

Atmospheric monitoring and detection of fugitive emissions for Enhanced Oil Recovery



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ABSTRACT

In Weyburn, Saskatchewan, carbon dioxide (CO₂) is injected into the Weyburn oilfield for Enhanced Oil Recovery (EOR). Cenovus Energy Inc. operates more than 1000 active wells, processing plants, and hundreds of kilometres of pipeline infrastructure over a >100 km² area. While vehicle-based atmospheric detection of gas leakage would be convenient for a distributed operation such as Weyburn, implementing atmospheric detection schemes, particularly those that target CO₂, are challenging in that natural ecosystems and other human activities both emit CO₂ and will contribute to regular false positives. Here we present field test results of a multi-gas atmospheric detection technique that uses observed trace gas ratios (CO₂, CH₄, and H₂S) to discriminate plumes of gas originating from different sources. This work is part of a larger project focused on multi-scale fugitive emissions detection and plume discrimination. During 2013 and 2014, we undertook vehicle-based mobile surveys of CO₂, CH₄, H₂S, and δ¹³CH₄, in the Weyburn oilfield, using customized Cavity Ring Down Spectroscopy (CRDS) instruments that also alternated as stationary receptors. Mobile surveys provided georeferenced observations of atmospheric gas concentrations every 20–30 m, along a route driven at roughly 70 km h⁻¹. Data were uploaded to remote servers and processed using visualization tools that allowed us to constrain the location and timing of potential emission events. Results from one day of mobile surveying, September 24, 2013, are presented here to illustrate how industrial activities, combustion engine and flare stack source emissions can be discriminated on the basis of excess mixing gas ratios, at distances from a few hundreds metres, to kilometres, in the Weyburn oilfield.

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1. Introduction

In the petroleum industry Enhanced Oil Recovery (EOR) through the injection of carbon dioxide (CO₂) or water (H₂O) has been used for decades (Emberley et al., 2005) as a method for displacing and recovering additional fractions of subsurface oil (Blunt et al., 1993). As a result of EOR, the production life of many oil fields has been extended, while at the same time shifting greenhouse gases from the atmosphere to geologic reservoirs for permanent storage. There were more than 130 active CO₂ EOR operations globally (GCCSI, 2012), and because it is a mechanism of production first, and CO₂ capture and storage second, EOR research has naturally tended to focus on increasing oil production rather than understanding

the fate of CO₂ in reservoirs and unintended atmospheric releases (Thomas, 2007). While this is still generally the case, atmospheric releases are increasingly being recognized as a diagnostic tool for production-related issues, including environmental performance. Even minor releases contribute valuable information about production factors, including the condition of infrastructure, and the care with which maintenance activities are done. In many cases, understanding small releases may help avert larger releases down the road. Detecting small fugitive EOR emissions is, however, challenging because several of the same gases involved in EOR operations are also produced naturally from a variety of sources distributed across the landscape. In this paper 'fugitive' emissions are defined as escaped reservoir gases with a composition (multi-gas signature) specific to the geochemistry of activities in the Weyburn oilfield, including CO₂ injection (Emberley et al., 2004). Further, we note that geochemistry can vary from site to site in ways that may limit, for example, the abundance of hydrogen sulfide (H₂S).

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Thus, a priori knowledge of a site's formation geochemistry will be vital prior to adaptation of techniques such as that presented here.

During the production, processing, and transportation of oil and natural gas, including EOR, unintended seepage can occur at a variety of points such as along well casings, pipeline, and other infrastructure. These components may include CO₂, methane (CH₄), and H₂S and other hydrocarbon species. In the case of CH₄, the US EPA estimates that over 60% of global CH₄ emissions are tied to human activities, a large portion of which comes from the energy sector (US EPA, 2010). This has been supported by a number of recent studies. The teams of Miller et al. (2013) and Pétron et al. (2012) used multi-year atmospheric measurements of hydrocarbon species from oil and gas fields to suggest that the amount of CH₄ leaked from the fields under study might be underestimated currently in national inventories by as much as a factor of two, although there is some disagreement on the exact magnitude of emissions (Allen et al., 2013).

As in the case for Carbon Capture and Storage (CCS) sites, CO₂ comprises the bulk of injected gas in EOR. Though CO₂ seems a target for monitoring, studies have found that bulk CO₂ is not a conclusive indicator of leakage by itself and therefore other indicators are required, because CO₂ is readily exchanged by most living organisms (Risk et al., 2013). This means that seepage events, especially those at smaller scale, may be masked by natural variations in CO₂ between the biosphere, atmosphere, and also by fossil fuel burning activities in the area. Recent studies have also examined other gases such as H₂S, which do occur naturally within these oil-bearing reservoirs, and the low natural abundance of such gases in the free atmosphere means that they can serve as valuable tracers in leak detection.

Table 1 lists four potential emission sources identified across the Weyburn oil field. The CO₂ injected by Cenovus is sourced from the Dakota Gasification Company (DGC) and transported via a ~300-km pipeline. At Weyburn, a water-alternating-gas (WAG) injection strategy is used, which increases oil fluidity and recoverability at production wells (Lombardi et al., 2006; Asghari et al., 2007). Following fluids separation and recycling (REC, mostly CO₂), surplus fluids and gases are mixed with new DGC CO₂ and re-injected back into the formation. This closed-loop, recycle system continually re-injects recovered fluids back into the reservoir at high pressure. Thus, each emission source (DGC, REC, etc.) has a unique gas composition and mixing ratio 'fingerprint' potentially allowing atmospheric plumes originating from these sources to be differentiated from one another, and also from natural signals within the field.

