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TECHNOLOGY ASSESSMENT REPORT: AIR MONITORING TECHNOLOGY NEAR UPSTREAM OIL AND GAS OPERATIONS

ENVIRONMENTAL DEFENSE FUND
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Figure 1: Number of low cost air quality sensor publications over time

ACRONYMS AND ABBREVIATIONS

AB	Assembly Bill
AQ-SPEC	Air Quality Sensor Performance Evaluation Center
ARPA-E	Advanced Research Program Administration-Energy
BAAQMD	Bay Area Air Quality Management District
BTEX	Benzene, Toluene, Ethylene, Xylene
CAIRSENSE	Community Air Sensor Network
CARB	California Air Resources Board
CEAS	Cavity-Enhanced Absorption Spectroscopy
CFCs	Chlorofluorocarbons
CO	Carbon Monoxide
CO2	Carbon Dioxide
CRDS	Cavity Ring-Down Spectroscopy
CW-CRDS	Continuous Wave Cavity Enhanced Absorption Spectrometry
DIAL	Differential Absorption Lidar
DoE	Department of Energy
DPM	Diesel Particulate Matter
EC	Electrochemical
EDF	Environmental Defense Fund
EPA	Environmental Protection Agency
ES&T	Environmental Science & Technology
ES&T Letters	Environmental Science & Technology Letters
FEM	Federal Equivalent Method
FID	Flame Ionization Detectors
FRMs	Federal Reference Methods
FTIR	Fourier-Transform Infrared Spectroscopy
GC	Gas Chromatography
JPL	Jet Propulsion Laboratory
LOD	Limit of Detection
M	Meter
MEMS	Microelectro-Mechanical Systems
MESA	Embedded Systems and Automation

MOS	Metal Oxide Semiconductor Detectors
NAAQS	National Ambient Air Quality Standards
NASA	National Aeronautics and Space Administration
NDIR	Non-Dispersive Infrared
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NOx	Nitrogen Oxides
O_3	Ozone
OA-ICOS	Off-Axis Integrated Cavity Output Spectroscopy
OF-CEAS	Optical Feedback Cavity Enhanced Absorption Spectroscopy
OPLS	Open Path Laser Spectrometer
ORS	Optical Remote Sensing
PARC	Palo Alto Research Center
PID	Photoionization Detectors
PM	Particulate Matter
ppb	Parts Per Billion
ppm	Parts Per Million
PTR-TOFMS	Proton Transfer Reaction Time of Flight Mass Spectrometry
SCAQMD	South Coast Air Quality Management District
SO_2	Sulfur Dioxide
SOF	Solar Occultation Flux
TDLAS	Tuneable Diode Laser Absorption Spectroscopy
U.S.	United States
VOCs	Volatile Organic Compounds
XRF	X-ray fluorescence spectrometer

1. INTRODUCTION

1.1 Objectives of this Report

This report is intended to provide an introduction to the landscape of air monitoring technologies that can be utilized near upstream oil and gas activities for monitoring targeted compounds on fencelines, detecting leaks, or for deployment within neighboring communities. Additionally, this report provides more in-depth reviews of emerging and promising low and mid-range cost monitoring technologies that may be used in the future for the purpose of minimizing site emissions, loss of product, and for the protection of the climate and health of communities.

Reviews contained herein provide brief descriptions of the mechanism of sensing, highlight important parameters to consider when deploying monitors in this context, and present advantages and disadvantages of each technology. The report discusses the commercial availability of monitoring technology and gives recommendations on the best uses and applications of each technology reviewed in-depth. Recommendations provided in this report are based on the information of today and should be considered time-sensitive due to the ongoing changes to the landscape of monitoring technologies.

1.2 Abbreviated summary of findings

- This report provides an overview of different monitoring categories and different price points for monitors for three categories of pollutants: methane, BTEX and NMOCs that can provide a range of monitoring options for upstream oil and gas operations.
- Specifications of 18 different monitoring technologies/applications are summarized and 9 technologies are reviewed in detail, providing information on important parameters to consider during sensor selection as well as advantages and disadvantages associated with each technology.
- While sophisticated optical remote sensing technologies are well established and can provide high resolution data with low detection limits, lower cost technologies are emerging with more powerful capabilities than before, at a fraction of the cost of typical optical remote sensing technologies.
- There are a wide variety of monitoring options on the market, and the field of inexpensive sensors, in particular, is rapidly evolving in terms of sensor availability, price points and information on sensor quality. The availability of inexpensive wireless communication and networking capabilities enhance the available choices among monitoring systems.
- A wide variety of sensing technologies are available and ready for deployment depending on the compound of interest and desired detection limit. The goals of any monitoring plan must be clearly defined and considered when selecting the most appropriate sensor technology.
- When evaluating monitoring technology, it is critical to match the monitoring and sensor qualities to the desired usage.
- Information in this report is presented in table format with easy to analyze categories and break points. This report is intended to aid in the selection of the most appropriate sensor technology for a defined monitoring plan or goal.

2. HISTORICAL APPROACHES TO AMBIENT AIR MONITORING NEAR UPSTREAM OIL AND GAS OPERATIONS

2.1 Pollutants of Interest

Since 2005, there has been a rapid increase in the number of upstream oil and natural gas wells, and activity to increase and / or maintain productivity at existing wells. There are more than 900,000 active oil and gas wells in the United States, and more than 130,000 have been drilled since 2010.[1] There was a significant decrease in the number of active wells in 2015 due to economic conditions with a subsequent recovery in 2017.[2] President Donald Trump has indicated that he plans to facilitate further increases in drilling by lifting regulations and allowing drilling on federal land. [3]

Much of the most recent development can be attributed to the shale oil and gas boom and emerging methods and technologies for extracting product, which has intensified drilling and production operations in many places and introduced it in others. Operations often include, alongside well pads, the processing and transportation facilities needed to move the gas and oil to market. Despite the recent dip in operations, industry, state and federal state government projections continue to plan for increased development in the coming years. [4,5,6]

