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Natural Seepage of Methane and Light Alkanes at Three Locations in Southern California

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Abstract: Methane and light (C_2 – C_5) alkane fluxes were measured from three geologic seepage sites in Southern California during May and June of 2019. Samples were collected from visible macroseeps in Carpinteria, McKittrick, and Ojai using an aluminum flux chamber with attached stainless-steel canisters and were analyzed for C_1 to C_5 alkanes via gas chromatography. Carpinteria fluxes were characterized by a lower percentage of volatile organic compounds relative to methane but greatly enhanced (~20:1) ratios of *i*-butane to *n*-butane. McKittrick and Ojai exhibited less methane-rich emissions and *i*-butane to *n*-butane ratios of less than 2:1. The differences between gas ratios observed at the surface and those previously reported from underground gas deposits at Ojai suggest that gases undergo alterations to their molecular composition between deposit and surface. The ratios of emitted gases in this study show that not only does geologic seepage have a much different volatile organic compound profile than oil and natural gas extraction and pipeline natural gas, but also that individual geologic seepage locations exhibit large variability.

Keywords: geologic seepage; macroseepage; methane; light alkanes; oil and natural gas

1. Introduction

Geologic seepage from underground oil and natural gas deposits is a source of methane and volatile organic compounds (VOCs) to the atmosphere that is sometimes overlooked. This seepage can occur in marine and terrestrial environments. Terrestrial seepage can occur in three ways, via microseepage, macroseepage, or miniseepage. Microseepage occurs when seepage from underground oil and natural gas deposits exit the earth's surface with no accompanying visible signs. Macroseepage (Figure 1) is observed when there is a visible escape of gases from underground deposits. Macroseepage is caused by pressure and buoyancy bulk fluid flow in locations where significant cross-stratal migration occurs [1]. It is capable of moving large amounts of liquids and gases and is often characterized by co-emission of oil or asphalt from the seeps [1]. Miniseepage is invisible seepage that occurs in an area where macroseeps are present. Though microseepage has the ability to occur globally in all places where underground deposits exist [2,3], macroseepage occurs in a much more limited number of discrete locations [3]. A recent database reports over 2100 global macroseeps in 89 countries [4]. However, even though macroseepage is more limited geographically than microseepage, individual macroseeps typically emit several orders of magnitude more methane and VOCs than microseeps [4,5]. Along with methane, the VOCs that are most commonly associated with geologic seepage are light alkanes, namely ethane, propane, *i*-butane, *n*-butane, *i*-pentane, and *n*-pentane. Although these gases react relatively slowly with hydroxyl radicals compared to other VOCs, they can nevertheless affect the hydroxyl radical reactivity, ultimately contributing to ozone formation in urban areas [6,7].



Figure 1. Example of macroseepage, as the asphalt bubble forming shows gas escape. Picture taken at the Carpinteria sample site.

A number of studies measuring terrestrial microseepage have been carried out in Europe, North America, and Asia. These studies have observed daily positive microseepage fluxes ranging from μ g m⁻² to hundreds of mg m⁻² [8]. A smaller number of studies have measured emissions from terrestrial macroseepage; these studies have reported daily fluxes from individual seeps in the kg m⁻² range [9]. Recent studies have estimated that global macroseepage contributes 3–4 Tg of methane annually, compared to an annual global contribution of 25 Tg of methane from microseepage [10]. Though previous studies have mainly focused on methane emissions, it has been estimated that annual global ethane and propane emissions from all types of geologic seepage are in the range of 2–4 Tg and 1–2.4 Tg respectively [11].