Given our knowledge about the multi-gas proportions of different sources and by measuring the concentrations of several gases simultaneously, it is in principle possible to distinguish these sources in the field based on multi-gas signatures (Romanak et al., 2012). This study field-tests a technique that associates known multi-gas ratios from different sources to anomalies recorded by mobile gas analyzers in the field. In our study, we chose to use recycled gas (REC) as an indicator of containment loss in this closed loop EOR system, whereas (Romanak et al., 2012) used a different set of ratios (CO₂, CH₄, vs. N₂:O₂). Here we present the results from a field campaign at Weyburn during late September 2013, where we test our ability to detect REC plumes in the free atmosphere, above background variation, and without prior knowledge of their presence.

2. Study methods

Our surveys focused on measuring atmospheric gas composition inside and outside the unit boundary in a grid-like search pattern, and in post-processing to identify atmospheric plumes of elevated concentrations of CO₂, CH₄, and H₂S that originated from upwind service rig activity. Service rig activities are known to occasionally generate emissions, including both emissions from service truck combustion and flare stacks (BURN), and also potentially reservoir-type gases (such as REC). We did not know the specifics of any service rig activities until after the survey, and thus the survey was conducted blind. Here, our primary interest was to test whether a geochemical fingerprinting technique could identify any service rig activities that were generating emissions that could be distinguished from natural background (e.g., BURN, REC).

2.1. Site description

The Weyburn oilfield in Saskatchewan Canada is the site of one of the World's largest EOR projects, injecting 2.4 Mt per annum of anthropogenic CO₂ (GCCSI, 2012). Over 18 Mt CO₂ has been stored since fall 2000 (GCCSI, 2012; Beaubien et al., 2013). This region is perforated by more than 1000 active wells that tap the oil-bearing zone of the Williston Basin. Although these wells are sealed, the integrity of the seal may degrade over time, and wells are the most likely source of seepage to the atmosphere (Bowden et al., 2013). An extensive pipeline infrastructure carries fluids back and forth from wells to processing plants, which is why REC gas is a main target for leak detection. Other non-industrial type emissions found in the Weyburn field are from the various wetland areas scattered across the landscape. This work is a natural follow-up to the decade-long International Energy Agency Greenhouse Gas Weyburn-Midale CO₂ Monitoring and Storage Project, led by the Petroleum Technology Research Centre (Hitchon, 2012). Despite the wealth of monitoring techniques used in that project for detecting potential CO₂ seepage, little atmospheric monitoring was included in the program. However, operator Cenovus Energy has recently been interested in developing atmospheric detection strategies, in particular where this environmental information can assist in optimizing aspects of production.

2.2. Field methods

To measure the atmospheric abundance target gases (CO₂, CH₄, δ¹³C-CH₄, and H₂S), we used two Picarro Cavity Ringdown Spectroscopic (CRDS) trace gas analyzers (Picarro Inc, Santa Clara, CA USA), included a G-2201i (with 1σ instrumental errors of 1 ppm, 5 ppb, and 1.15σ respectively) for CO₂, CH₄, and δ¹³C-CH₄, and a G-2204 for H₂S which is a specialized instrument with instrumental errors comparable of the G-2201i. Lag time between the tube inlet and gas analyzer was corrected for the 880 cm of tubing and 12 c.f.m. pre-pump flow rate. During the 2013 field season, five mobile surveys were completed. The instruments were mounted in thermostatically-controlled waterproof housings, and placed in the bed of a pickup truck with an inlet tube connected to the windshield. Measurements were collected at 1 Hz frequency at about 70 km h⁻¹ in a grid-like route that surveyed all areas accessible

Table 1
Four potential emission sources found across the Weyburn oil field, their estimated mixing ratio values, and references to those sources of information are given. This study focuses on REC and BURN and experimentally uses a range of 20–40 eCO₂/eCH₄ for REC and >1000 eCO₂/eCH₄ for BURN.

Source	Acronym	eCO ₂ /eCH ₄	eCH ₄ /H ₂ S	δ ¹³ CH ₄	Source
CO ₂ sourced from Dakota Gasification Company	DGC	110	0.12	-20	Trium (2011)
Recycle gas	REC	30	0.32	-20	Trium (2011)
Combustion-General	BURN	20,000	1	-20	US EPA (2014, 2013)
Natural aerobic soil	NAT	>220	10 ⁻⁶	-60	Trium (2011), Phillips et al. (2013)