Methane is the second most prevalent greenhouse gas emitted (by carbon dioxide equivalence) in the United States. [7] It is a potent greenhouse gas and the primary component of natural gas. One of the largest sources of methane emissions in the United States (U.S.) comes from the oil and gas industry, with the top 5% of emitters accounting for about 50% of emissions.[8, 9] There has been an exponential growth of research into the environmental impacts of the unconventional oil and gas industry in line with the expansion of extraction operations, mostly in the U.S. but also in Canada, South America and China. For example, of the 180 studies published on this topic between 2010 and 2016 in Environmental Science & Technology (ES&T) and

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[1] Washington Post, 2017. *The United States of oil and gas.* Available at: https://www.washingtonpost.com/graphics/national/united-states-of-oil/ February 2017

[2] Earthworks Oil & Gas Accountability Project, 2016. *Community Air Monitoring of Oil and Gas Pollution: A Survey of Issues and Technologies.* March 2016

[3] Washington Post, 2017. *The United States of oil and gas.* Available at: https://www.washingtonpost.com/graphics/national/united-states-of-oil/ February 2017

[4] Earthworks Oil & Gas Accountability Project, 2016. *Community Air Monitoring of Oil and Gas Pollution: A Survey of Issues and Technologies.* March 2016

[5] US Energy Information Administration, July 2017, U.*S. crude oil production forecast expected to reach record high in 2018,* Available at: https://www.eia.gov/todayinenergy/detail.php?id=32192

[6] U.S. Energy Information Administration, 2017. U.S. crude oil production expected to increase through end of 2017, setting up record 2018. Available at: https://www.eia.gov/todayinenergy/detail.php?id=33332

[7] U.S. Energy Information Administration, 2011. Emissions of Greenhouse Gases in the U.S. Available at: https://www.eia.gov/environment/emissions/ghg_report/ghg_methane.php

[8] Environmental Defense Fund, 2016. New EPA Stats Confirm: Oil & Gas Methane Emissions Far Exceed Prior Estimates. Available at: https://www.edf.org/media/new-epa-stats-confirm-oil-gas-methane-emissions-far-exceed-prior-estimates

[9] Brandt, Adam., et al. "Methane Leaks from Natural Gas Systems Follow Extreme Distributions" *Environ. Sci. Technol., 2016, 50 (22), pp 12512–12520*

Environmental Science & Technology Letters (ES&T Letters), 75% were published after 2013.[10]

Although our understanding of emission sources from the oil and gas industry has greatly increased, literature studies indicate that basin- and site-level measurements result in emissions that are consistently higher than those reported in inventories, which they hypothesize is caused, in part, by emissions from abnormal conditions that are not accounted for in inventories.[11] Leaks and releases occur throughout the oil and natural gas supply chain, but it can be very difficult to detect and quantify the actual emissions. Emissions from oil and gas operations can also constitute a safety hazard because of the flammability of gases such as methane, or the toxicity of certain gases like hydrogen sulfide. For example, a recent explosion related to activities (a cut pipeline that was supposed to be isolated from active production wells) surrounding natural gas and oil operations in Colorado resulted in two deaths in a nearby house,[12] though this is not the only such documented occurrence of impacts from oil and gas operations.

Air emission constituents from oil and gas operations have been generally understood for some time. Table 1 shows typical sources of airborne emissions from oil and gas production (upstream) activities which are broken down into four source categories.[13] Yet, studies to allow a complete understanding of the range and magnitude of emissions from drilling, well completion, and other activities are ongoing.[14]

Table 1: Source Categories of Airborne Emissions from Upstream Activities

Source Category	Type of emissions	Example sources of emissions
Combustion Sources	Nitrogen oxides (NOx) and carbon monoxide resulting from the burning of hydrocarbon (fossil) fuels. Air toxics, particulate matter (PM), uncombusted volatile organic compounds, and methane are also emitted.	Engines, compressors, heaters, flares, incinerators, and turbines.
Vented Sources	Volatile organic compounds (VOCs), air toxics, and methane resulting from direct	Tanks; well testing, completions, and workovers; pneumatic devices, dehydration

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[10] Vengosh, Avner., et al. “Environmental and Human Impacts of Unconventional Energy Development” *Environ. Sci. Technol., 2017, 51 (18), pp 10271–10273*

[11] Zavala-Araiza, Daniel., et al. “Super-emitters in natural gas infrastructure are caused by abnormal process conditions” *Nature Communications 8, Article number: 14012 (2017) doi:10.1038/ncomms14012*

[12] Denver Post, 2017. *Deadly Firestone explosion caused by odorless gas leaking from cut gas flow pipeline.* Available at: http://www.denverpost.com/2017/05/02/firestone-explosion-cause-cut-gas-line/

[13] United States Environmental Protection Authority, 2013. *EPA Needs to Improve Air Emissions Data for the Oil and Natural Gas Production Sector – Report No 13-P-0161* February 2013

[14] Macey, Gregg P., et al. "Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study." *Environmental Health* 13.1 (2014): 82.

Table 1: Source Categories of Airborne Emissions from Upstream Activities

Source Category	Type of emissions	Example sources of emissions
	releases to the atmosphere.	processes, gas sweetening processes, chemical injection pumps and compressors.
Tank Flashing	VOCs, air toxics, and methane	Storage tanks and Flash Tanks
Fugitive Sources	VOCs, air toxics, and methane resulting from evaporative sources and leaks and operational upsets.	Equipment leaks through valves, connectors, flanges, compressor seals, seals, and related equipment and evaporative sources including wastewater treatment, pits, and impoundments.

This report focuses on monitoring for VOCs – though the types of VOCs emitted from upstream oil and gas production activities vary widely based on the source. For the purposes of this report, we will focus on monitoring three separate VOC categories (benzene, methane, and non-methane organic compounds), as surrogates for other VOCs that fall within a similar class.

In discussing monitoring technology within this report, the following initial observations and assumptions will be made:

- Benzene will be used as a surrogate for detecting benzene, toluene, ethylene, xylene (BTEX) compounds. BTEX is a class of pollutants with the potential for causing health impacts;
- Methane will be used as a proxy detecting the climate change impact of oil and gas operations and in detection of co-emitted pollutants, though the make-up and magnitude of co-emitted pollutants may not be easily determined. Methane is the most commonly emitted constituent of oil and gas operations; and
- Non-methane organic compounds is a category meant to encompass non-methane organic compounds (NMOC) such as heavier alkanes that are commonly found in upstream activities. This category includes BTEX compounds which are typically a small fraction of total NMOCs.

