

Multimethod Approach to Investigate the Factors Influencing High-Temperature Fuming of Bitumen

Zachary Deller, Stephen Grist, Filippo Giustozzi,* and Subashani Maniam*

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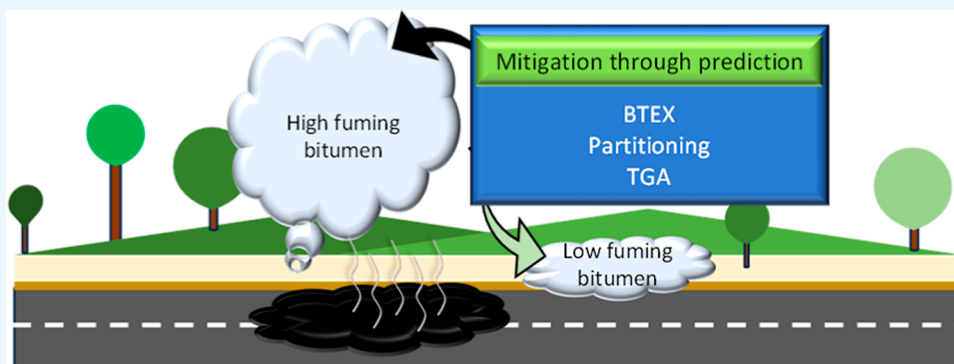
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ABSTRACT: Bitumen is heated at high temperatures during asphalt paving applications. In these circumstances, there is the possibility for fuming. These fumes can vary in intensity and, if significant, may attract complaints. The bitumen's chemical composition depends on the crude oil from which it originates. A tool to screen bitumen and evaluate its potential to release fumes would be highly beneficial. In this study, three methods have been employed to investigate a series of bitumen samples that were known to produce complaints by (a) quantifying benzene, toluene, ethylbenzene, and *m*, *o*, *p*-xylene (BTEX), (b) measuring the partition coefficients of these analytes, and (c) measuring the volatile mass of bitumen exposed to isothermal heating. It was found that the concentration of BTEX varied significantly between bitumen samples. The partition coefficients of these analytes are substantially the same between samples. Finally, the volatile mass of each sample varies significantly between samples, independent of bitumen grade or country of origin. These volatile masses correlate strongly with fuming complaints from bitumen and can be used as predictors of bitumen fuming risk.

1. INTRODUCTION

Bitumen is a heavy residue that remains after crude oil processing in a refinery. It is a product containing residual amounts of many organic compounds considered pollutants.^{1,2} The primary application of bitumen is as a binder in asphalt for road construction.¹ Asphalt comprises a mixture of roughly 5 wt % bitumen to 95 wt % aggregate, predominantly inorganic material such as crushed stone. When asphalt is prepared, bitumen is first heated to allow mixing with the aggregate. Depending on the type of bitumen used and the manufacturing process, the bitumen could reach temperatures above 200 °C, especially if overheating occurs.^{3,4} During the mixing and laying of asphalt at high temperatures, fumes are emitted from the bitumen containing a range of organic compounds in the form of gases or particulate matter.^{5,6} Through anecdotal reports and complaints, the material has been known to produce large quantities of fumes in isolated cases.⁷ Large clouds of visible fume can be unsettling to nearby communities and businesses and disruptive to workers handling bitumen. There is also a range of saturated and unsaturated hydro-

carbons that may cause respiratory irritation, making work difficult without personal protective equipment.⁸

The complex matrix of bitumen, while consisting predominantly of heavy oil fractions categorized as saturates, aromatics, resins, and asphaltenes,^{9,10} can emit organic chemicals ranging from low-molecular-weight volatile organic compounds (VOCs) to high-molecular-weight polyaromatic hydrocarbons (PAHs).^{11,12} Among these are compounds, which include certain PAHs^{13,14} and VOCs^{12,15–18} that can exhibit carcinogenesis. As bitumen is a natural product containing variations in its chemical composition, it has been reported that the levels of the emitted VOCs and PAHs can vary notably between samples.^{12,16} The matrix of bitumen and

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its unique physiochemical properties have been explored in literature, while the microstructure of bitumen is often modeled as a colloidal structure. It is a complex field of research and a universal model of its microstructure is yet to be embraced while various notions exist.¹⁹ Given its complexity, the effect of the microstructure on emissions and fumes is still poorly understood. While large aromatic systems are present in the asphaltene fractions and large hydrophobic hydrocarbons exist in the mixture, it is unclear how any variations in concentration, molecular structure, and distribution could influence the emission potential of VOCs and PAHs.^{19–21} The emissions of PAHs and VOCs have been extensively studied and are well established in bitumen.^{8,10,11,22–27} The emissions of PAHs and VOCs in bitumen generally remain low, and their emissions are classified as “possibly carcinogenic to humans” (group 2B) by the World Health Organization’s International Agency for Research on Cancer (IARC). In 2011, the IARC working group concluded that there was insufficient evidence to determine the carcinogenicity of hard and straight-run bitumens in humans.²⁸

To accurately investigate bitumen emissions, nonvolatile compounds within the bitumen complex matrix must be addressed. Consequently, sample preparation methods are essential for isolating the volatile analytes of interest from the heavier fractions, ensuring a focused analysis of the desired volatile components. A range of sample preparation methods have been used to analyze bitumen emissions. In the laboratory, this includes sampling through the use of filters to concentrate emissions, headspace sampling, headspace solid-phase microextraction sampling, and nonseparative real-time sampling.²⁹ Many current laboratory methods used to examine bitumen emissions rely on the extraction and concentration of emissions onto filters. When using this method, bitumen is heated and mixed in a closed vessel, while air is pulled through the vessel’s headspace and subsequently through filters to collect and concentrate the emissions.^{10,11,30–40} This method has expanded significantly upon the understanding of bitumen fumes and has been essential in establishing health advice for persons that are regularly exposed to bitumen emissions.^{41–43}

Comparing the amount of emitted analyte and the net concentration of analyte in a bitumen sample can help in understanding the behavior of the bitumen emissions. Depending on the sample preparation method, the amount of analyte is often expressed by the mass of analyte per volume (mg/m^3) if extracted from fumes. Otherwise, the net concentration of an analyte in the sample is typically expressed by the mass of the analyte per mass of the sample ($\mu\text{g}/\text{g}$). Comparing net concentrations of chemicals with their emitted concentrations may provide insight into how bitumen emits different chemicals and factors that influence this, such as the chemical composition of the bitumen, its physical properties, and the working conditions in which it is used.

The relationship between the amount of emitted analyte and the net concentration of analyte in a bitumen sample may be complex, and a range of factors may influence it. These factors may include the volatility of the analyte, the affinity of the analyte for the bitumen matrix, and the volatile mass of the bitumen. Understanding these parameters is essential for comprehending bitumen emissions behavior and devising effective strategies to mitigate associated emissions.

Headspace gas chromatography mass spectrometry (HS-GC-MS) sampling is a technique that analyzes the gas phase of an associated solid or liquid sample, therefore restricting the

analysis to the volatile chemicals present in the gas phase. It requires no solvent extraction or enrichment methods, making it a simple and clean preparation method. It allows for the highly sensitive and specific detection and quantification of volatile compounds in complex samples.⁴⁴

In HS-GC, partition coefficients (PCs) are the distributions of a compound between the headspace above a sample and the sample itself. The PC plays a crucial role in HS-GC as it can impact the concentration of an analyte in the gas phase that is being extracted from the sample before being introduced into the instrument and, therefore, affects its detection sensitivity. Compounds with higher PCs are more present in the headspace and, therefore, are more easily detected. In comparison, compounds with lower PCs can be more challenging to detect as less analyte partitions into the headspace. The PCs of compounds can be influenced by many factors, such as the chemical properties of the compound, the sample matrix, and the temperature and pressure used in the headspace analysis.^{45,46} Using the PC values, this method can measure both the gaseous concentrations of chemicals and the net concentration of chemicals in a sample.

