.1[8]	Aromatic, sweet, solvent	61,000[2,8]	10,000 -	6 4 3[8]	0.04	A
Toluene	6.30	0.6	0.27 - 7.98 Median: 2.88[9]	Sour, burnt, benzene-like	8,000[9] 2,800[2]	50,000 -	1000 - 80[9]	-	-
***m,p*-Xylene**	2.90	0.12	1 - 30 Median: 2.8[10]	Sweet	50[10] 730[2]	100,000 150,000	2000 600 50[10]	-	-
Naphthalene	25.0	0	0.08 - 32.43 Median:	Tar, creosote, mothballs	84[11] 38[2]	10,000 15,000	- -	-	C

			0.18[11]				0.7[11]		

Definitions of Health Thresholds

TLV: American Conference of Governmental and Industrial Hygienists' (ACGIH) threshold limit value expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed eight hours per day without adverse effects

STEL: ACGIH's short-term exposure limit; a 15-min time-weighted-average exposure which should not be exceeded at any time during a workday

MRL: Minimal risk level; an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure

Acute MRL: minimal risk level for acute-duration inhalation exposure (14 days or less)

Intermediate MRL: minimal risk level for intermediate-duration inhalation exposure (15-364 days)

Chronic MRL: minimal risk level for chronic-duration inhalation exposure (365 days or more)

E-6 Cancer Risk Level: the concentration to which a lifetime of exposure will cause no more than a one-in-a-million increased chance of developing cancer

Cancer Risk Categories: A - known human carcinogen, B - probable human carcinogen, C - possible human carcinogen, D - not classifiable as a human carcinogen, E - evidence of non-carcinogenicity

References

[1] (ATSDR, 1999), [8] (ATSDR, 2007a), [9] (ATSDR, 2000), [10] (ATSDR, 2007b), [11] (ATSDR, 2005)

[2] (EPA, 1992)

[3] (Lewis R.J., 2001)

[4] (EPA, 2013f)

[5](Jia, Batterman, & Godwin, 2008)

[6] (OSHA)

[7] (Amoore & Hautala, 1983)

Figure 1. Map of the Globeville boundary and the location of residents that reported a tar/asphalt odor. Sampling locations are also shown.

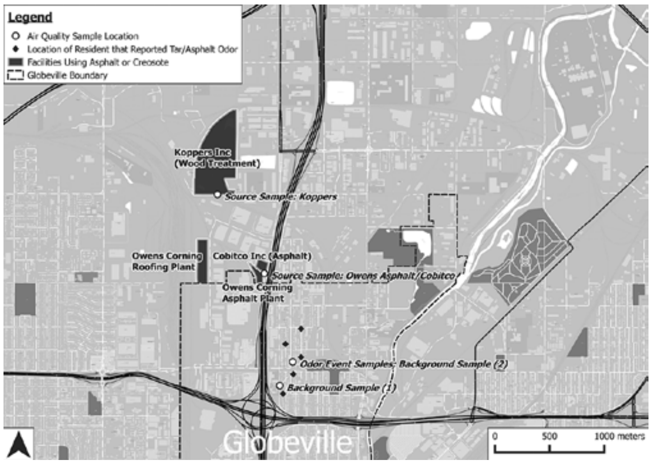

Figure 2. Odor, background, and industrial sample concentrations of compounds detected in odorous air. Odor indicates samples that were collected during an odor episode in a residential yard in Globeville; background indicates samples that were collected in a vacant lot and residential yard in Globeville when there was no odor episode; industrial samples were collected directly adjacent to a wood treatment facility, Koppers Inc., and on the fence line between two asphalt plants, Owens Corning Trumbull Asphalt and Cobitco Inc., when tar/asphalt odors were present. See Figure 1 for sampling locations.