2.2 Regulatory Framework

Historically, local, state and federal environmental and regulatory agencies have not regularly undertaken air quality monitoring or imposed monitoring requirements directly around well sites and other upstream facilities. One reason for this may be related to the fact that prior to the early 2000’s, the upstream oil and gas sector was considered by some jurisdictions to be an insignificant contributor to VOC emissions.[15] For example in Colorado, until 2003, condensate storage tanks at oil and gas production facilities were exempt from reporting and permitting requirements.[16]

State and federal environmental and regulatory monitors are mainly located in populated areas to track ground-level air quality impacts on people from traffic, major stationary sources, and other ongoing sources across broader regions. Even in urban areas, where wells may be located in close proximity to people, monitoring of well sites and other upstream facilities has tended to be done as required due to an event or as required by individual authorities as part of reporting or demonstrating compliance. In either case, rural or urban, traditional regional monitoring approaches are generally not intended to measure or detect at a site-level the contribution of local source emissions to surrounding areas.

As part of the new federal policy on oil and gas, the Trump administration has tried to delay and/or undo several Obama-era federal regulations and policies designed to reduce methane leaks, or collect data from existing and new oil and gas facilities.[17] At the same time, states like Colorado, Utah and Ohio have continued to act to cut emissions from oil and gas activities. Similarly, California adopted new standards to reduce greenhouse gas emissions from the upstream oil and gas sector with the adoption of a new methane rule in early 2017. The California regulation requires quarterly monitoring of methane emissions from oil and gas wells, natural gas processing and storage facilities, compressor stations and other equipment used in the processing and delivery of oil and natural gas.[18] Some have described these California standards as the most comprehensive of their kind in the country.

In addition to regulations designed to directly reduce oil and gas emissions through requirements to inspect sites and fix leaks, there appears to be an increased emphasis on monitoring air quality, with technologies becoming more sophisticated and lower in cost. Monitoring not only creates several drivers for overall lower emissions, it provides an extra level of compliance assurance. Continuous monitoring may not prevent leaks, but it may act as an early warning to the presence of an emissions event (depending on the detection limit of the monitor being used, among other things) and can alert operators so they can fix equipment quickly and reduce the chance of offsite impacts. However, it is important that the technologies be suited to the desired use and that proper communication be disseminated regarding the interpretation of data recorded by a monitor.

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[15] Kaufman, Garry, "SLIDES: Regulating Oil and Gas Emissions in the Denver Julesberg Basin" (2014).Water and Air Quality Issues in Oil and Gas Development: The Evolving Framework of Regulation and Management (Martz Summer Conference, June 5-6).

[16] Hart LLP, 2015. *Air Quality Regulation of the Oil and Gas Production Sector in Colorado and Beyond* Garry Kaufman Holland & Hart LLP Presentation

[17] The Washington Post, 2017. Federal judge reinstates Obama-era rule on methane emissions. Available at: https://www.washingtonpost.com/business/interior-moves-to-delay-obama-era-rule-on-methane-emissions/2017/10/04/7b08488c-a965-11e7-9a98-07140d2eed02_story.html?utm_term=.838a310313ca

[18] California Air Resources Board, 2017. CARB approves rule for monitoring and repairing methane leaks from oil and gas facilities. Available at: https://www.arb.ca.gov/newsrel/newsrelease.php?id=907

Presently, several research projects are planned by state agencies related to air quality monitoring including some projects at or near oil and gas production sites.[19,20] Also, community monitoring near industrial operations is increasingly required in California. California is developing an air study in communities located near oil and gas production operations called the Study of Neighborhood Air near Petroleum Sources (SNAPS). This study will include limited-term, intensive air quality monitoring with a particular focus on oil and gas production facilities.[21] Additionally, California Assembly Bill 617 (AB 617) was approved by the Governor in July 2017, and is intended to bring additional ambient air monitoring to high-priority communities throughout the state. And California Assembly Bill 1647 (AB 1647) was approved in early October 2017, requiring refinery-related community air monitoring systems for every refinery in the state. As evidenced by its language, this bill was meant to supplement, and at times, further local air district efforts. For example, Bay Area Air Quality Management District (BAAQMD) Rule 12-15 requires Air Monitoring Plans and the operation of fenceline and community air monitoring systems around refineries, while South Coast Air Quality Management District (SCAQMD) has proposed Rule 1180 which would accomplish similar goals. Air monitoring plans have also been required in the event of large releases or failure of compliance, on an ad-hoc basis, described below.

2.3 Episodic/Ad-hoc Monitoring Plans

There are several incidences of monitoring being conducted for the purpose of following up after an emissions event or in the event of a lawsuit. While the events below do not represent an exhaustive list, they provide an example of the types of monitoring conducted related to these circumstances.

In 2003, a highly publicized lawsuit having to do with a well-field operating near the Beverly Hills High School, in Beverly Hills, California, resulted in one of the defendants, (Venoco Inc.) undertaking an air quality monitoring campaign including installation of a continuous monitor for methane and other hydrocarbons.[22] Annual monitoring for VOC's was also conducted. Samples were collected over an 8-hour period at 11 locations and then analyzed according to USEPA standards. [23]

In 2012, in response to complaints by community members, an air monitoring study was conducted at the Inglewood oil field in Los Angeles,[24] and monitoring required as part of any new drilling operation at the site (though no monitoring has been performed due to

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[19] California Energy Commission, October 2017, GFO-17-502, Grant Funding Opportunity, Enhancing Safety, Environmental Performance, and Resilience of California's Natural Gas System, http://www.energy.ca.gov/contracts/pier.html#GFO-17-502

[20] California Air Resources Board, May 2017, Air Monitoring Near Oil and Gas Operations, https://www.arb.ca.gov/cc/ab32publichealth/meetings/052317/lozo.pdf

[21] California Air Resources Board *"Study of Neighborhood Air near Petroleum Sources (SNAPS)"*

https://www.arb.ca.gov/cc/oil-gas/snaps/snaps.htm?utm_medium=email&utm_source=govdelivery