There is a clear indication that the temperature strongly influences the rate and amount of organic material released from bitumen. An increase in temperature can drastically increase emissions and influence the PC values of analytes.^{6,40,47} Besides this relationship between temperature and emissions, previous work has had difficulty in establishing clear indicators for predicting high-fuming bitumen.^{6,40}

Work by Brandt and De Groot,⁴⁰ focusing on the mass of PAHs emitted from bitumen, measured as benzene soluble matter (BSM), showed that the actual BSM could be predicted with reasonable certainty based on the fuming index, which they defined as a measure of heating temperature and volatility. Volatility in their work was defined as the percentage mass of bitumen lost below set temperature thresholds. As the temperature increases, a greater BSM would be predicted for the bitumen product. These predictions were also confirmed with in-field testing consistent with the model’s predictions. Although this method effectively predicted the BSM in bitumen samples, it did not specifically address the prediction of fuming risk in bitumen.

In a separate study conducted by Stroup-Gardiner et al.,⁶ the prediction of fuming was the primary focus. They examined the weight loss and opacity at temperatures ranging from 130 to 190 °C for various bitumen samples. The samples were categorized into low, medium, or high levels of fuming complaints based on real-world usage. The researchers utilized weight loss and opacity measurements to identify bitumen samples with emission issues. However, their approach had some limitations as it relied on modified equipment and necessitated two metrics to assess fuming risk, making replication of their method challenging.

This work investigated historic bitumen samples from various locations worldwide that have attracted fuming complaints to understand the factors that may contribute to high-fuming events. These were compared to normal samples that did not attract any complaints. This investigation was performed employing three main procedures. First, developing a method for measuring the weight loss percentage of samples at 200 °C to create a measure for the volatile mass of bitumen samples. Second, the quantification of benzene, toluene, ethylbenzene, and *m*, *o*, *p*-xylene (BTEX) in bitumen using

HS-GC-MS. Finally, the calculation of the PC values for each BTEX analyte. By employing these three procedures, this study wanted to provide a more comprehensive understanding of the chemical factors that contribute to bitumen producing high levels of fume, thereby mitigating the use of “poor” quality products in the industry. Additionally, this study evaluated a series of bitumen samples supplied from several refineries in various countries.

2. METHODS

2.1. Chemicals. Analytical-grade methanol was purchased from Sigma-Aldrich. Analytical standards for BTEX and the kerosene surrogate mixture were purchased from Agilent. Glass headspace vials and all GC consumables listed were also purchased from Agilent.

2.2. Bitumen Samples. The bitumen samples used were provided by Puma Energy (Australia) Bitumen Pty Ltd. and were taken from a library of samples with known performance spanning two decades. During this time, samples were stored in sealed tins on the scale of milliliters to liters. Temperature ranges were in the range of typical ambient temperatures. The information provided for each sample included the product grade and whether the bitumen had received any complaints. Nineteen unique samples were provided and analyzed for this work. All the samples (Table 1) have previously been used in

Table 1. Bitumen Samples Used in This Study and Their Status, Fuming (Complaints), or No Concerns (No Complaints)

sample reference	grade	comment
117	160/220	fuming
43369	160/220	fuming
207	160/220	no concerns
327	250/330	fuming
227	35/50	no concerns
237	40/60	no concerns
120	50/70	fuming
204	50/70	no concerns
198	50/70	no concerns
46559	650/900	fuming
217	70/100	no concerns
43368	70/100	fuming
23762	70/100	no concerns
25249	70/100	no concerns
C170	70/100	no concerns
33248	70/100	no concerns
22707	70/100	no concerns
44771	80/100	no concerns
180	10/20	no concerns

projects. The samples contained no modified bitumen, and they did not contain any additives or polymers. Reports of fuming were instances of customer complaints during either mixing with aggregate at an asphalt plant or the laying of asphalt on site. These complaints were substantiated and assembled by Puma Energy (Australia) Bitumen Pty Ltd. as part of a survey including users of the bitumen products. The data that were provided for this work were binary qualitative data. The collection of these data is not part of this work.

2.3. Thermogravimetric Analysis. All thermogravimetric analysis (TGA) testing was done on a PerkinElmer TGA 8000 instrument with automated attachments and PerkinElmer

software. Additional equipment includes ceramic pans from PerkinElmer that are compatible with the TGA 8000 and nitrogen gas.

Bitumen samples were stored at room temperature in sealed tins. Gram quantities of bitumen were collected from 1 to 3 cm below the surface layer. Samples were not heated to be transferred to the ceramic sampling pans. This was done to reduce variations in weight loss from the evolution of fumes.

The bitumen was collected with a stainless-steel spatula, and 15–20 mg was added to the center of each ceramic pan. The accurate weighing was carried out automatically by a TGA instrument before the start of each run. Reproducibility was consistent in the 15–20 mg range. The mass range appears sufficiently small to minimize variation in the surface area to volume ratio of samples to achieve consistent results.

After weighing, the temperature program was automatically carried out as follows. The nitrogen flow was initiated, and the temperature was maintained at 35 °C for 3 min. This was then increased at 20 °C/min until reaching 200 °C. This temperature was then maintained for 1 h, the nitrogen flow was maintained throughout this program, the sample purge flow was set to 20 mL/min, and the balance purge flow was set to 40 mL/min. Isothermal temperatures can be maintained with a precision of ± 0.1 °C. The precision while ramping at 20 °C/min is $\pm > 1$ °C.

2.4. Head Space Gas Chromatography Mass Spectrometry. To prepare the sample, 1 g of bitumen was placed in a sealed headspace vial with an incubation time of 90 min to establish equilibrium. The samples were collected from room-temperature bitumen using a metal spatula. Gram quantities were removed from the tins without heating and manually mixed to produce homogeneous samples. The replicates of the samples showed good repeatability. All samples were measured in triplicate. The method was carried out on an Agilent 8890 GC/5977B GC/MSD instrument fitted with CTC PAL RSI 120 attachments, including a headspace sampler and sample heating and agitation. Headspace sampling was completed automatically with the CTC PAL systems 8010-0265 2500 μ L headspace sampler. The samples were heated at 150 °C for 90 min in the agitator before gas was extracted with the automated syringe. A headspace sample volume of 500 μ L was used. The injection mode was set to split (1:10), constant flow mode. The injection port was set to 250 °C and was fitted with an Agilent 5190-3983:800 μ L (single taper) linear. The GC was fitted with a J&W DB-624 GC column (30 m, 0.25 mm, 1.40 μ m). Flow was 1.525 mL/min, and pressure was 12.685 psi through the column.

This method was used for qualitative and quantitative analysis. Qualitative analysis used scan mode with mass ranges between 33 and 300 m/z . Quantitative analysis was run with selective ion monitoring (SIM). The ions are displayed in Table 2; a dwell time of 100 ms was used for each ion.