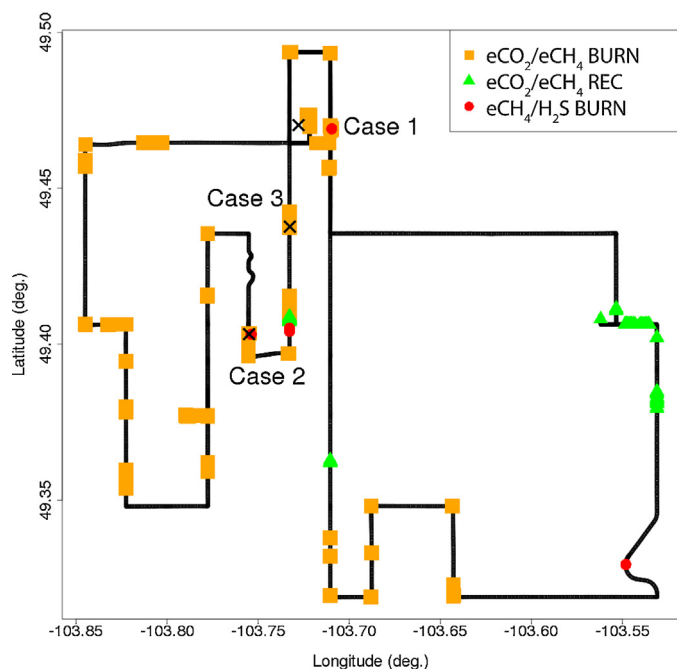


Fig. 1. Map of September 24, 2013 afternoon mobile survey that shows locations where BURN and REC anomalies were detected along route. Black line show the geographical coordinates where data were sampled. Orange squares represent 1 Hz measurements corresponding to $e\text{CO}_2:e\text{CH}_4$ BURN anomalies. Green triangles indicate $e\text{CO}_2:e\text{CH}_4$ REC anomalies. Red circles indicate $e\text{CH}_4:\text{H}_2\text{S}$ anomalies. Black X's represent the locations of service events and the general locations of Cases 1–3 along route are also labelled. 0.05 degree of latitude = 5.57 km. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

by road representing a 100-km² area. Mobile surveys generally lasted about three hours, resulting in roughly 7000 geo-located data points, per gas species. Before and after each survey, gas standards were used to establish analyzer drift, if any. One mobile survey was completed during the June field campaign and two rounds of both day and nighttime surveys were completed in September. Cellular telemetry allowed analyzer data to be viewed in real-time on a handheld device throughout each survey, though in raw form without calculated ratios. In between surveys, the instruments act as stationary measurement points, though these data are not discussed here. Analyzer drift was monitored daily using tanks of compressed air, though CRDS calibrations are extremely stable and generally need to be refreshed only every few months. Also, since our detection technique is a differential one in which we measure a departure from in-situ value, the technique is tolerant of some daily drift if it were to occur.

2.3. Calculation of excess concentrations

To quantitatively increase the visibility of fugitive emission events, the global background minimum concentration value from this survey was subtracted from each measured value to create a dataset of differences, or excess concentration beyond what might be considered normal. “Excess” (e) concentrations here are defined as the concentration minus background and represent the remaining residual concentration, or excess above ambient for a gas species (CO_2 , CH_4 , H_2S). The background minimum value in this study was obtained from the entire mobile survey dataset of roughly 2.5 h of 1 Hz measurements. Our measurement site was ideal for this application because of extremely flat topography, and the short timeframe of measurements, both of which would maximize the likelihood that the ambient background concentrations

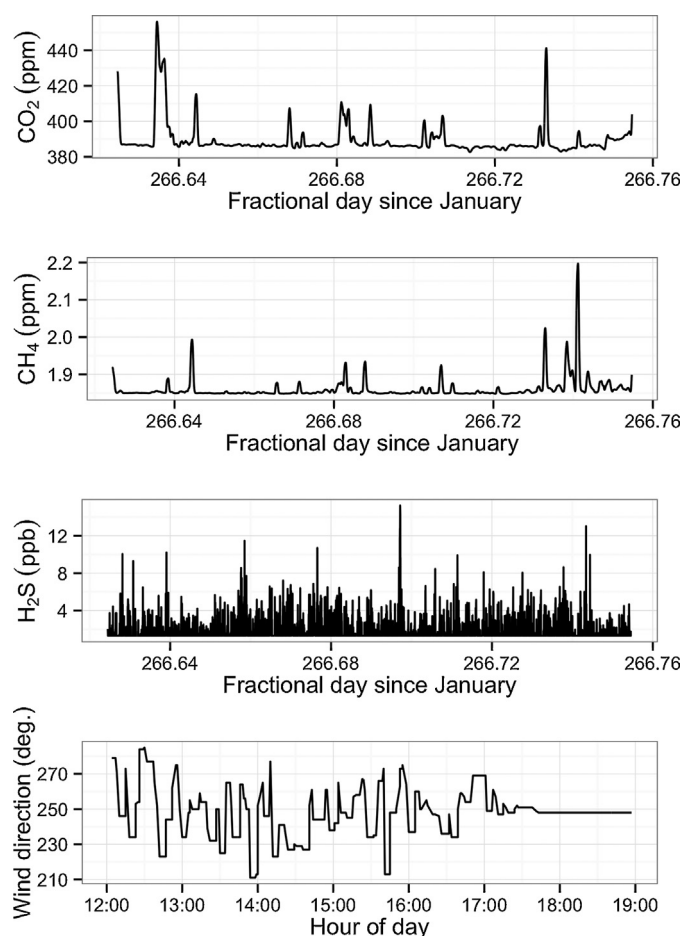


Fig. 2. Time series of CO_2 , CH_4 , H_2S and wind direction (from Halbrite meteorological station) for the survey of September 24, 2013.