[22] AQMD *"Venoco to Monitor Air Quality at Beverly Hills High School"*. *https://web.archive.org/web/20120206060308/http://www.aqmd.gov/news1/2003/venocosettlementpr.html*

[23] CDM, 2005. *Summary of Findings Ambient Air Investigation Beverley Hills High School 241 South Moreno Drive Beverley Hills, California November 21, 2005.* – Prepared by CDM

[24] Sonoma Technology, Inc., 2015. Baldwin Hills Air Quality Study. Available at: http://planning.lacounty.gov/assets/upl/project/bh_air-quality-study.pdf

the lack of drilling there).[25,26] The study aimed to quantify air toxics emissions from the oil field operations and assess health risk due to exposure to those air toxics. The study also attempted to determine and distinguish air toxics emissions from other nearby major sources surrounding the oil field. Four types of monitors were utilized during this one-year study: (1) Aethalometers to measure black carbon (as a proxy for diesel particulate matter (DPM)); (2) X-ray fluorescence spectrometer (XRF) for metals; (3) Proton Transfer Reaction Time of Flight Mass Spectrometry (PTR-TOFMS) for VOCs; and (4) meteorological sensors to help assess the wind patterns, temperature, and humidity that might influence pollutant concentrations. All air monitoring equipment used in this study would be considered high-cost, research or regulatory-grade equipment. Researchers were able to estimate the oil field contributions to cancer risk on a per-pollutant basis. Excess cancer risk was primarily attributed to DPM, and oil field contributions to DPM concentrations were a small fraction compared to other major sources in the area.

AllenCo Energy Inc. has a drilling site located in the City of Los Angeles surrounded by residences including low income housing units, a high school, and a college. In response to community members' and neighbors' complaints, in October 2013, the SCAQMD initiated monitoring at sites around the AllenCo facility. Regularly scheduled VOC samples were collected on the roof of an apartment building across the street from AllenCo, and there was a remote-controlled sampler capable of collecting a VOC grab sample should an odor complaint be called into the SCAQMD odor complaint line. After EPA officials investigating the odors fell ill while visiting the site,[27] the company suspended operations. Operations were suspended in November 2013 and SCAQMD thereafter moved the continuous Non-Methane Hydrocarbon Measurements to support the Aliso Canyon monitoring efforts, but continues to collect VOC samples while AllenCo is shut down. When AllenCo resumes operations, SCAQMD intends on resuming continuous monitoring briefly to assess air quality.[28] Additionally, a court order issued in 2016 details specific regulations and further approvals that AllenCo must follow and obtain prior to re-opening, in particular, an innovative, state-of-the-art health and safety monitoring systems with emergency shutdown provisions.[29]

Similarly, the Jefferson drill site in South Los Angeles run by Sentinel Peak Resources was required to conduct continuous air monitoring for methane and hydrogen sulfide in

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[25] Baldwin Hills Community Standards District, Los Angeles County Code, Title 22, Division 1, Chapter 22, Part 22, 22.44.142

[26] Sonoma Technology, Inc., 2015. Baldwin Hills Air Quality Study. Available at: http://planning.lacounty.gov/assets/upl/project/bh_air-quality-study.pdf

[27] L.A. Times, 2013. EPA officers sickened by fumes at South L.A. oil field. Available at: http://www.latimes.com/local/la-me-1109-fumes-20131109-story.html

[28] SCAQMD, 2017. Air Quality Monitoring Network Plan. Available at: https://www.epa.gov/sites/production/files/2017-10/documents/caplan2017-southcoast.pdf

[29] Los Angeles City Attorney, Mike Feuer, 2016. City Attorney Mike Feuer Obtains Court Order with Key Guarantees Before South L.A. Oil Facility is Ever Allowed to Re-Open. Available at: https://www.lacityattorney.org/single-post/2016/06/09/City-Attorney-Mike-Feuer-Obtains-Court-Order-with-Key-Guarantees-Before-South-LA-Oil-Facility-is-Ever-Allowed-to-ReOpen?__hsfp=1773666937&__hssc=259341397.1.1473465600127&__hstc=259341397.73866753dac91b459be33ada5c72a03b.1473465600124.1473465600126.1473465600127.2

October, 2017 and inform the public of the results online in real time.[30] Sentinel Peak Resources would also have to alert the Los Angeles Fire Department if hydrogen sulfide or methane were detected.

Another high profile event in 2015 occurred at the Aliso Canyon natural gas underground storage facility where a natural gas leak emitted 109,000 metric tons of methane into the atmosphere from late October 2015 to mid-February 2016. Analysis of the event concludes that the Aliso Canyon facility likely resulted in the largest man-made release of methane in California's history.[31] This event triggered the installation and operation of 9 continuous monitoring stations by the California Air Resources Board (CARB) and, at the same time as continuous fixed site monitoring deployment, SCAQMD initiated methane surveys using a LI-COR-equipped mobile platform in the nearby communities. SoCalGas also commenced air monitoring on October 30, 2015 and collected over 3,700 grab samples, and over 2,200 time integrated samples for laboratory analysis of VOC's. In addition, SCAQMD collected 24-hr integrated canister samples from four locations for laboratory analysis. SCAQMD also conducted daily scheduled inspections and mobile platform monitoring on–site at the Facility. Examples of the technologies used at or near the Aliso Canyon site include:[32]

Continuous methods

- Flame Ionization Detector – Methane and Non Methane Hydrocarbon Detectors
- Cavity Ring Down Spectroscopy – Methane and Hydrogen Sulfide
- Chemiluminescence - Total Sulfur
- Gas Chromatography Flame Ionization Detector – Benzene

Samples

When a continuous monitor measured concentrations of a pollutant above a specified concentration threshold, it automatically triggers an instantaneous grab sample to be collected and analysed according to the following methods:

- VOC's – Canister using Gas chromatography Flame Ionization Detector and Mass Spectrometry
- Methane, Carbon monoxide (CO), Carbon dioxide (CO_2) and Ethane – Total Carbon Analyzer
- Sulfur species – Chemiluminescence

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[30] L.A. Times, 2017. City orders tougher rules for oil drilling site near South L.A. homes. Available at: http://www.latimes.com/local/lanow/la-me-ln-jefferson-drilling-20171013-story.html