Table 2. SIM Ions and Elution Time Ranges for Ion Scanning

analyte	qualifier ion (m/z)	target ion (m/z)	SIM time window (min)
benzene	77	78	5.5–9.0
toluene	91	92	9.0–13
ethylbenzene and <i>m</i> , <i>o</i> , <i>p</i> -xylenes	91	106	13–20

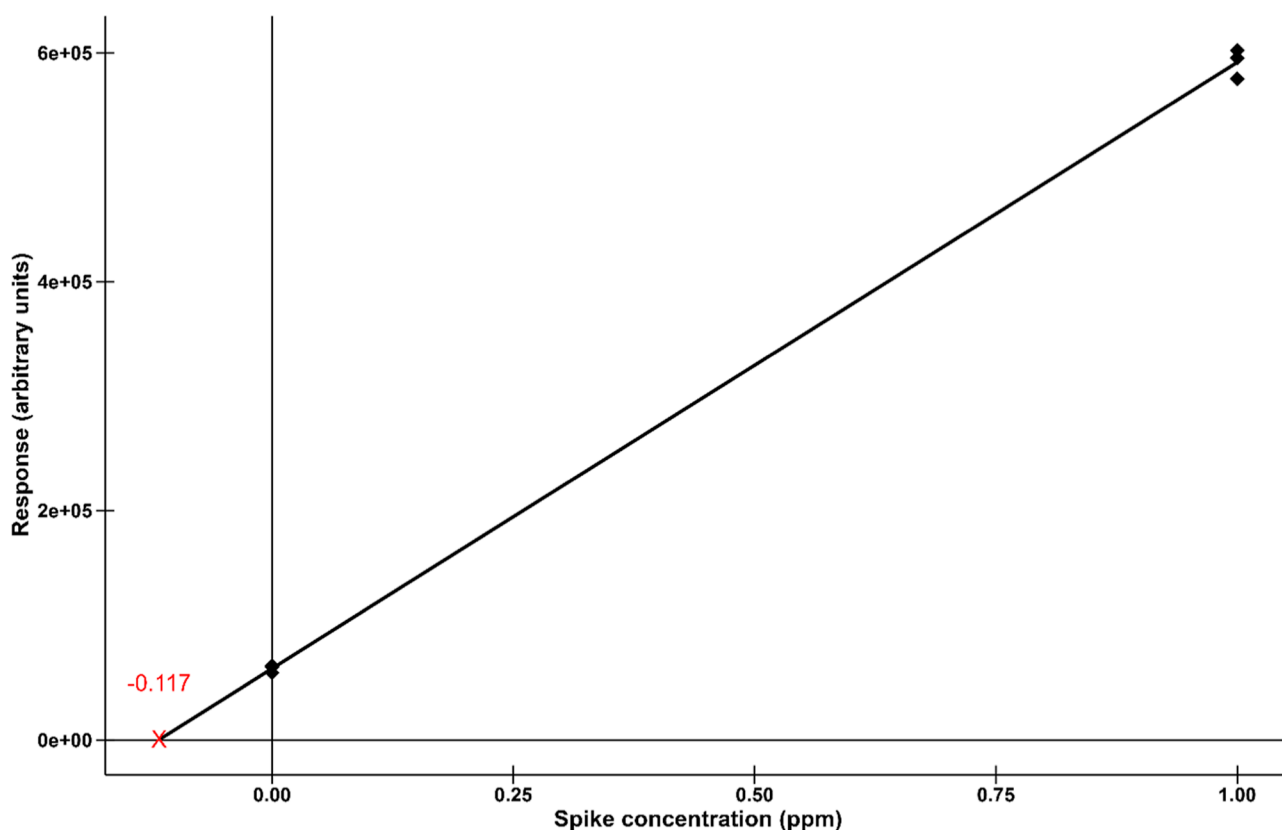


Figure 1. Extrapolated linear regression to the x intercept (-0.117 ppm) for 3 spiked and 3 neat samples of bitumen 46559, where the x intercept is equal to the absolute value of the sample concentration. The y -axis is response intensity in arbitrary units, and the x -axis is the concentration of standard added to the sample.

A two-point standard addition method was used to quantify BTEX. Three neat and spiked samples were prepared for each sample as above. All three spiked samples were prepared by the addition of $0.5 \mu\text{L}$ of the $2000 \mu\text{g/mL}$ BTEX standard in methanol, and the vial was quickly sealed. The neat samples were spiked with $0.5 \mu\text{L}$ of methanol to match the volume of the spiked samples. The concentration of BTEX analytes was calculated by determining the x intercept according to eq 1, where $[X]_i$ is the initial concentration, I_X is the signal intensity of X initial, $[S]_f$ and $[X]_f$ are the concentrations of the analyte in the final sample and final spike, respectively, and I_{X+S} is the signal from the spiked sample. According to eqs 3 and 4, where $[S]_i$ is the concentration of standard in the final samples and V_i and V_s are the volumes of the initial sample and standard, respectively, if the spike volume is considered negligible or is accounted for by dilution of the neat sample, then $[X]_f = [X]_i$ and $[S]_f = [S]_i$ can be substituted into equation one to derive eq 2. With this substitution, a plot of I_{X+S} vs $[S]_i$ is constructed, and the x intercept is equal to $-[X]_i$ (Figure 1). The error of the x intercept was calculated according to eq 5. The 95% confidence interval was then calculated using a student's t value, eq 6.^{48,49} Outliers were removed, where appropriate.

$$\frac{[X]_i}{[X]_f + [S]_f} = \frac{I_X}{I_{X+S}} \quad (1)$$

$$\frac{[X]_i}{[X]_i + [S]_i} = \frac{I_X}{I_{X+S}} \quad (2)$$

$$[X]_f = [X]_i \left(\frac{V_i}{V_i + V_s} \right) \quad (3)$$

$$[S]_f = [S]_i \left(\frac{V_i}{V_i + V_s} \right) \quad (4)$$

$$u_x = \frac{s_y}{\text{lm}} \sqrt{\frac{1}{n} + \frac{\bar{y}^2}{m^2 \sum (x_i - \bar{x})^2}} \quad (5)$$

$$\pm t u_x \quad (6)$$

3. RESULTS AND DISCUSSION

3.1. Weight Loss TGA. The TGA testing was designed to measure the volatile mass of each bitumen sample, and this is the weight loss observed under these conditions. While 200°C is slightly higher than the operational temperatures of many bitumen samples in this study (i.e., $145\text{--}185^\circ\text{C}$), this temperature was chosen to ensure the evolution of a range of VOCs in each sample. At 200°C under an inert atmosphere, oxidation reactions are negligible, and the more volatile constituents of the bitumen, those with a boiling point below or around 200°C , should account for the majority of weight loss observed as these are evolved from the bitumen. The inert atmosphere is essential to the weight loss method to eliminate oxidation and avoid potential negative weight loss results seen in other mass loss methods.⁶ Through the use of these parameters, the method is optimized to volatilize all VOCs present in the bitumen. The results of the graphs can be seen