would be constant through the observation interval. Assuming the minimum CO_2 value recorded during a mobile survey was 380 ppm then the excess CO_2 ($e\text{CO}_2$) was: $e\text{CO}_2 = \text{CO}_2 - 380$. Excess ratios are useful for capturing the undiluted ratio of the added gas, and to subtract a baseline value that is appropriate to that day, time, and place. Thus, our excess ratios use the measured concentration of H_2S . The $e\text{CO}_2:e\text{CH}_4$ and $e\text{CH}_4:\text{H}_2\text{S}$ ratios were compared to the mixing ratios of known emission sources. Note that H_2S is exceptionally rare in areas without significant geologic activity, thus we do not subtract a background from it. The excess approach reduces the need for significant baseline data, and generally minimum values for the 2.5 h survey were used because (1) they best represented actual conditions on the day of sampling, and (2) it was highly improbable that we would detect anything other than background for most of our driving across the large domain. Since the surveyed area is flat, windy, and managed under large-scale cropping regimes typical of industrial agriculture, the background concentrations of all target gases were found to be spatiotemporally stable during our surveys, as indicated by (1) measurements within the field distant from possible oilfield emission sources, and (2) measurements outside the EOR operating area.

2.4. Supporting data

Company records were obtained from all 2013 field activities, to cross-reference against detected anomalies. We did not know about these service activities a priori. Service rig activities ranged from well abandonment, repairs of pump jack rod, to flushing wax buildup from lines. Some activities could last for multiple days.

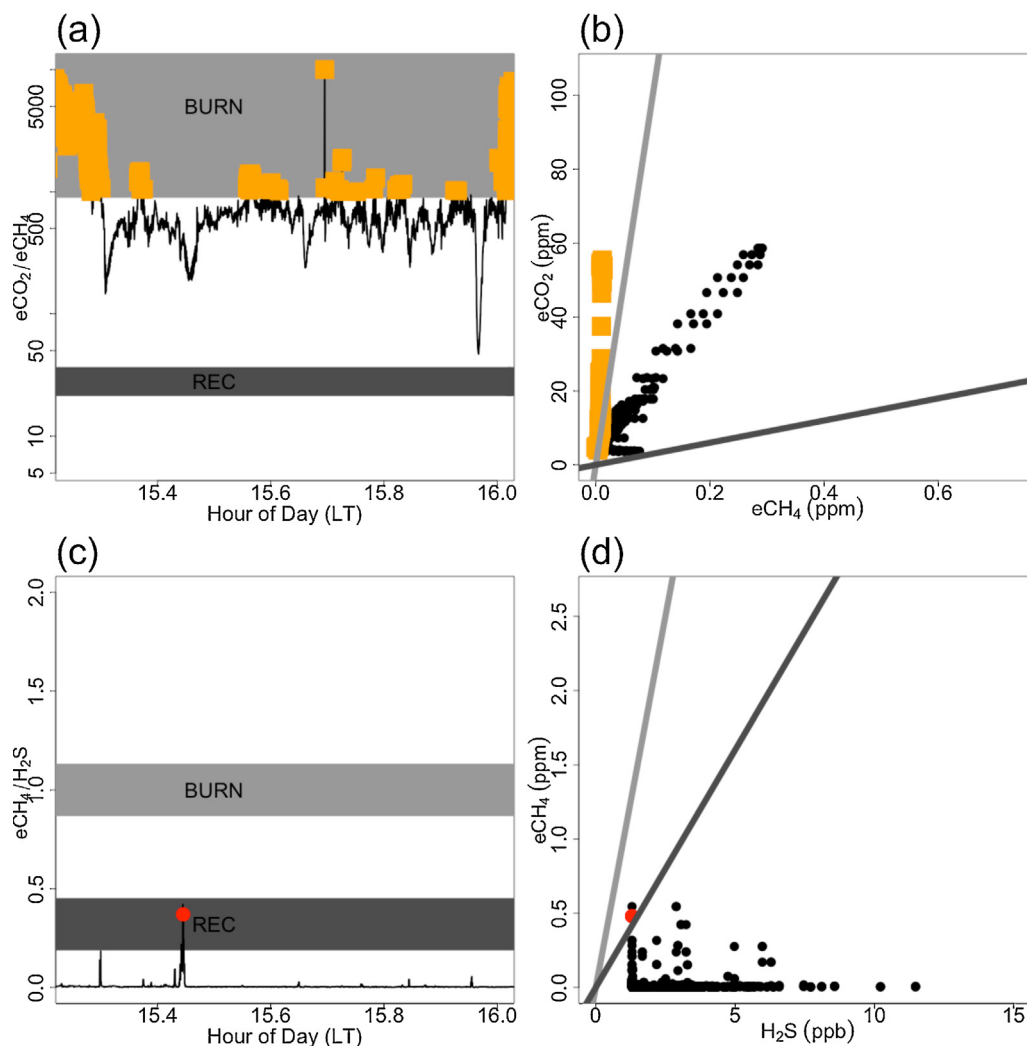


Fig. 3. Combination time series and scatter plots for Case 1 showing a positive REC anomaly detection during the September 24, afternoon mobile survey. Top row: $e\text{CO}_2:e\text{CH}_4$ time series (a) and scatter plot (b). Bottom row: $e\text{CH}_4:\text{H}_2\text{S}$ time series (c) and scatter plot (d). The gray bands in the time series indicate the acceptable ranges indicating BURN and REC ratios. These correspond to the angled gray lines in the scatter plot, though these do not also indicate acceptable range. Note that for comparison the scatter plots show all ratios collected during the survey.