[31] California Air Resources Board, 2016. *Aliso Canyon leak emitted 109,000 metric tons of methane.* News Release, available at: https://www.arb.ca.gov/newsrel/newsrelease.php?id=868

[32] South Coast Air Quality Management District, 2016. *Aliso Canyon Facility Monitoring Network Plan.* August 2016

Community monitoring[33]

- Open-path Ultraviolet Monitor – Benzene, toluene, and xylene
- Tunable Diode Laser Absorption Spectroscopy – Methane (ongoing[34])

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[33] Los Angeles Daily News, 2016. "Private company offers real-time community air monitoring in Porter Ranch." Available at: http://www.dailynews.com/2016/02/01/private-company-offers-real-time-community-air-monitoring-in-porter-ranch/

[34] Real-time community monitoring continues in the Porter Ranch community. A website with real-time methane concentrations is available to the public at: http://fenceline.org/porter/data.php

3. PARADIGM SHIFT TO UTILIZE LOWER COST SENSORS

The monitoring technologies being used in the various monitoring rules, regulations, and episodic events described above generally involve sophisticated equipment. For example, historically, approaches for monitoring air pollution use expensive, complex, stationary equipment that have rigorous standards of data quality assurance. Additionally, the EPA and U.S. states uses a national air quality network to evaluate compliance with the National Ambient Air Quality Standards (NAAQS). Monitors in this network use Federal Reference Methods (FRMs) to ensure air quality data collected at different sites are gathered in a similar manner and are of known accuracy. To foster innovation and advance new technologies, EPA also reviews, tests, and approves other methods, called Federal Equivalent Methods (FEMs), which are based on different sampling and/or analyzing technologies than FRMs, but are required to provide similar decision-making quality when making NAAQS attainment determinations.

This paradigm of ambient air monitoring using the most sophisticated equipment available is shifting due to increased availability and awareness of low-cost air pollution sensors that are capable of providing highly time-resolved data in real-time (sampling as often as once every 1-5 seconds). For air monitoring rules and regulations that aim to capture release events and protect people and the environment, there are obvious advantages to using low-cost sensor networks which can provide greater spatial resolution as compared to a small number of sophisticated, stationary monitoring technologies that presume that air quality in a single location is characteristic of a much larger area.

The paradigm shift of air monitoring is being catalyzed by increasing availability and decreasing cost of sensors, due in part to advances in (1) microfabrication techniques; (2) microelectro-mechanical systems (MEMS); (3) energy efficient radios and sensor circuits that have extremely low power consumption; and (4) advanced cloud-computing power suitable for handling extremely large datasets and user-friendly data visualization at lower costs.[35] Since 2005, the number of peer-reviewed publications studying low cost air quality sensors has increased dramatically. Figure 1 displays the number of search results using the search term “low cost” “air quality” “sensors” in Google Scholar.

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[35] Snyder, Emily G., et al. "The changing paradigm of air pollution monitoring." (2013): 11369-11377.

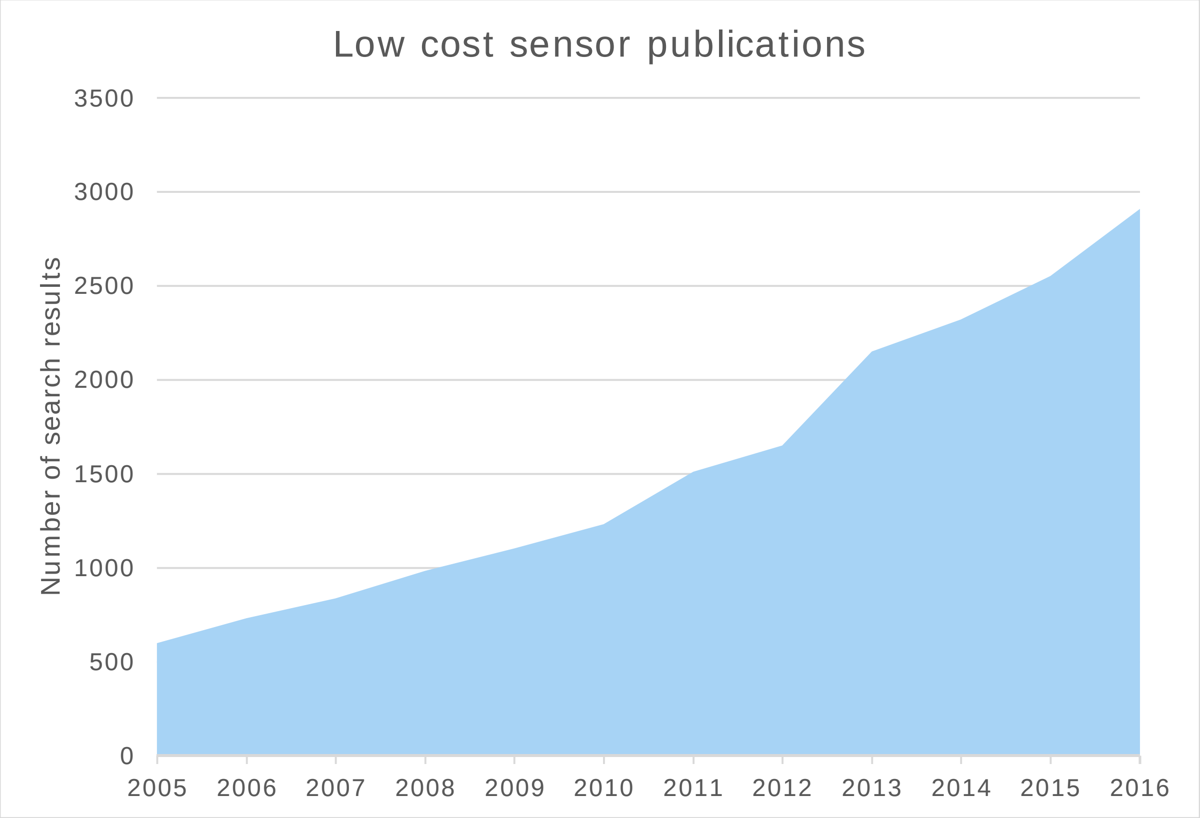

Figure 1: Number of low cost air quality sensor publications over time

Despite the great potential of this technology, the overwhelming majority of research points to two critical issues associated with this new trend:

1. How accurate, stable and reliable are the new sensors?
2. What new data analysis techniques are needed to properly analyze the data?