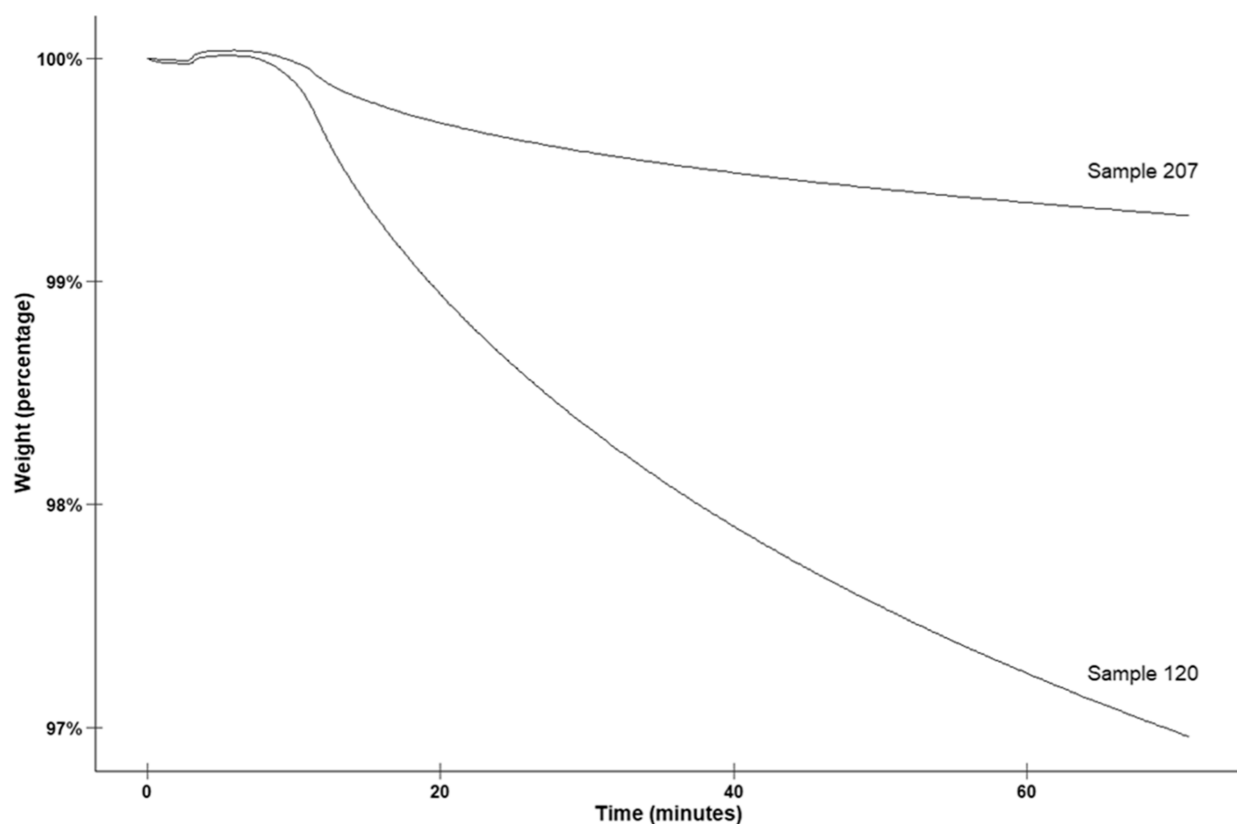


Figure 2. Weight loss graphs of samples 120 and 207 are for comparison. The plot is weighted in percentage vs time in minutes; the samples reach 200 °C at 11.3 min, whereby this is maintained for 60 min.

in Figure 2 where samples 207 and 120 are compared, with volatile masses of 0.74 and 3.31%, respectively. Samples with greater weight loss in the 60 min time frame clearly have a greater rate of weight loss vs time.

The differences between the observed weight loss results were considerable (Table 3). While, to some extent, lower volatile masses were recorded in lower penetration grade bitumen (i.e., greater viscosity at ambient temperature), this was still far from consistent, and significant variations in volatile mass were observed within penetration grades. This contrast of weight loss is seen in samples 117 and 207, 3.28 and 0.74%, respectively, where weight loss differs significantly between bitumen samples of similar penetration grades. These differences between penetration grades may be due to differing treatments and the management of fractions during the refinement process.⁵⁰ A clear separation between samples of bitumen products with fuming concerns and those without fuming concerns was observed in the results of the TGA testing. The five highest weight loss measurements were all found in samples reported as fuming, 46559, 120, 117, 327, and 43369, with percentages of 8.92, 3.31, 3.28, 3.15, and 2.68, respectively. Sample 43368, reported as fuming, recorded a slightly lower weight loss percentage of 2.49%, while sample 217, which recorded a higher weight loss of 2.68%, did not attract any fuming complaints.

These results suggest that the degree of mass change during the TGA testing is a valuable indicator of the potential of a bitumen product to emit fumes. Therefore, as the weight loss percentage increases, so does the probability of the bitumen producing significant fumes. This association, however, cannot fully explain the instances of fuming. Reports of fuming

Table 3. TGA for Weight Loss Measurements of Bitumen Samples at 200 °C after 1 h under Nitrogen Flow, Average of Three Repeats, and Standard Deviation in Weight Loss Percentage Units

sample reference	grade	comment	weight loss (%)	standard deviation
46559	650/900	fuming	8.92	0.53
120	50/70	fuming	3.31	0.24
117	160/220	fuming	3.28	0.24
327	250/330	fuming	3.15	0.33
43369	160/220	fuming	2.68	0.15
217	70/100	no concerns	2.64	0.33
43368	70/100	fuming	2.49	0.15
44771	80/100	no concerns	2.38	0.09
204	50/70	no concerns	2.01	0.15
198	50/70	no concerns	1.31	0.15
23762	70/100	no concerns	0.94	0.05
227	35/50	no concerns	0.89	0.08
25249	70/100	no concerns	0.79	0.04
207	160/220	no concerns	0.74	0.07
C170	70/100	no concerns	0.57	0.06
237	40/60	no concerns	0.42	0.01
33248	70/100	no concerns	0.31	0.01
180	Oct-20	no concerns	0.26	0.03
22707	70/100	no concerns	0.21	0.02

bitumen are highly dependent on the manifestation of fumes in practice. Other factors may contribute to the generation of fumes in addition to weight loss measures, such as working conditions or the composition of the emitted material. Fuming could easily be aggravated or reduced by weather conditions,