While these may allow for REC leakage, there are typically additional emission sources on site including, large tank trucks, a flare stack, personal pickup trucks, and other rig equipment which may generate BURN emissions. Natural emissions from local biota are also of course present everywhere. At the time of a mobile survey, visible service activities were targeted and in some instances we diverged from our grid-like surveys to drive additional roads when rigs were seen onsite. In some cases, we had limited access to well pads where service activity was ongoing, and on occasion we would drive towards the well pad, but be forced to reverse. In these instances, the vehicle exhaust was an additional source of atmospheric gas anomaly, though this was straightforward to identify based on timing and excess ratios. The coordinates of all field activities in 2013 were projected onto Google Maps and overlaid with recycled gas and combustion ratios for a visual comparison. Weather data from a nearby Environment Canada station (Halbrite) was used to determine wind speed and direction for each mobile survey. Although simultaneous measurements of wind direction and speed should be prioritized for this kind of survey, we consider that wind information collected at the Halbrite meteorological station would be sufficient since the weather station is only ~ 10 km northeast of our survey area, and in between

there is neither topography nor trees, and vegetation consists only of low-height crops.

To positively identify measurements as anomalies, (1) plumes had to conform to the target gas ratio of $e\text{CO}_2:e\text{CH}_4$, (2) measurements had to contain more than two successive points along route, (3) plume geometry and wind directional information had to be consistent, and finally (4) plume geochemistry ideally conformed to the targeted gas $e\text{CH}_4:\text{H}_2\text{S}$ ratios when these were available.

3. Results and discussion

This section presents three different cases in which measured $e\text{CO}_2:e\text{CH}_4$ and $e\text{CH}_4:\text{H}_2\text{S}$ ratios met the required criteria for an anomaly as described above, and could be associated with service rig events. As expected, in all three cases we observed complex signals, with anomalies of both REC and BURN. All cases were observed on the same afternoon, September 24, during mobile surveying as can be seen in Fig. 1. Fig. 2 shows the survey time series. During that day, we measured peaks in concentration related to the oilfield emissions, with otherwise relatively flat profiles of background variation, which is expected given the relatively short timeframe of these surveys, and the totally flat topography. The maximum peaks

for CO_2 , CH_4 , and H_2S were 456 ppm, 2.2 ppm, and 15 ppb, respectively. The H_2S was inherently more variable than the other gases, as a consequence of its low concentrations near the threshold of detection, but peaks rising above the background are clearly evident.

3.1. Case 1: Observation of drilling event anomaly

Case 1 represents a survey that approached a drill rig from the east, and turned north onto a road that was just east of the drilling event (Fig. 1). Winds were from the southwest. A mild sulfurous smell was present in the air, and rig trucks were visible, as was a flare. The most proximal measurement locations were at 0.5 and 1.3 km from the rig. Fig. 3 highlights the significant events that correspond to Case 1. Concentrations of CO_2 peaked at ~ 462 ppm, or only some tens of ppm above natural well-mixed air. Ratios revealed $\text{eCO}_2:\text{eCH}_4$ consistent with combustion (i.e. BURN in Table 1). These ratios correspond to the orange squares in the Fig. 3(b) scatter plot, and move along a combustion-type mixing line. At 0.5 km from the source, combustion signatures were detected continuously over an interval of 115 m. The proximity of this route to a drill rig and close correspondence of these multi-gas mixing ratios to fossil fuel combustion strongly indicate that this plume originated from the vehicles and flare stack onsite, and the tailpipe of the survey vehicle (during the U-turn).

At another point crosswind 1.3 km from the drilling rig, a sulfur odour was still present. Elevated H_2S , CH_4 , and CO_2 concentrations were recorded at 1.3 ppb, 2 ppm, and 440 ppm, respectively. The $\text{eCO}_2:\text{eCH}_4$ ratios did not conform to the mixing ratio of REC, though a REC-type anomaly was recorded in the $\text{eCH}_4:\text{H}_2\text{S}$ data (Fig. 3c). There were five sequential measurements within 15 m showing $\text{eCH}_4:\text{H}_2\text{S}$ ratios ranging from 0.24 to 0.42, or within the REC signature range. This anomaly plots along the mixing ratio of recycled gas (Fig. 3d).

Overall, this first case helped illustrate that even within small areas, we were able to differentiate plumes from the various sources, and that our observations were consistent with the site activities.