Previous geologic seepage studies have been carried out by our research group at the La Brea Tar Pits in Los Angeles, California [12,13]. The second of these studies measured not only macroseepage but also associated miniseepage at La Brea. This study estimated that approximately 1000 kg of methane, more than 10 kg of ethane, and more than 4 kg of propane were emitted daily from the La Brea area. Another finding from these La Brea studies was that ratios of emitted gases not only varied at the surface, but also differed significantly from alkane ratios that are typically associated with oil and natural gas production and pipeline natural gas [14–16]. Furthermore, the gas wetness, or the relative amount of C_2 – C_5 alkanes to methane, differed throughout the sampling locations. Most notably, the largest seep measured was significantly less methane-rich and gave a much lower *i*-butane to *n*-butane ratio of gases in the underground reservoir, which had been measured in a previous study [17]. This suggested that the gas from this largest seep underwent less alteration between the reservoir and the surface, as the gases had a more direct, and thus faster, pathway to the surface. This alteration or 'processing' of the gas as it makes its way up through the soil was suggested as a contributing factor for the anomalous ratios of gases emitted at the surface seeps.

These findings at La Brea were not necessarily novel as similar uncommon ratios had been previously observed in other seepage studies. Unusually high *i/n*-butane ratios of approximately 5 were found in a marine seep off the coast of Alaska [18]. These findings fit with other studies that suggest that *n*-alkanes are preferentially degraded by microbes compared to *i*-alkanes [19,20]. Additionally, studies of leakage gas from underground storage tanks have noted chemical fractionation during migration that can preferentially remove heavier (C_2 +) alkanes compared to methane [21].

The current study seeks to further expand the database of macroseepage emissions of methane and C_2 – C_5 alkanes. Three macroseepage sites in Southern California were sampled and the observed seepage rates and seepage ratios were compared to the previous results at La Brea.

2. Experiments

2.1. Description of Sampling Sites

All three sampling sites were located within 200 km of Los Angeles, Figure 2. Despite their geographic proximity, each site was unique in terms of its geological features and climate. Additionally, individual seeps at each sampling location had differing physical characteristics.



Figure 2. Map showing location of the three sampling sites plus La Brea.

Carpinteria is located approximately 20 km east of Santa Barbara, and approximately 130 km west-northwest of downtown Los Angeles. The seepage sampling location is located almost equidistant (3–4 km) from four mapped oil fields, the Summerland and Carpinteria Offshore Fields and the Rincon and Rincon Creek Onshore Fields. Though the sampling area was first mined in the 1850s and subsequently drilled starting in the 1920s, no active extraction currently takes place at the site. Previous wells were drilled to depths between 100 and 300 m [22]. However, the nearby Carpinteria Offshore Field, operational since the 1960s, is currently being drilled [23]. A number of natural offshore seeps also occur in this area and have been studied previously [24]. The Carpinteria climate is typical of coastal California, and the area is relatively dry, receiving approximately 48 cm of rainfall annually. During the sampling dates in June, weather conditions were typical for the season, with daily temperature maximums of approximately 20 °C and cloudy skies. Samples were collected from a series of seeps located in Tar Pits Park (34°23′15.7″ N, 119°30′46.4″ W) as well as seeps directly located on beach sand in Carpinteria State Park (34°23′14.9″ N, 119°30′50.3″ W and 34°23′21″ N, 119°31′0″ W).

McKittrick is located approximately 50 km west of Bakersfield and approximately 200 km north-northwest of Los Angeles. The seeps are located above the McKittrick Oil Field [25]. The oil deposits are capped by a layer of Monterey shale that is up to 600 m in depth [26]. The field has been extensively drilled since the late 1800s and remains active [23]. Current active oil and gas wells that are closest to the seeps studied are drilled to depths of at least 300 m [27]. Additionally, the tar pits of the area are well known, as they are the second most extensive tar pits in California (after La Brea) and have been studied for their fossil record [28]. The sampling location is surrounded by scrubland and characterized by its dryness (approximately 17 cm of rainfall annually) and hot summers

(average maximum July temperature of 37 °C). Samples were collected from McKittrick in late May on a sunny dry day with temperatures of approximately 25 °C. Samples were collected from mainly two areas. The first was a mostly dry creek bed adjacent to Highway 58 (centered around 35°17′40″ N, 119°37′46″ W), while the second was a mostly dry creek bed next to a service road just south of Highway 58 (centered around 35°17′34.7″ N, 119°37′51.8″ W).