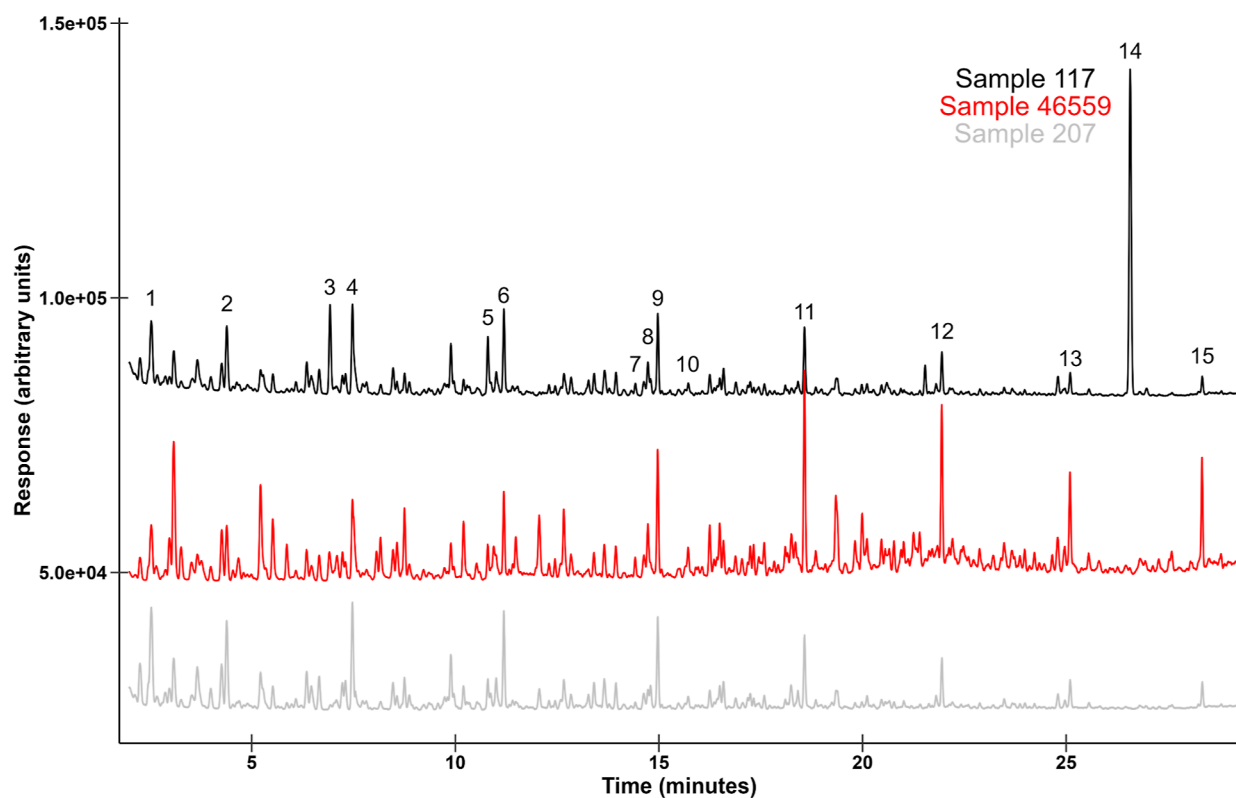


Figure 3. Chromatograms of “fuming” samples 117 and 46559 and “no concerns” sample 207, scan data. Peaks, 1: pentane, 2: hexane, 3: benzene, 4: heptane, 5: toluene, 6: octane, 7: ethylbenzene, 8: *m*, *p*-xylenes, 9: nonane, 10: *o*-xylene, 11: decane, 12: undecane, 13: dodecane, 14: naphthalene, and 15: tridecane.

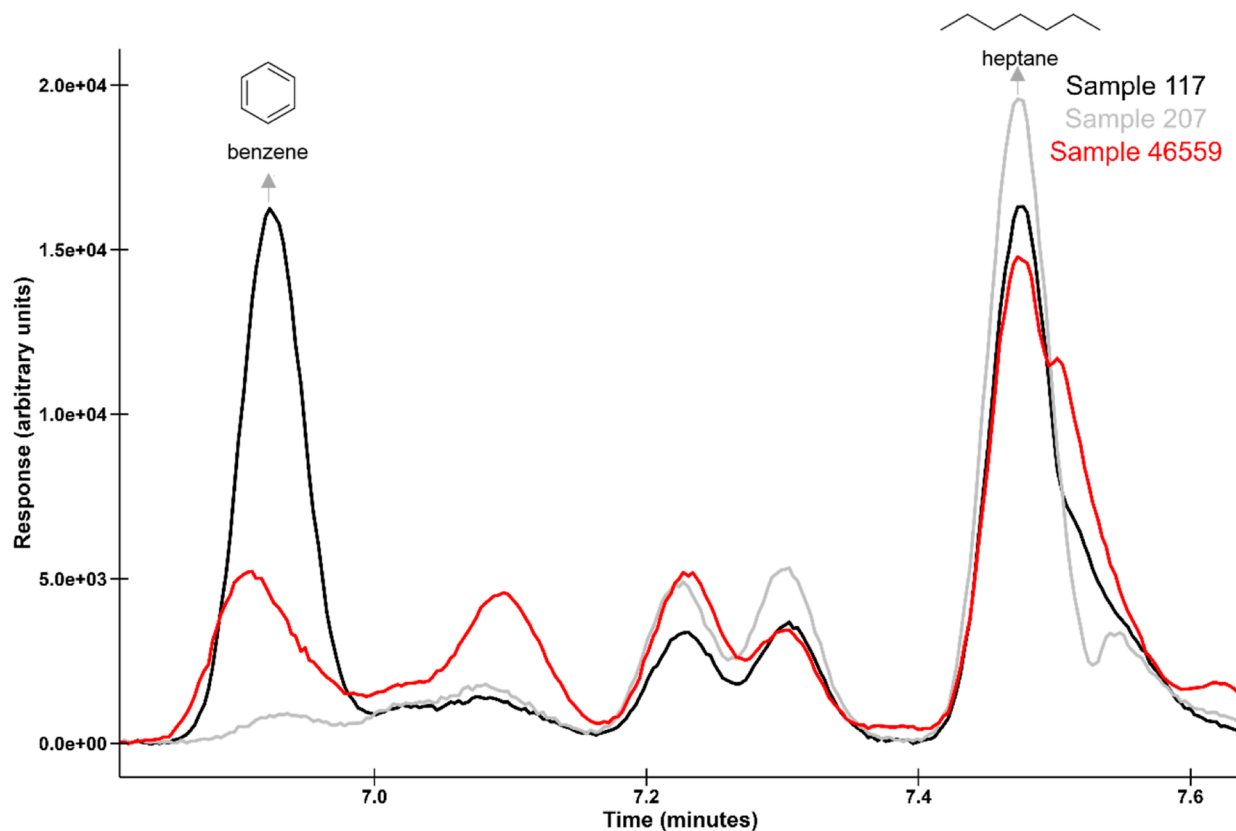


Figure 4. Chromatogram comparison of samples 207 (gray), 117 (black), and 46559 (red), scan data. Peaks, 1: benzene and 2: heptane.