3.2. Case 2: Observation of a service rig anomaly

Case 2 presents data from an area near the center of the field (Fig. 1), in which we approached a service rig that was east of our survey route. The duration of data collection for this particular case investigation was only about fifteen minutes (Fig. 4a). Winds were from the south-southwest. This case also starts with a tailpipe anomaly from our idling vehicle, near the entrance to the well pad where we waited several minutes to gain access. While the vehicle idled, the road became peak CO_2

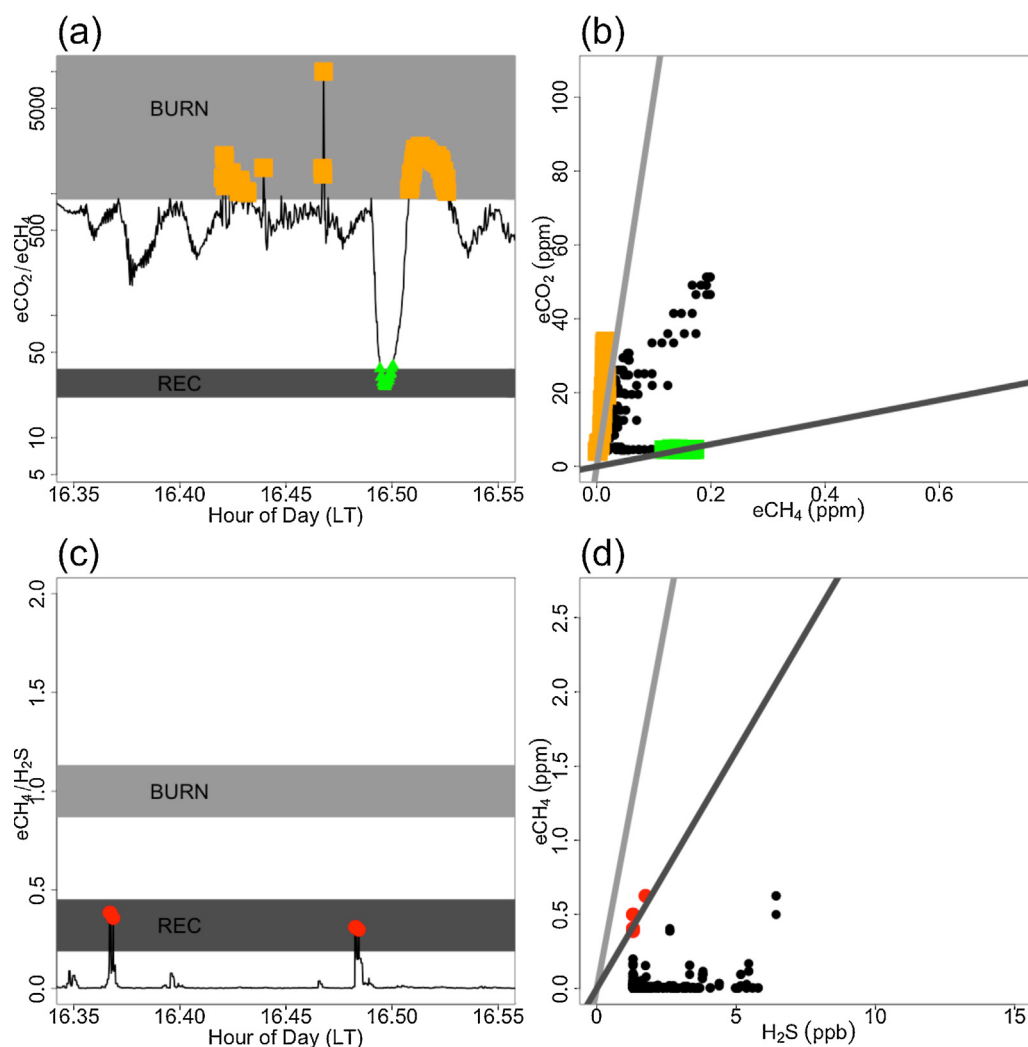


Fig. 4. Combination time series and scatter plots for Case 2 that show combustion and REC anomalies that were detected. Both REC anomalies were detected by $\text{eCO}_2:\text{eCH}_4$ and $\text{eCH}_4:\text{H}_2\text{S}$. (a) and (c) indicate REC anomaly detection by $\text{eCO}_2:\text{eCH}_4$ (green triangles) and $\text{eCH}_4:\text{H}_2\text{S}$ (red circles), corresponding also to the green and red groupings in (b) and (d). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