Ojai is located approximately 100 km northwest of Los Angeles. Samples were collected above the Sisar Creek area and Tip Top area in the Ojai Valley Oil Field [29]. These fields are part of the broader Ventura Petroleum Basin [30]. Both the Sisar Creek area and Tip Top area have been drilled for oil and gas production in the past, with the Sisar Creek (~225 m) deposits being deeper than those at Tip Top, which naturally rose to the surface. Known faults in the Ojai Valley give the asphalt a migration pathway to the surface. Oil extraction has occurred in the area since the 1800s, and although the Sisar Creek area is still active, the Tip Top area has not had active extraction since the early 1900s [27,31]. Geologic seepage in Ojai was the subject of a previous study that looked at emissions of methane, carbon dioxide, and C_2 – C_4 *n*-alkanes from two seepage sites in the area [32]. In terms of climate, Ojai is similar to Carpinteria in annual rainfall (48 cm), but typically has warmer summers, with average high temperatures of approximately 30 °C. On the day of sample collection in mid-June, it was an unseasonably hot day with sunshine and a high temperature of 38 °C. Samples in Ojai were collected from two general areas. Some samples were collected in the Sisar Creek area on the eastern side of the Ojai Oil Field directly on the side of Highway 150 (centered around 34°26'01.0" N, 119°07'30.1" W). Other samples were collected in the Tip Top area beside a trail that was the old Sulphur Mountain Road south of the town of Ojai (centered around 34°22′48.4″ N, 119°17′54.7″ W). Both Ojai sample sites had much larger nearby seeps in the vicinity that were visible, but not sampled due to a lack of access.

2.2. Sample Collection and Analysis

Samples were obtained by placing a 0.5 m by 0.5 m by 0.5 m aluminum chamber above active seeps, which were identified by visual bubbling or movement of wet asphalt. The chamber was not fitted onto already placed collars in the soil, as is the case with true quantitative flux chambers. However, the chamber was sealed on its outer edges with loose debris and dirt to attempt to trap all seeping gases. A pre-evacuated 2 L stainless-steel sampling canister was attached to the chamber via an ultratorr connection to a 1/4" (outer diameter) aluminum tube. In order to determine flux measurements from seeps, a reference canister was collected immediately after the deployment of the aluminum chamber. Then, the reference canister was removed and a second canister (termed "sample") was connected to the chamber. The sample canister was then collected after 10 min. Flux measurements were determined via the difference between the sample and reference canisters. Subtraction of the reference canister from the sample canister also had the effect of background-correcting the data. Twenty-two samples were collected in this manner.

Unfortunately, the lack of a permanent collar made it impossible to ensure an airtight seal. Therefore, data collected with this sampling technique should be considered to be biased low, in that if a tight seal with the ground was not present, it is likely that some seeped gases escaped from the chamber leading to an underestimate of total flux. However, it is important to emphasize that this escape of gases does not affect the ratios of gases that were measured. Additional information on the chamber and canister system, including a picture of the setup and discussion about possible error introduced, is included in [13].

After collection, sampling canisters were analyzed on two analytical systems within the Loyola Marymount University laboratory. For C_2 – C_5 hydrocarbons, 1105 cm³, at standard temperature and pressure were pumped from each canister and cryogenically pre-concentrated and then injected onto a PLOT column (Agilent J&W Scientific, Santa Clara, CA, USA) within a Varian 3400 gas chromatography oven equipped with a flame ionization detector. The data were then analyzed on a PC utilizing Star Chromatography software. The reproducibility of this non-methane hydrocarbon (NMHC) analytical system was determined by measuring the relative standard deviation (RSD) of each compound; this was

found to be less than 6% for all compounds measured in this study. The GC-FID was calibrated using air standards obtained from the Blake laboratory, prepared in lab at University of California, Irvine. Methane was analyzed on a separate system consisting of a 1 m packed column with 1/8" tubing filled with Carbosphere 80/100 (Grace Davison, Deerfield, MA, USA). This column was located inside of a Bruker 430 GC-FID. These methane measurements had an RSD of less than 5%. Additional information on the analytical system can be found in [33].

Following quantification of chromatograms, fluxes for each sample site were determined. In order to report results for this study in a similar fashion as previous studies, magnitudes of fluxes are reported by mass, whereas all ratios that are presented are calculated by volume.