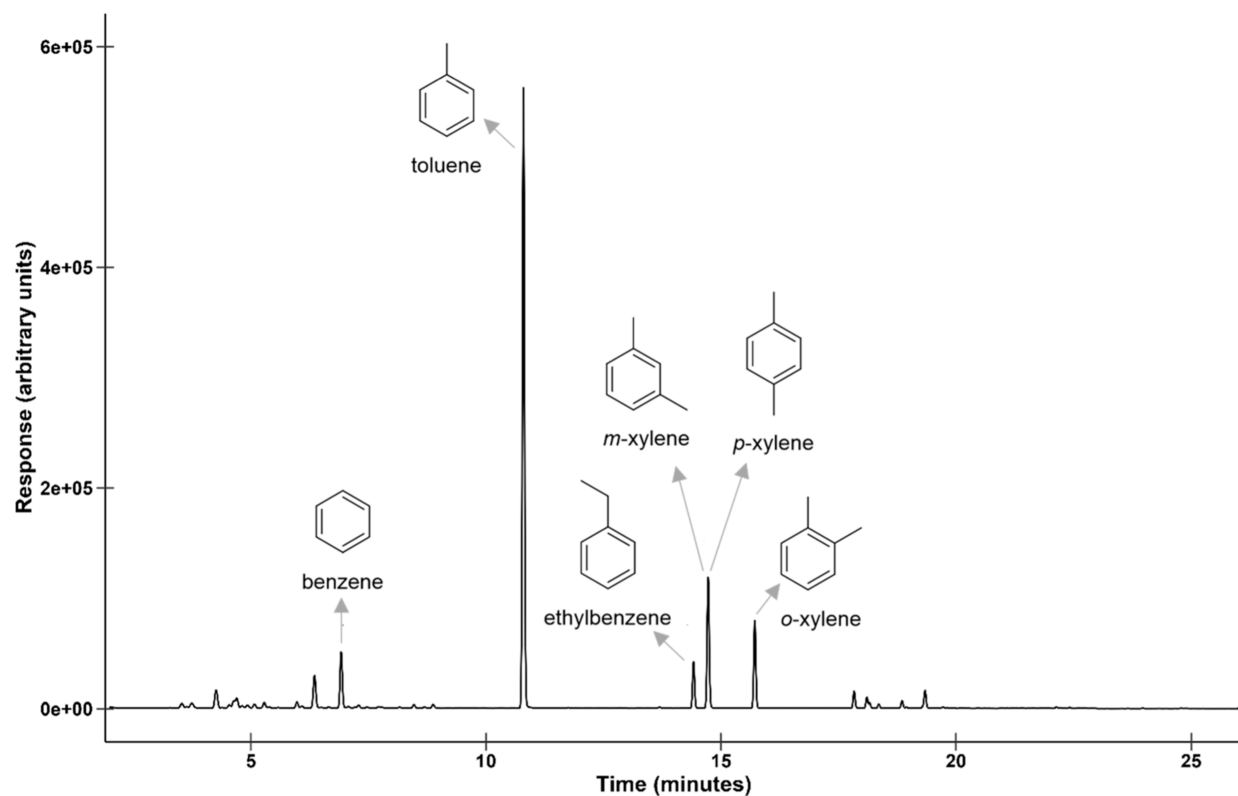


Figure 5. SIM data: chromatogram of “nonfuming” sample 204. Peaks, 1: benzene, 2: toluene, 3: ethylbenzene, 4: *m*, *p*-xylenes, and 5: *o*-xylene.

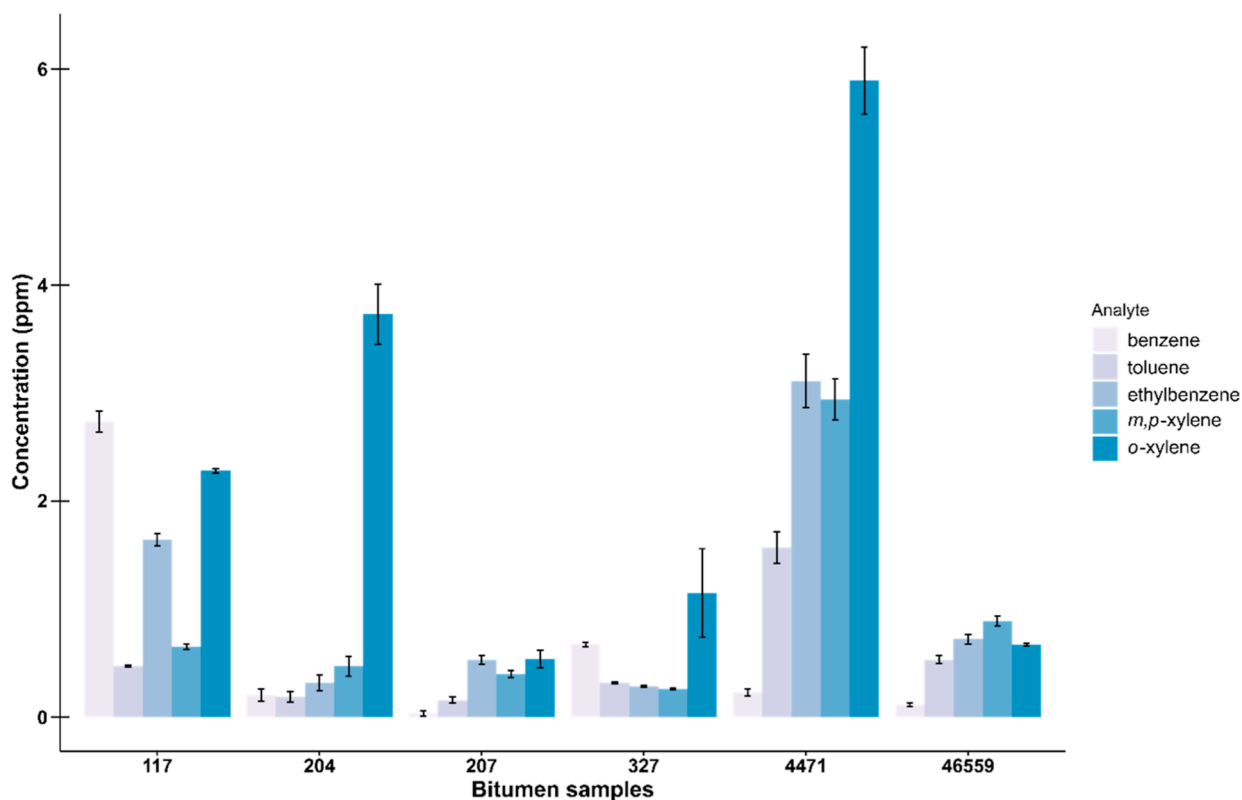


Figure 6. Concentration of BTEX analytes (ppm) in each sample. Samples 46559, 117, and 327 are fuming samples.

wind speed, and ambient temperature, affecting the diffusion of evolved gases.³⁵ Nevertheless, these findings have important implications for the quality control of bituminous products. TGA is a bulk analysis technique; it provides a mass for all

compounds that can be emitted under these conditions, but it does not provide information about the specific types or concentrations of individual VOCs present. To further detail the emissions, chromatographic methods are required to

isolate specific chemicals from the complex mixture of bitumen.

3.2. Head Space Gas Chromatography Mass Spectrometry. Using HS-GC-MS to analyze bitumen qualitatively revealed a range of aliphatic hydrocarbons, and aromatics were identified using library matching (Figure 3). Examples of chromatograms are shown for samples 117, 46559, and 207 in Figure 3. Upon comparison of the samples, it was observed that many contained similar chemicals, but their relative intensities varied between all samples (Figure 4). Hydrocarbons of varying saturation make up the majority of bitumen emissions by mass, while arene compounds are a minor component.^{25,31} However, arene compounds, particularly benzene, are of greater interest due to their higher toxicity.¹⁵ To further investigate these samples, we chose to quantify the levels of benzene, toluene, ethylbenzene, *m*, *o*, and *p*-xylene (BTEX) (Figure 5) as these compounds have been shown to pose a greater adverse health risk than other VOCs such as many alkanes.^{51,52}

A representative selection of the bitumen samples that had been analyzed for weight loss using TGA was further analyzed by quantitative HS-GC-MS. A wide range of concentrations were observed for various analytes, including benzene and toluene, in bitumen samples (Table 2). The concentration of benzene, for instance, varied from 0.04 ppm in sample 207 to 2.7 ppm in sample 117, highlighting that the risk of exposure to benzene associated with bitumen may vary depending on the specific product. Additionally, variations in toluene of around ten times were observed between samples 207 and 44771, with values of 0.54 and 5.9 ppm, respectively (see Supporting Information, Table S1). These findings indicate that while the concentration of BTEX compounds is generally low in the samples, the concentration range is quite large (Figure 6). Consideration for the wide range of BTEX concentrations, particularly toluene, may be due to its presence in asphalt and bitumen cleaning agents and may become present as a contaminant.⁵³

By comparing these values to both the volatile mass measurements and fuming incidents, we find that there are no strong relationships between BTEX concentrations and instances of fuming or weight loss. This is seen in samples 204 and 44771, which have similar volatile masses and notably different BTEX concentrations (Figure 6). As BTEX represents only a small portion of the bitumen samples' overall emissions profile, these measurements alone may not be sufficient to differentiate samples. Further research is needed to gain more insight into these variations and how they might affect the safety and quality of bitumen products. These results demonstrate a valid option for a rapid and solvent-free method to quantify selected VOCs in bitumen products by using small sample sizes.