While these issues can limit the use of these sensors as compliance sensors, they can still be used to set additional sampling or a review of potential leak sites into motion. The availability of low cost sensors depends on the compound of interest and the desired detection limit. Low cost sensors are much less available for individual BTEX compounds than for methane, for example.

Low cost air quality sensors are now widely available directly to consumers, even before sensor performance has been adequately characterized or certification protocols have been developed. They vary widely in quality, measurement reliability, and ease of use. Some are intended for personal use, and others are intended to democratize data availability, where each sensor is incorporated into visualizations and maps including all sensors of the same type.

3.1 Current State of Sensor Science and Performance Evaluations

There are a number of sensors and devices that hit the market before there was a clear understanding of their reliability, applications, or accuracy. There is a need to characterize the actual performance of air monitoring sensors as well as to educate the public about the advantages of such devices and their potential limitations.

In 2014, the SCAQMD created the Air Quality Sensor Performance Evaluation Center (AQ-SPEC) program as an objective way to evaluate the performance of a range of new devices. Until the advent of the AQ-SPEC program, there was no opportunity to uniformly evaluate precision and overall quality outside of the standard scientific literature. AQ-SPEC tests air quality sensors that are commercially available and measure common criteria pollutants such as CO, Ozone (O_3), nitrogen dioxide (NO_2), PM and sulfur dioxide (SO_2). Although VOCs, hydrogen sulfide, and methane are listed as qualifying pollutants for sensor evaluation selection, no sensors have been tested for those pollutants at this time. Most of the focus to date has been on PM sensors. Until now, the AQ-SPEC program has focused on “out-of-the-box” sensor performance evaluations to provide clarity and guidance on the current sensor market. Based on a presentation at an AQ-SPEC conference at SCAQMD in September 2017, the program is considering a sensor certification program to help standardize data quality and reliability of low cost sensors.[36] No formal information is available on this effort at this time.

In order to understand the reliability of commercially available new monitors, in 2014, EPA established the Community Air Sensor Network (CAIRSENSE) project, which involves testing the feasibility of a wireless sensor network application as well as collocation of multiple identical sensor devices with reference monitors over an extended period of time. The CAIRSENSE project is a multi-year effort, involving field testing emerging air quality sensors in multiple locations across the U.S.

There are other programs that are also testing newer monitoring techniques, such as the Environmental Defense Fund’s (EDF) Methane Detector Challenge. This program is a collaboration between oil and gas companies, U.S. based technology developers, and other experts, and is intended to accelerate the development and deployment of methane monitors to reduce leakage, pollution and product loss. The focus of this program was on near-market-ready technologies that are inexpensive and rugged monitors capable of detecting large leaks. This offers another platform for testing and verifying new technologies.

Similar to the EDF Methane Detectors Challenge, EDF and Stanford University’s Natural Gas Initiative have launched the Mobile Monitoring Challenge, a competition calling for technology developers to participate in a blind study showcasing the capabilities of their mobile technology to quickly find and assess leaks while in motion and while off-site. This challenge is focused on mobile solutions for methane leak detection – solutions that are rapid, low-cost, and able to survey large areas for detecting and quantifying leaks.

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[36] AQ-SPEC Presentation: Evaluation of “Low-cost” Sensors for Measuring Gaseous and Particle Air Pollutants: Results from Three Years of Field and Laboratory Testing, 2017. Available at: http://www.aqmd.gov/docs/default-source/aq-spec/2017-conference-presentations/3-scaqmd-polidori_scaqmd-sensorconf17.pdf?sfvrsn=4

There are several publications evaluating the use of mobile sensors to find natural gas leaks.[37,38]

Yet another program for testing and validating sensors is sponsored by the Department of Energy (DoE). The Advanced Research Program Administration-Energy (ARPA-E) is intended to initiate deployment and evaluation of novel means of methane detection to reduce the overall emissions from natural gas production sites, particularly, emerging technologies for locating and quantifying emissions. The ARPA-E MONITOR[39] program (Methane Observation Networks with Innovative Technology to Obtain Reductions) includes evaluation of a wide range of sensors, including advanced infra-red detectors and imaging, lightweight spectrometers, optical fibers, and tunable laser diodes.

3.2 Emerging Capabilities of Networked or Crowdsourced Sensors Utilizing Data Analytics

The next frontier involves using data analytics to make sense of variable data. Data can tell stories, particularly if you have a great deal of it. Data analytics assist with analyzing a great deal of data, and use intelligent ways to find patterns in the data. The patterns identified can be used to start to solve problems, but to find and assess complex patterns, data analytics tools must be used. In pursuit of new data analysis tools to evaluate large data streams coming from sensors, there is a robust amount of activity at the university level and within the private sector. These efforts in the aggregate, can develop and refine information into usable chunks that previously had too much scatter to be of real use. For example, data analytics and calibration methods have allowed researchers to capture diurnal changes in methane concentrations (varying in 10’s of ppb) using low cost metal oxide semiconductor sensors.[40] There is also active research in how denser data can be used in a feedback loop to improve air quality modeling.

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[37] Phillips, NG, et al. Mapping urban pipeline leaks: Methane leaks across Boston. Environmental Pollution. V. 173, February 2013, Pages 1-4.

[38] Eapi, G.R., Sabnis, M.S. and Sattler, M.L., 2014. Mobile measurement of methane and hydrogen sulfide at natural gas production site fence lines in the Texas Barnett Shale. Journal of the Air & Waste Management Association, 64(8), pp.927-944.

[39] https://arpa-e.energy.gov/?q=arpa-e-programs/monitor

[40] Eugster, W. and Kling, G.W., 2012. Performance of a low-cost methane sensor for ambient concentration measurements in preliminary studies. Atmospheric Measurement Techniques, 5(8), p.1925.

4. CHALLENGES

Despite the recent advances and rapid commercialization of low cost sensors, many technical and practical challenges remain in this emerging area. For example, data quality is the key hurdle left to tackle. Additionally, commercially available sensors are lacking for a variety of pollutants, specifically for direct-reading of PM mass as well as specific hazardous air pollutants. Many low cost sensors also have short expected lifetimes, which may present challenges for large-scale deployment of sensors in remote areas. These challenges are consistently being tackled by technology developers, academic and governmental programs.