3. Results and Discussion

3.1. Overview

Of the twenty-one samples collected, not all the samples exhibited positive fluxes. Samples that exhibited negative or negligible fluxes were excluded from further analysis. Of the six samples collected at McKittrick, four showed positive fluxes, of the nine samples collected at Carpinteria, five presented positive fluxes, and all six samples at Ojai were positive. The negative or negligible fluxes were likely due to one of two causes. First, as previously mentioned, flux chambers without fixed in-ground collars were deployed. In some sample locations, it was difficult to achieve an adequate seal with the ground. This was especially problematic at the Carpinteria site, as there were many large branches at the asphalt seeps. If a sizeable seep of gas were made into the chamber prior to the reference sample being collected, large gaps between the ground and the chamber bottom would have allowed these gases to escape throughout the ten-minute sampling interval and led to vastly underreported, or even negative, fluxes. A second possibility for the negative and negligible fluxes would be the temporal nature of the seeps. The episodic nature of seepage has been previously observed [34]. It is possible that during the ten-minute flux chamber deployment the seep was not active.

Magnitudes of fluxes varied significantly within and between sites for both methane and VOCs and are presented in Table 1. Again, each sample in Table 1 was a result of a flux measurement from two individual sample canisters. Table 2 shows reference and sample canister concentrations for sample number 20 which was collected in Carpinteria. The high levels of methane and other gases in the reference canister in Table 2 are primarily caused by seepage occurring after placement of the chamber but prior to collection of the reference canister. It is worth pointing out that even small mass fluxes that are reflected in Table 1 are generally associated with large concentration differences (greatly above measurement uncertainty and detection limits) between the reference and sample canisters. In general, the magnitude changes shown in Table 1 were consistent with visual observations, as the Carpinteria sampling sites exhibited the most vigorous surface bubbling. The largest fluxes were observed at Carpinteria, with maximum methane and ethane fluxes of 840 mg h^{-1} and 6.4 mg h^{-1} , respectively. Maximum fluxes at the other sites were between two and three orders of magnitude smaller, with maximum fluxes of methane and ethane of 8.2 mg h^{-1} and 20 μ g h^{-1} at McKittrick and 3.8 mg h^{-1} and 1.9 μ g h⁻¹ at Ojai. The maximum fluxes found in this study are generally small compared to previous studies at La Brea, where fluxes reached up to 17 g h^{-1} for methane and 270 mg h^{-1} of ethane [12]. However, it is difficult to infer conclusions regarding flux strength or overall emissions from each site given the small numbers of samples collected in the current study and potential errors introduced by unsealed chamber leakage.

Location	Sample	Methane	Ethane	Propane	<i>i</i> -Butane	<i>n</i> -Butane	<i>i</i> -Pentane	<i>n</i> -Pentane
McKittrick	1	590	0.27	0.37	0.052	0.095	0.13	0.19
McKittrick	3	10.6	1.8	2.9	0.61	0.66	0.88	1.3
McKittrick	4	360	0.92	3.7	0.88	0.71	0.88	1.1
McKittrick	5	8200	20	1.9	0.31	0.18	0.17	0.28
Carpinteria	11	840,000	6400	104	21	1.08	0.33	0.35
Carpinteria	20	3300	2.2	6.9	15	1.1	37	0.75
Carpinteria	21	23,000	3.1	7.0	16	0.53	24	0.39
Carpinteria	22	7500	2.4	6.5	14	0.69	27	0.44
Carpinteria	23	11,000	3.1	9.4	23	1.11	44	0.67
Ōjai	13	3300	1.12	1.5	0.42	1.00	0.68	1.07
Ojai	14	160	1.4	1.8	0.46	1.3	0.43	2.9
Ojai	15	290	0.35	0.67	0.103	0.35	0.13	0.099
Ojai	17	3800	1.5	0.50	0.0052	0.57	0.15	0.30
Ojai	18	910	1.9	2.2	0.59	0.95	0.57	0.94
Ojai	19	110	0.86	0.99	0.027	1.2	0.15	0.31

Table 1. Flux magnitudes by mass (μ g/h) for each of the fifteen positive-flux seeps that were sampled in this study.