3.3. Partition Coefficients. PCs are the principal factors that must be considered when performing multiphase analysis. In this analysis, PCs measure the distribution of a substance between the headspace, defined as the gaseous phase, and the sample, defined as the liquid phase. The coefficient determines the amount of the substance available for analysis in the headspace. If the PC is low, then the majority of the substance will be present in the liquid phase and will not be available for analysis in the gas phase. Alternatively, if the PC is high, then the majority of the substance will be present in the headspace and available for analysis. The PC can be affected by a number of factors, including temperature, pressure, and the matrix of

the sample.^{45,46,54–57} The sample matrix and its effects can be investigated by controlling the other variables that affect the PC. The matrix effect is the physical and chemical characteristics of the sample on the partitioning of the gases. When the relevant settings, such as heat, agitation, and pressure, are controlled, the main factor influencing the chemical partitioning will be the sample itself, specifically the matrix. In controlled experimental conditions, where external parameters are kept constant, any variations in the chemical partitioning of compounds, including BTEX, can be primarily attributed to the characteristics of the bitumen sample under study. Under these conditions, the partitioning of chemicals can be assessed, either by absorbing more of the chemical and sequestering it into the sample or the reverse by releasing more into the headspace.^{56,58} The PC equation, $K = C_S/C_G$, describes the equilibrium of an analyte between the liquid and gas phases, where C_S is the concentration of analyte in the liquid phase at equilibrium, C_G is the concentration in the gas phase at equilibrium, and K is the PC value (see Supporting Information, Table S2). As the PC value has no unit, the percentage distribution is also included in this work as this provides a more straightforward conceptual metric for gas-phase partitioning. The percentage distribution is the concentration in the gas phase (C_G) divided by the net concentration (C_{net}), where $C_{net} = C_S + C_G$, representing the percentage of analyte that has migrated out of the bitumen and into the gas phase.

$$\text{Percentage distribution} = C_G / C_{net}$$

In this work, the percentage distributions were used to investigate whether selected analytes have the same values for all bitumen samples or whether each bitumen has a unique distribution for each analyte depending on the bitumen's unique matrix.¹⁰ A bitumen's chemical composition can vary, and while some physical characteristics are attributed to the content of specific fractions such as saturate, aromatic, resin, and asphaltene (SARA),⁵⁹ the effect on emissions is unclear.

The percentage distribution values for each analyte in each sample show minor variations between samples (Table 4), with

Table 4. Percentage of Total BTEX Analytes Present in the Headspace for the Bitumen Samples

sample	percentage of analyte present in headspace				
	benzene	toluene	ethylbenzene	<i>m</i> , <i>p</i> -xylenes	<i>o</i> -xylene
46559	42.9	33.6	24.4	47.5	20.4
204	41.4	22.5	25.7	51.0	22.4
44771	35.4	25.7	25.3	52.5	24.9
327	33.1	24.3	21.0	39.9	17.4
117	30.9	24.0	16.9	15.8	13.7
207	30.3	22.7	13.8	12.4	11.2
mean	35.7	25.5	21.2	36.5	18.3
range	12.6	11.1	11.9	40.0	13.7

most analytes having a range between 11.1 and 13.7% across the samples. The single exception is the values for *m* and *p*-xylenes, where the range is 40%. Samples 117 and 207 possess these xylene isomers' two lowest headspace percentages. These two samples have the lowest headspace partition percentages across all of the BTEX analytes. While there are some variations in the partitioning of benzene, toluene, ethylbenzene, and *o*-xylene with a range varying from 11.1 to 13.7% in samples, in general, the effect of the natural bitumen matrix

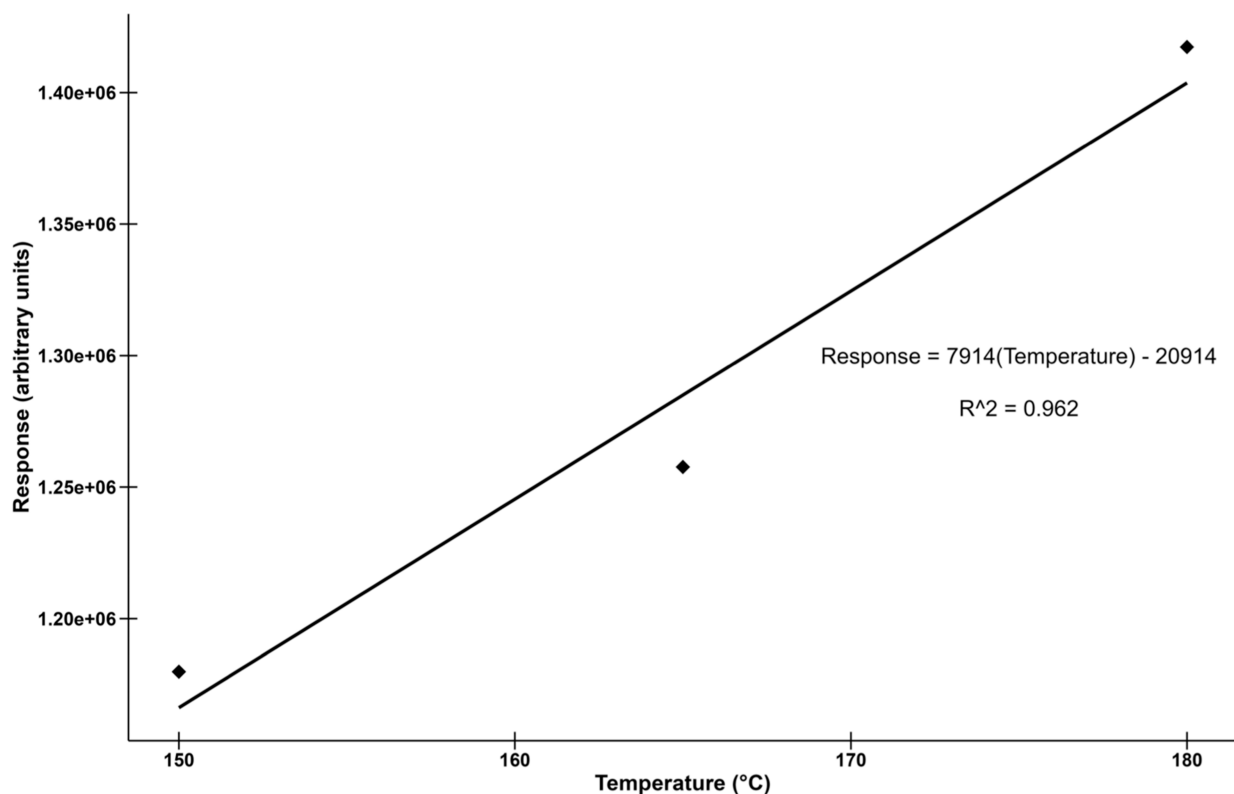


Figure 7. Benzene peak area vs temperature after incubation at three temperatures for 90 min each, bitumen sample 217. The trend line demonstrates the positive correlation.