The discussion in Section 3.1 describes the various programs and research studies that have performed evaluations of emerging low cost air quality sensors. Evaluations show across-the-board performance results, from R-squared values of 0.0 to 0.99 and sensors that match regulatory monitors quite well to others that severely over or under-estimate concentrations.[41]

As evidenced by the results of sensor studies and evaluations, many sensors on the market would not meet US Environmental Protection Agency (EPA) Federal Equivalent Method (FEM) criteria for monitoring equivalency certification. However, an important question to ask is whether these sensors *need* to comply with the restrictive FEM criteria for uses other than determining compliance with air quality standards. For example, many applications of low cost sensors may not need the high level of data quality required by an FEM. Conversely though, there remains a need to develop standards or certifications that set the bar for data quality and reliability for emerging low cost sensors for each particular use mode.

Great advances have also been made in the area of mid-range cost VOC monitoring technologies, particularly optical spectroscopy techniques. Although costs have decreased along with increased detecting precision, many emerging technologies have a limited rate of scalability, which remains a challenge for deploying a large number of monitors at upstream oil and gas sites in a short period of time. These types of technologies often use sophisticated components (such as high-reflectivity mirrors, multi-pass cells, and coherent lasers) and manufacturing techniques that may present challenges if there is a sudden demand for large-scale deployment. Additionally, more sophisticated technologies with higher power demand may be more difficult to power remotely. For wide-spread distribution of monitoring networks; and to ensure adequate data capture, analysis and visualization; it is likely that a diverse mix of monitoring technologies deployed on a site-by-site basis, with consideration for site specific conditions would be needed.

For technologies intended to detect leaks, sensors may be exposed to high concentrations of flammable gases. For safety, technologies deployed for monitoring near oil and gas operations (or within homes near operations, see footnote 15 above) will require Class 1/Division 1 capabilities, adding to the complexity and challenges of low-cost, large-scale deployment in the upstream oil and gas industry.

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[41] An R-squared value of 0.0 represents no correlation between monitor results and actual concentrations, while an R-squared value of 0.99 represents a near perfect correlation

5. OVERVIEW OF PRIMARY SENSING CATEGORIES

As a result of the historic monitoring work outlined above, and as a result of the emerging trend of low-cost high precision monitoring sensors reaching the market today, several sensor types are commercially available now for the detection of VOCs. Generally, the categories of sensor technologies presented in Table 2 are based on one of the six principles of operation listed below:

- Optical absorption spectroscopy
- Gas Chromatography
- Photoionization
- Electrochemical
- Semiconductor
- Thermal conductivity

Optical absorption spectroscopy: The optical absorption spectroscopy techniques measure the interaction of electromagnetic energy (i.e., different wavelengths of light) with the sampled air to determine the composition and the concentration of contaminants. There are different types of optical absorption spectroscopy techniques (i.e., Fourier-transform infrared spectroscopy (FTIR), tunable diode laser absorption spectroscopy (TDLAS), cavity ring-down spectroscopy (CRDS), and non-dispersive infrared (NDIR)) that are suitable for various air monitoring applications. For example, FTIR and TDLAS are suited to open-path air monitoring, CRDS provides enhanced detection sensitivity to target analytes, and NDIR offers a low-cost alternative to other optical absorption spectroscopy techniques.

For air quality monitoring, the light sources commonly used in optical absorption monitoring instruments range from infrared through ultraviolet, with different ranges of the light spectrum used for detecting multiple compounds simultaneously or to match the absorption wavelength of specific target analytes. Flammable gases and vapors from the VOCs group are subjected to characteristic absorption from the infrared range.

Optical absorption spectrometry is often applied in open-path air monitoring, where a concentrated beam of electromagnetic energy is emitted into the air along the open path to provide an average concentration over a line of sight, although the technology can also be used with extractive sampling to monitor at discrete location points. The EPA developed a handbook on optical remote sensing (ORS) technologies that serves as an excellent reference document explaining uses and limitations of data generated by optical remote measurement approaches.[42] ORS technologies are commonly used in limited quantities, typically one or two, to be used along a fenceline, in a short-term campaign, for a research study, or by an enforcement agency like the SCAQMD or CARB. This is in part due to the high cost associated with these types of technologies and in part due to the expertise needed to operate these technologies.

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[42] EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux, 2011. Available at: https://www3.epa.gov/ttnemc01/guidlnd/gd-052.pdf

Open-path technologies are the most common monitoring approach for remote fenceline systems at this time. They provide the benefit of quantifying concentrations across a long path length, sometimes as far as 1 kilometer. Although a few of the technologies reviewed here are open-path technologies, many are not. Techniques do exist to artificially create a path in order to sample at many locations with just one discrete sensor or monitor. Sensing devices that offer real-time or near real time analysis capabilities can be used as multi-port sensors. A multiport sensor is one where numerous (up to 10) samples can be manifolded into the sample port and the sensor can offer rapid evaluation of concentrations at a series of locations, say, along a fenceline. In this manner, a single unit that measures concentrations at a location can be effectively used as an area or fenceline monitoring system, but with the low detection limits associated with a point sampler. With this approach, spatial variation can be resolved with just one monitor and there is the flexibility to orient ports in other configurations than a straight line, around a well head, for example. A multiport system is only useful when the sensors are sufficiently expensive, such that manifolding a series of ports is less expensive than buying additional sensors. Care must be taken to flush previous samples from the manifold before analyzing the next port in the manifold.

Although different than other open path systems, gas imaging technology also falls within the category of optical detection equipment. Gas imaging cameras such as that supplied by FLIR Systems (using optical imaging) and Rebellion Photonics (using hyperspectral imaging) use camera optics and internally mounted heat detection devices to convert externally measured infrared energy (heat) signatures into electric signals that can be displayed on a video screen. Traditionally used in hand held applications, but now available as fixed mounted systems, these devices produce thermal images that can be viewed by operators or in automatic alarm systems on imaging software, and can be paired with emissions quantification algorithms to calculate pollutant flux rates and volumes.