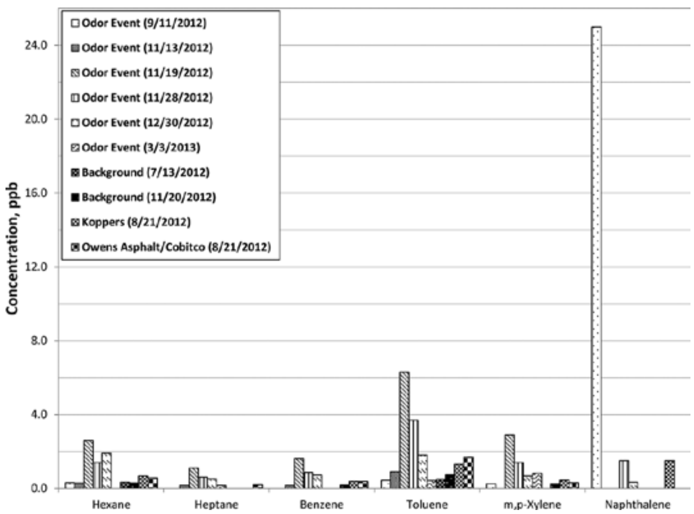

Figure 3. Wind rose summarizing wind speed and direction for the air monitoring period.

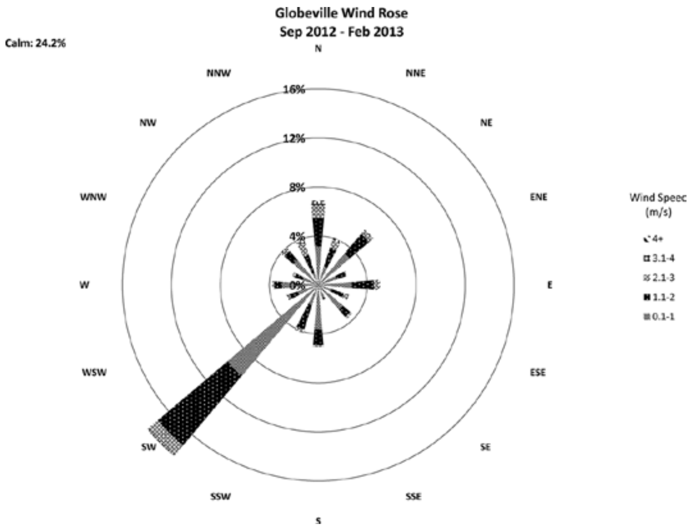

Figure 4. Wind direction versus time of day for odor sample collected on 11-13-12 (sample collected from 4:05 p.m. to 4:25 p.m.).

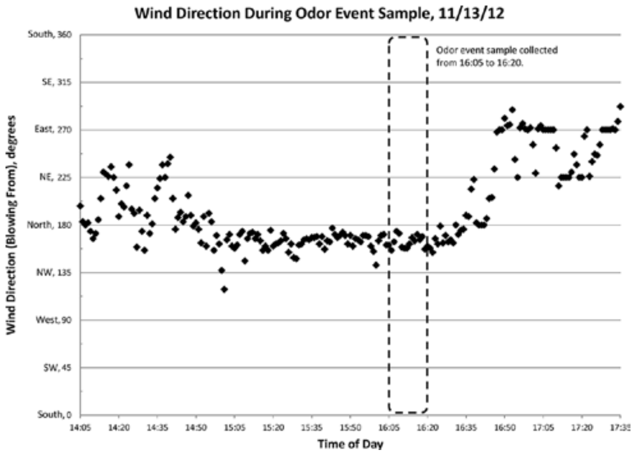

Figure 5. Industrial facilities near to Globeville.

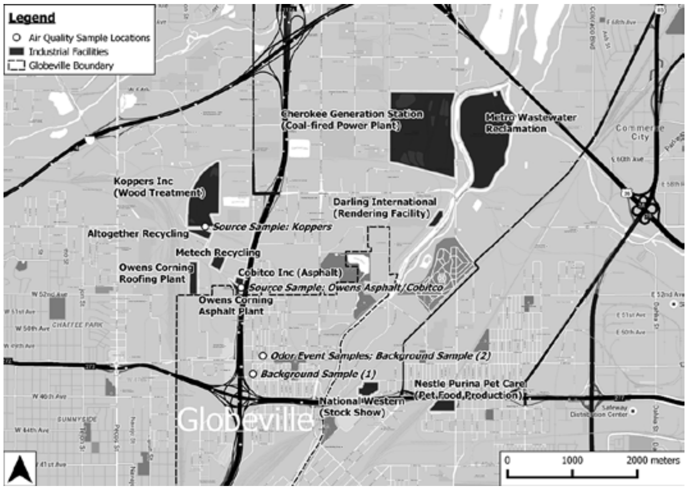

Figure 6. Modeled naphthalene **e**missions from treated wood storage, reproduced from data in (Wikstrom et al., n.d.).