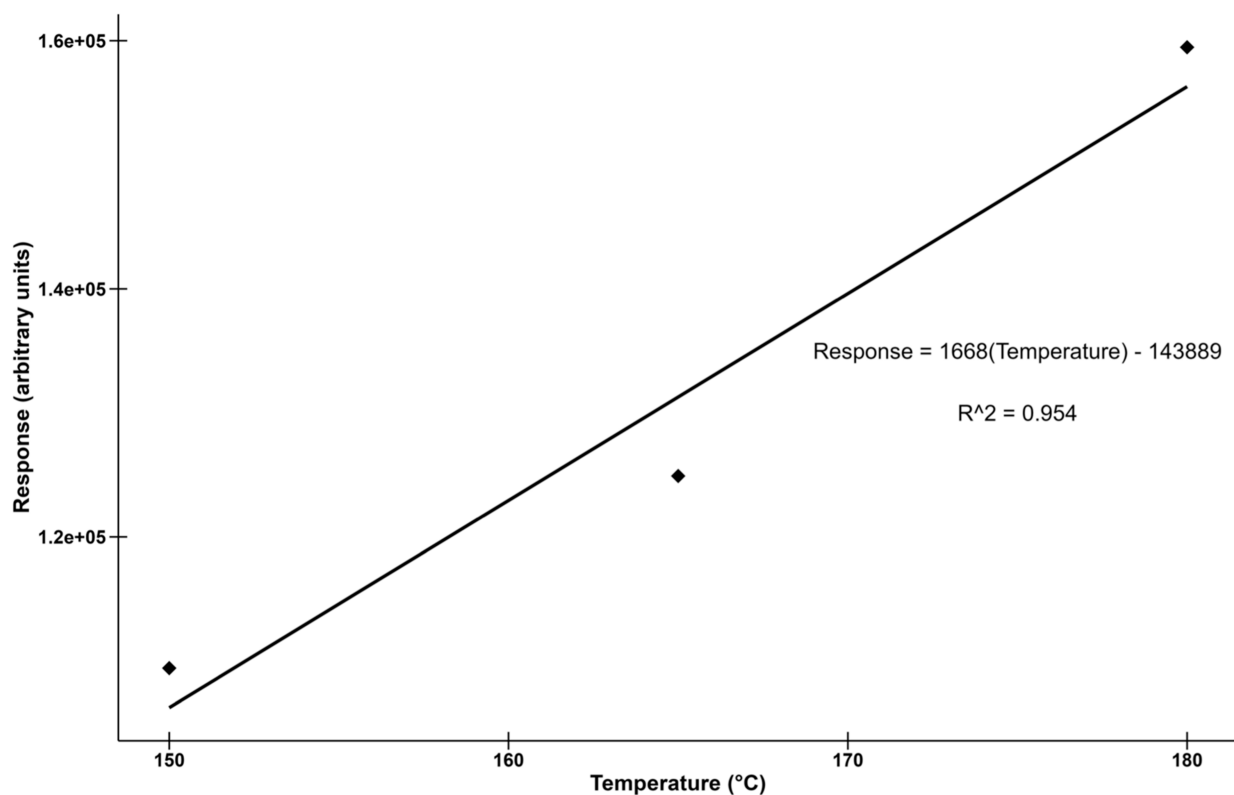


Figure 8. Hexane peak area vs temperature after incubation at three temperatures for 90 min each, bitumen sample 217. The trend line demonstrates the positive correlation.

appears to have minimal influence on the emission or sequestration of these chemicals regardless of the grade or

refinery location. However, the meta and para isomers of xylene show a significant range in the analyte distribution.

From the values obtained, the natural fluctuations in the composition of refined bitumen have a minimal impact on the partitioning of BTEX analytes between the liquid phase and the gaseous phase and thus are unlikely to affect the emission rate significantly. Although variations in the physical properties of bitumen relevant to its grading are significant for its suitability in road applications, these differences do not appear to impact the emission of BTEX from bitumen material significantly. Since similar percentages of analyte are emitted from bitumen, one of the most significant factors influencing the concentration of emitted VOCs may be the net concentration in the bitumen before mixing commences.

The observed slight variations in the emission percentages of the BTEX analytes may be attributed to several factors, including variations in the bitumen matrix and potential interactions with the BTEX molecules. One possible absorption method in bitumen is through the π - π interactions between the cyclic aromatic systems of BTEX molecules and other aromatics, such as asphaltenes, present in the bitumen. These π - π interactions can facilitate the sequestration of BTEX within the bitumen matrix.^{60,61}

Furthermore, additional interactions that may contribute to the variation in emissions involve π - π electron-donor-acceptor mechanisms between the delocalized π electrons of BTEX and the π electrons in carboxylic acid groups or heteroatoms within the bitumen. Such interactions could influence the behavior of BTEX molecules and their potential for emission from the bitumen.^{62,63}

As mentioned previously, temperature increases the emission rates of chemicals from bitumen.^{10,64} Increased temperatures in HS-GC should emit more analytes and push the PC value toward a smaller value and greater gas phase and fewer liquid phase analytes.⁴⁵ To test this, the HS-GC-MS qualitative procedure was carried out on sample 217 at temperatures of 150, 165, and 180 °C, and the area counts were measured. A linear correlation between the response and temperature was observed. As the response is proportional to concentration, this demonstrates the significant effect temperature has on the distribution of analytes and how increased temperatures can lead to increased emissions when mixing bitumen. The qualitative results for benzene and hexane are displayed in Figures 7 and 8, respectively.

4. CONCLUSIONS

Despite bitumen being utilized for various purposes throughout history,⁶⁵ there remain a limited number of methods available to quantify and analyze the emissions of VOCs from bitumen.^{8,24} As such, there is a need for comprehensive techniques to describe the characteristics of VOC emissions from bitumen, particularly to identify sources with excessive emissions and fuming issues.

During our research, a strong connection was discerned between the substantial mass loss observed during the isothermal TGA testing of bitumen samples and the tangible fuming issues reported by people in real-world scenarios. This link illuminates a critical threshold: bitumen samples undergoing a mass loss equal to or surpassing 2.4% are markedly predisposed to emit overwhelming fumes. These emissions often result in numerous complaints and concerns regarding air quality.

This work presents an efficient method for determining fuming. Our research has provided a concrete basis for categorizing bitumen samples according to their fuming

potential by identifying this specific mass loss threshold. This categorization is an invaluable tool for industry professionals, enabling them to assess bitumen samples before deployment. It acts as an early warning system, allowing for the proactive identification of high-fuming-potential samples, thereby preventing potential environmental disturbances and public grievances.

One avenue for future exploration could involve integrating modified bitumen samples into this predictive model. This extension of the research could offer nuanced insights into how various modifications might impact fuming tendencies. Expanding this method could provide a precise analytical method for tailored bitumen formulations that mitigate fuming issues, enhancing both the efficiency of construction projects and the well-being of communities in their vicinity.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c04673>.

BTEX analyte concentration (ppm) with confidence intervals and partition coefficient values (K) for BTEX analytes and samples (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Filippo Giustozzi – *Civil and Infrastructure, School of Engineering, STEM College, RMIT University, Melbourne, Victoria 3001, Australia*; Email: Filippo.giustozzi@rmit.edu.au

Subashani Maniam – *Applied Chemistry and Environmental Science, School of Science, STEM College, RMIT University, Melbourne, Victoria 3001, Australia*; orcid.org/0000-0002-0272-864X; Email: Subashani.maniam@rmit.edu.au

Authors

Zachary Deller – *Applied Chemistry and Environmental Science, School of Science, STEM College, RMIT University, Melbourne, Victoria 3001, Australia*

Stephen Grist – *Applied Chemistry and Environmental Science, School of Science, STEM College, RMIT University, Melbourne, Victoria 3001, Australia*

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.3c04673>

Author Contributions

Zachary Deller did the conceptualization and writing of the original manuscript draft. Stephen Grist did the primary method development of GC-MS. Filippo Giustozzi and Subashani Maniam did the supervision, funding acquisition, and project development.

Notes

The authors declare no competing financial interest.

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