Table 2. Concentrations (in ppbv, except methane) for reference and sample canisters that were used to calculate sample number 20.

Canister	Methane (ppmv)	Ethane	Propane	<i>i</i> -Butane	<i>n</i> -Butane	<i>i</i> -Pentane	<i>n</i> -Pentane
20-reference	3.20	1.6	1.1	0.75	0.31	1.2	0.06
20-sample	9.82	4.1	6.3	9.4	0.94	18	0.40

3.2. Gas Ratios

Various ratios were determined for the three reported sites and compared to previously reported seepage studies and are shown in Table 3. The relative amount of methane in each sample was investigated using C1/(C2 + C3), which is known as the Bernard ratio. This ratio is closely related to the inverse of the true gas wetness, which would also include butane and pentane. However, in this case the Bernard ratio was used to facilitate comparison with previous studies that did not measure C_4 + gases. The C1/(C2 + C3) ratio varied by location as well as within locations. Figure 3 shows how this ratio changed for individual sampling locations versus the mass of seeped methane. In general, there did not appear to be a strong correlation between the strength of the seep and the $C_1/(C_2 + C_3)$ ratio for the three locations in this study. However, it must be noted that the lack of a strong relationship could be due to bias introduced in the sampling method. Though the limited number of samples showed that McKittrick was the wettest gas followed by Ojai and Carpinteria, each location had at least one individual sample that was within the range of the other two locations. Variability of the Bernard ratio could be due to several factors. First, this ratio can vary based on the composition of the oil or gas deposit [35]. Secondly, this ratio has been observed to increase during migration from underground deposit to surface [9]. Therefore, if all deposits contained the same wetness of oil/gas, it could be expected that deeper deposits would emit more methane-rich gas at the surface, as a greater percentage of the ethane and propane would be lost during migration. However, in this study, the deposit composition is not well known at all three sites, making further analysis on the causes of differing surface C1/(C2 + C3) ratios difficult.



Table 3. Gas ratios by volume (v/v) observed by site in this and previous studies [30].

 $c_1 + c_3 + c_3$ McKittrick 1000 Ojai Carpinteria 500 0 10² 105 107 10⁸ 1 10 10^{3} 10^{4} 106 $C_1 \; (\mu g \; h^{-1})$

Figure 3. Plot of methane flux vs. C1/(C2 + C3) ratio at the three sites and La Brea.

A second gas ratio investigated was the relative amount of *i*-alkanes to *n*-alkanes. Classically, it is observed that there is a higher ratio of *n*-butane and *n*-pentane in emissions from hydrocarbon deposits in comparison to their *iso* counterparts. Specifically, ambient ratios of *i*-butane to *n*-butane in the U.S. are approximately 0.5, while ratios from natural gas fields are typically even lower [36,37]. *i*-Pentane to *n*-pentane ratios of approximately 2 are typical for ambient U.S. samples while ratios from raw natural gas and oil and natural gas impacted areas have been reported as 0.86 and less than 1 respectively [6,15,36,38–41]. However, studies have suggested that during gas migration to the surface, the *iso* gases become more enhanced. One explanation for this has been that microbes preferentially degrade *n*-alkanes [19,20]. The current study showed wide variability of *i*-butane/*n*-butane and *i*-pentane/*n*-pentane ratios at the three sites, as shown in Figure 4. Similar to the $C_1/(C_2 + C_3)$ ratio, the i/n ratios did not seem to be strongly influenced by the strength of the individual seep. Again, it should be noted that the lack of a strong relationship could be affected by sample collection bias. Ojai samples exhibited an i/n ratio for both C_4 and C_5 of less than one; this sort of ratio is typical of what has been reported from oil and gas extraction emissions previously. McKittrick showed slightly higher ratios, but still near 1 for *i/n*-butane and under 1 for *i/n*-pentane. Carpinteria samples showed significantly different ratios, with an *i/n*-butane ratio of 21 and an *i/n*-pentane ratio of 48. These Carpinteria ratios are even more enhanced than the large *i*/*n* ratios seen during the La Brea studies. These greatly enhanced *i*/*n* ratios at Carpinteria suggest that microbial degradation is occurring between subsurface reservoir and surface emissions that is not occurring to the same degree at McKittrick or Ojai. This suggestion is further supported by the greater amounts of *i*-butane and *i*-pentane relative to ethane and propane in Carpinteria sample numbers 20 thru 23. Normally, it would be expected that C_2 and C_3 gases would exceed levels of C_4 and C_5 from hydrocarbon deposits. The fact that this is not observed in these samples hints that all *n*-alkanes are being consumed as the gases migrate from