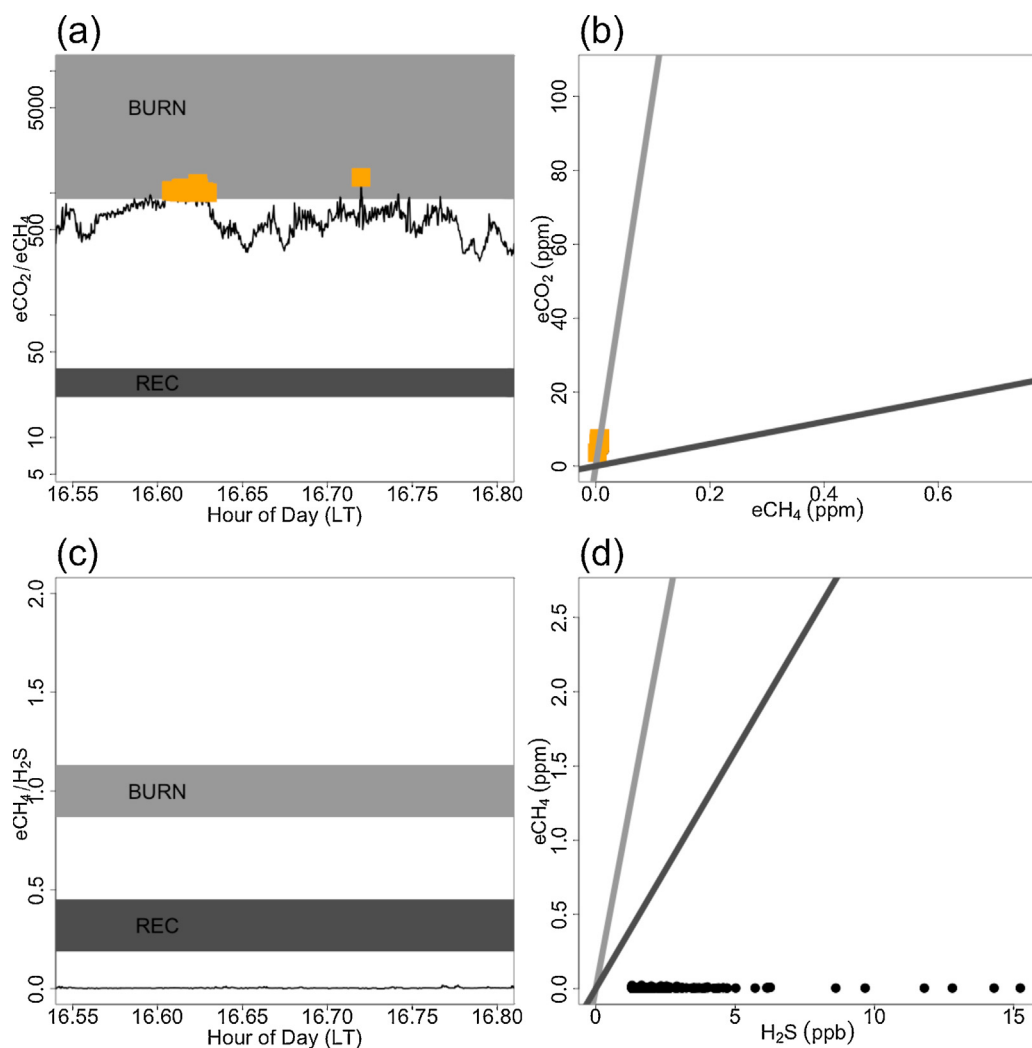


Fig. 5. Combination time series and scatter plots for Case 3 that show a combustion gas anomaly in (a) that conforms to $e\text{CO}_2:e\text{CH}_4$ signature of BURN and plotted along the mixing line in (b).

concentrations were 413 ppm and conformed to $e\text{CO}_2:e\text{CH}_4$ ratios of BURN as would be expected. Once access was allowed, measurements were made at close range to the rig and was circled twice. On the first pass, peak CO_2 and CH_4 concentrations, measured at about 50 m from the rig, were 417 ppm and 2.0 ppm, respectively. This event did not initially reveal $e\text{CO}_2:e\text{CH}_4$ ratios that corresponded to REC even though the rig was circled at a close range. Peak H_2S and CH_4 concentrations on the second pass were, however, 1.3 ppb and 2.4 ppm, respectively, and $e\text{CH}_4:\text{H}_2\text{S}$ did in fact suggest a weak REC anomaly (Hour of day 16.35 in Fig. 4c). This anomaly plotted along the line of REC (Fig. 4d).

Following the proximal survey, observations 10 min later at a greater distance also revealed elevated H_2S and CH_4 . At 1.4 km from the service rig (Fig. 1, Case 2) CO_2 , CH_4 , and H_2S concentrations peaked at 386 ppm, 2.3 ppm, and 1.7 ppb, respectively. Although concentrations of CH_4 were more dilute further from the rig and H_2S concentrations increased, the composition of the REC plume retained its signature. In this instance, concentration of H_2S likely increased with increasing distance from the rig due to variations in the strength of emission through time, though other factors could have contributed including shifting wind, or (less likely) the presence of an enhanced natural flux of H_2S in the region. Fig. 4(a and c) show time series with ratios of $e\text{CO}_2:e\text{CH}_4$ and $e\text{CH}_4:\text{H}_2\text{S}$ both conforming to REC near hour 16.5. Ratios of $e\text{CH}_4:\text{H}_2\text{S}$ ranged from

0.28 to 0.31 and $e\text{CO}_2:e\text{CH}_4$ from 26 to 40 representing about for 400 m along the road. Fig. 4(b and d) scatter plots show both green triangles and red circles that again follow the mixing lines of REC. Towards the end of the survey the survey vehicle stopped to reverse, which resulted in $e\text{CO}_2:e\text{CH}_4$ ratios indicating BURN from the survey vehicle tailpipe (orange squares in Fig. 4a).