underground deposit to surface. Carpinteria samples also exhibited interesting intra-site variability of these i/n ratios, which is further discussed in following sections.



Figure 4. Plots of methane flux vs. (**a**) *i*-butane/*n*-butane ratio and (**b**) *i*-pentane/*n*-pentane ratio at the three sites and La Brea.

3.3. Ojai Comparison

As previously mentioned, the Ojai site had been previously studied by Duffy et al. between 2003 and 2005 [32]. This previous study made measurements in the North Sulfur Mountain and Silverthread oil fields; these fields are approximately 15 km northeast of the Tip Top oil field where four samples were collected in the current study. However, the two samples collected in this study as part of the Sisar Creek Oil Field were collected only a distance of 1.3 km from the North Sulfur Mountain samples collected in the earlier study. The previous study had access to some of the largest seeps in the area, and the observed methane seepage rates of up to 300 g h⁻¹ were approximately five orders of magnitude greater than the maximum Ojai flux rates observed in this study. In terms of gas composition, the earlier study found relatively greater ethane and propane amounts (average C1/(C2 + C3) ratio of 220) compared with this study's observations (average C1/(C2 + C3) ratio of 1360). Perhaps most interestingly, the earlier study was able to measure the composition of the reservoir gas for both the North Sulfur Mountain and Silverthread fields. The reservoir gas samples were much less methane rich, exhibiting a C1/(C2 + C3) for North Sulfur Mountain and Silverthread of 10.9 and 8.1 respectively. This indicates that the gas is changing character as it migrates from deposit to the

9 of 13

surface, becoming more methane rich. This is likely due to a combination of microbial degradation and the preferential loss of ethane and propane because of their adsorption and solubility properties that has been previously observed at seepage sites [9,21]. This may also explain the more methane-rich flux gases that were observed in this study; it makes sense that in larger seeps (where gas makes it to the surface in a shorter amount of time), the gas would undergo less change/processing and would maintain a composition that was closer to the original composition of the deposit. It should also be noted that differences in sample collection protocol could also contribute to observed differences between the current study and work carried out by Duffy et al.

3.4. Anthropogenic Versus Natural Seepage

The Carpinteria site allowed for an interesting look at how anthropogenically influenced emissions vary from natural seepage. At Carpinteria, one sample was collected from the top of an exposed pipe that contained bubbling asphalt, Figure 5. It is believed that this represents remains of an old oil well [20]. This pipe gives gases a preferred route to the surface, which theoretically means they spend less time making the journey from underground reservoir to surface. The isomer gas ratios observed coming from the pipe varied significantly from the other Carpinteria samples. Both the *i*-C₄/*n*-C₄ ratio and the *i*-C₅/*n*-C₅ ratio were greatly depressed compared to the ratios at the other seepage sites, as shown in Figure 6. This would suggest that the processing that gas undergoes on its way from deposit to surface is at least in part responsible for the elevated *i*/*n* ratios observed, since the gases emitted via the pipe would have not only a shorter processing time but less interaction with soil and water. Somewhat surprisingly, the C1/(C2 + C3) ratio did not vary significantly for gases coming from this exposed pipe. The *i*/*n* ratios observed are similar to earlier findings at La Brea, where gas emissions at very high emission sites (indicating ease in passage) varied greatly and seemed to exhibit less indications of gas processing than other seeps.



Figure 5. Exposed pipe with bubbling asphalt that was sampled at Carpinteria.