Overall, this case was again instructive, and showed how combined signals could be detected and differentiated within short timeframes, even at near-background concentrations. The detection of a REC plume indicates that this technique was able to detect combustion and recycled gas events using $e\text{CO}_2:e\text{CH}_4$ and $e\text{CH}_4:\text{H}_2\text{S}$ at kilometre-scales, providing some constraints on the downwind sensitivity. During Case 2, concentrations of H_2S ranged from 1.3 to 1.7 ppb, which (as for all observed emissions) fell far below any regulatory guidelines, yet still allowed anomalies to be identified and attributed. Again, the $e\text{CH}_4:\text{H}_2\text{S}$ indicated REC first, though synchronous anomalies exist in the $e\text{CO}_2:e\text{CH}_4$ records. The most likely reason for the differential sensitivity of the excess ratios ($e\text{CO}_2:e\text{CH}_4$ vs. $e\text{CH}_4:\text{H}_2\text{S}$) relates to the quality of background subtraction at each time point, plus possible source variation in time, and composition. REC is known to have a variable fingerprint, particularly for CO_2 concentration, and thus the expected window of e-ratios may have to be widened. In addition, the ratio of natural (NAT) systems varies spatiotemporally within small limits at

Weyburn. So, while the single background subtraction value is a useful simplification that works well for a region such as Weyburn, there is room for adaptive background algorithms. For these September surveys, $e\text{CH}_4:\text{H}_2\text{S}$ does appear to be the more useful of the two ratios for identifying REC, but at other times of year, particularly in the winter when background variations are smaller, $e\text{CO}_2:e\text{CH}_4$ is very useful because these gases are present at higher concentrations and thus may indicate with greater acuity when background variance is low. The dual indicators do, however, provide independent checks on one another, and ideally with the future development of improved background subtraction algorithms, we will seek to accommodate within-survey variations and improve precision for both fingerprints.

3.3. Case 3: Successful management of reservoir gases during flaring

In this case the mobile survey route travelled north towards a service rig that was actively flaring gas, meaning that reservoir gases of REC-type composition were likely being managed to avoid atmospheric release. The service rig was located to the west during this approach on an adjacent road (Fig. 1). A gradual increase in CO_2 concentrations was observed along route leading up to intersection with the cross wind from the flare stack. At the time of measurement, winds were from the south-southwest. Within the next 300 m, CO_2 concentrations ranged between 388 and 409 ppm, whilst CH_4 concentrations remained steady at 1.8 ppm. Fig. 5(a) shows values of $e\text{CO}_2:e\text{CH}_4$ from hour 16.65 to 16.80 during this Case. The increase and decline of concentrations matched general plume geometry. Ratios of $e\text{CO}_2:e\text{CH}_4$ conformed to the BURN mixing line in Fig. 5(b). This combustion anomaly appears to have originated from the flare stack located about 300 m away. Despite the faint odour of sulfur in the air downwind from the service rig, there was no record of a recycled gas plume in Fig. 5. As in both the previous cases, we again observed a group of data points again tracking along the combustion mixing line (Fig. 5b), which is consistent with observations of combustion activity. Normally our efforts were primarily focused on detecting anomalies that are compositionally similar to reservoir gases, not those originating from flare stacks or vehicles.

4. Conclusions

This study presents a compositional-based atmospheric sensing strategy that can be used to discriminate between industrial, natural, and combustion emissions on the basis of site-specific gas ratios. Results from each of the observed anomalies show positive identification of atmospheric anomalies that were attributed to combustion or recycled gas sources originating from a drilling or service rig activity, and are consistent with our expectations. Additionally our results show that continuously emitted plume retains its excess gas ratio fingerprint at distances of up to 1.4 km from the source.

During this particular 1-day survey from which these different case study examples were extracted, we recorded a large number of combustion anomalies, from oilfield activities, local industries, farms, and roads. These combustion anomalies dominated the above-natural emissions, and will have the potential to create recurrent false positives in low-level atmospheric monitoring campaigns that attempt to target CO_2 directly as an indicator of CCS containment at EOR (or CCS) sites. These combustion events also contribute to multi-scale temporal variability in the region's atmosphere, though this appears not to be problematic for detection of low-level anomalies by excess ratio. For this study to work, we did have to use spatially and temporally limited datasets so that

the background would be constant through the observation interval. For longer surveys, or for surveys in topographically diverse terrain (our survey area was totally flat), a defensible technique for determining an adaptive background value would be highly beneficial. Ideally this technique would take the form of a computational filtering algorithm that would recognize baseline concentrations from within the dataset itself. Of course baseline is always present, given the low probability of driving continuously through anomalies.

In this study, we presented results exclusively from an EOR site. However, ongoing projects also involve monitoring of other emerging unconventional energy sectors such as oil sand, shale gas and petroleum exploration. Future work should also try to further develop such techniques that would involve understanding atmospheric plume migration and dispersion for improved source area delineation, including from stationary analyzers undertaking temporal surveys. Simultaneous measurements of wind direction and speed should be incorporated into future mobile surveys to better understand local conditions. Additionally, real-time analysis would permit the driver to immediately distinguish false positives from REC-type anomalies. At last, future work that seeks to understand how this technique can be applied across sites may consider the effect that distance (depth) of leakage point to surface has on gas ratios, for example in cases of escaped $e\text{CH}_4:\text{H}_2\text{S}$ that follows fissures or permeable pathways to the surface.

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