Figure 6. Cartoon showing anthropogenic influence on i/n gas ratios at Carpinteria.

3.5. Implications and Future Directions

As seen within the study of McKittrick, Ojai, and Carpinteria macroseepage sites, there are significantly different gas ratio signatures depending upon the location of the seep. In addition to significant intra-site variability, there were also significantly different ratios within samples at the same site. The two largest Ojai fluxes, samples 13 and 17, exhibited C1/(C2 + C3) ratios approximately ten times higher (3400 versus 350) than the other four Ojai sites. Most interesting were the differences between Carpinteria sample sites. One sampling site was located approximately 300 m west of the other sites. Fluxes measured from this site were unique in two ways. First, the single site exhibited much greater amounts of the C₂+ alkanes, as its C1/(C2 + C3) ratio of 240 was more than ten times less than the average of the other four samples collected at Carpinteria. Second, the site was unique in that even though it was generally rich in C₂+ alkanes, it did not exhibit any appreciable amount of *i*-pentane, which resulted in a much lower *i*-pentane to *n*-pentane ratio (0.9) than the other four samples (average of 60). Future studies that employ more samples will be useful in determining if, how, and why ratios of emitted gases vary over relatively small distances or short time intervals.

Contributing factors for both these differing intra-site and inter-site ratios may include gas composition of the deposit, deposit depth, strength of seep, and degree of microbial degradation. Because of these variables, it can be stated that there is no one singular characteristic of geological seepage in terms of its gas ratios. This is also true of other emission sources, such as the percentage of ethane in U.S. pipeline natural gas, which may vary from 1.6% to 2.7% ethane in various cities [16,42] or the methane to ethane ratio from oil and natural gas fields which can change from approximately 11:1 to 1:1 [43]. Headspace vapor from gasoline samples can also vary up to an order of magnitude by season for butane components [44]. However, the variability of VOC ratios in these emission sources is smaller than the almost two orders of magnitude difference between *i/n* pentane ratios observed in this study. Thus, there is no one characteristic "fingerprint" that can be applied to macroseepage. This means that future estimates on the role that geologic seepage plays in VOC budgets in a given city or region should be based upon emission data from seeps in that same area. For global or national budgets, a range of macroseepage studies should be used. Moving forward, additional studies carried out at new sites are important to measure ratios of emitted gases and in order to better understand the role that geologic seepage plays in both local and global budgets of methane and VOCs.

Future studies at these and other sites in Southern California will build upon this preliminary study. These future studies will incorporate not only additional samples but will measure a wider suite of gases. Both isotopic measurements of C in methane and measurements of non-hydrocarbon gases (N₂, O₂, CO₂) can be used to obtain more information about gas sources and can specifically be used to better differentiate reservoir gas signals from possible contributions from biogenic methane [1]. The relative amount of C₅–C₉ gases can also potentially be used to better gauge the degree of degradation from the source that has occurred [45].

4. Conclusions

Flux measurements of methane and light alkanes showed wide variability in terms of magnitude and gas ratios from Carpinteria, McKittrick, and Ojai seepage sites in Southern California. These three sites also showed significant differences from previous seepage studies carried out at the La Brea Tar Pits in Los Angeles. Carpinteria samples showed the most evidence of 'processing' between the deposit and the surface, exhibiting highly elevated ratios of more than 20:1 for *i*-butane/*n*-butane and more than 45:1 for *i*-pentane/*n*-pentane. Large differences were also observed between sample seeps that were anthropogenic versus natural, with the anthropogenically-influenced samples showing less processing or alteration from ratios that are typical of underground oil or gas deposits.

The large differences in emitted gases at each site have important implications when estimating the relative importance of macroseepage in the atmospheric budget of a given gas. Unlike VOC emission sources that are relatively constant, geologic seepage appears not to have a single source fingerprint. This means that studies that seek to incorporate macroseepage into local or regional atmospheric budgets should not use generalized composition measurements that were made in other locations. Though composition of deposit, deposit depth, geology of region, and microbial environment may all play roles in shaping the gas ratios emitted at the surface, further research is needed in order to assess the relative importance of these variables in the studied locations.

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