Gas Chromatography: Gas Chromatography (GC) is commonly applied in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. GCs are most commonly found in a research laboratory setting, and they are often the size of a small refrigerator. Handheld GCs, which are fairly new to the market, combine micro columns with a variety of conventional detectors to reduce the size and weight of bench top instruments to offer a GC for portable use. These are not, however, intended for use as continuous monitors (at this time), rather, as a handheld surveying tool. Handheld GC units also can be deployed at a stationary field location and set up to analyze samples upon the triggering of an air sampling collection event, though this configuration would require an additional sensor and collection device to initiate air sampling.

Photoionization: Photoionization sensors, or Photoionization Detectors (PID), use an ultraviolet light source to break down chemicals into positive and negative ions (i.e., ionization) to detect the charge of the ionized gas which provides a measure of contaminant concentration. PIDs are most frequently used device for measurement of summary concentrations of VOCs, though the mechanism of sensing is not chemical specific. Due to their ease of use and small size, PIDs are commonly used in personal air monitoring for worker protection, and by both companies and local enforcement agencies during episodic on-site leak detection efforts.

Electrochemical and Semiconductor: Electrochemical and semiconductor sensors are based on detection of a response to a chemical reaction with the target analyte to provide a measure of contaminant concentration. Electrochemical sensors rely on an electrochemical reaction with the target analyte present in the sampled air to produce an electrical signal proportional to the contaminant concentration. Semiconductor sensors rely on a chemical reaction with a metal oxide surface that alters its conductivity or resistivity to provide a measure of contaminant concentration. Both electrochemical and semiconductor sensors are lower in cost than previously described technology but they also have lower sensitivity, high detection limits, and can suffer from poor data quality due to interferences, temperature and relative humidity sensitivity, or drift, making the data from these sensors sometimes inaccurate or unreliable. Some of these limitations may be quelled with the use of numerous sensors and data analytics, while others such as detection limits are limited by the technology capability.

Thermal Conductivity: Thermal conductivity sensors such as the pellistor gas sensor are used for the detection of gases with high thermal conductivities greater than air like hydrogen and methane, while gases with conductivities less than air cannot be detected. These sensors have been in use for many years, primarily for health and safety monitoring to detect combustible environments.

MEMS are resulting in advancements in the manufacturing techniques allowing sensors to become increasingly more compact, light-weight and inexpensive. Advancements in MEMS will affect the performance and capabilities of numerous types of technologies, particularly small sensors such as pellistor, electrochemical, metal oxide semiconductor, and PID sensors.

Table 2 provides a high-level summary of the many monitoring technologies suitable for upstream oil and gas operations, ambient air monitoring and leak detection and Table 3 a key for the color-coding within Table 2. As previously mentioned, the more costly optical remote sensing technologies (both open path and extractive) are commonly used for fenceline monitoring and leak detection systems in a regulatory setting.

Table 2: High-level Summary of Sensor Technologies

Sensor Categories	Monitoring Technologies	Compound Classes	Sampling rate	Simultaneous Detection of Multiple Compounds?	General Limit of Detection	Remote capability	Cost Range	Degree of Market Penetration
Sample Collection	Active Sampling	Methane, NMOC, Benzene	Discrete, time-weighted average	Yes	Methane: < 1 ppm Benzene: < 10 ppb NMOC: < 50 ppb	Yes	Under $1,000 each	Widespread use
	Passive Sampling	Methane, NMOC, Benzene	Discrete, time-weighted average	Yes	Methane: < 1 ppm Benzene: < 10 ppb NMOC: < 50 ppb	Yes	Under $1,000 each	Widespread use
Open Path Optical/Laser Absorption Spectroscopy	Differential Optical Absorption Spectroscopy (UV-DOAS)	Benzene, NMOC (monocyclic aromatic hydrocarbons)	Continuous	Yes	Benzene: < 10 ppb NMOC (monocyclic aromatic hydrocarbons): < 50 ppb	Yes	$60,000-$200,000	Commercially available, limited availability
	Differential Absorption Lidar (DIAL)	Methane, Benzene, NMOC	Continuous	No	Methane: < 1 ppm Benzene: < 10 ppb NMOC: < 50 ppb	Mobile-capable but requires an attendant to move the instrument's location	$295,000 - $445,000	Commercially available, limited availability
	Fourier Transform Infrared Spectroscopy (FTIR)	Benzene, Methane, NMOC	Continuous	Yes	Methane: 15-60 ppb Benzene: 30-100 ppb NMOC: 1-100 ppb	Yes	$75,000 - $120,000	Commercially available
	Tunable Diode Laser (TDL) Spectroscopy	Methane, Benzene	Continuous	No	Methane: 0.5-1 ppm Benzene: 10-30 ppb	Yes	$15,000 - $65,000	Commercially Available
	Infrared Camera	Methane, Benzene, NMOC	Continuous	No	Qualitative detection only, add-on devices allow for emission rate quantification	Yes	$50,000 - $75,000	Commercially Available

Table 2: High-level Summary of Sensor Technologies

Sensor Categories	Monitoring Technologies	Compound Classes	Sampling rate	Simultaneous Detection of Multiple Compounds?	General Limit of Detection	Remote capability	Cost Range	Degree of Market Penetration
	Solar Occultation Flux	Methane, NMOC, Benzene	Continuous	Yes	0.5 kg/hr from 50 m downwind *or* 0.3 mg/m^2 across a plane[43]	Mobile-capable but requires an attendant to move the instrument's location	New unit is approximately $1,000,000, one month study is $200,000	None in US, only in Sweden
Extractive (non-open path) Optical/Laser Absorption Spectroscopy	FTIR	Methane, NMOC, Benzene	Continuous	Yes	Methane: 15-60 ppb Benzene: 30-100 ppb NMOC: 1-100 ppb	Yes	$20,000-$50,000	Commercially Available
	Non-Dispersive Infrared Sensor (NDIR)	Methane, NMOC	Continuous	No	Methane: 1-500 ppm NMOC: 500-1,000 ppm	Yes	$1,000-$10,000	Commercially available
	Tunable Diode Laser (TDL) Spectroscopy	Methane, Benzene	Continuous	No	Methane: 0.5-1 ppm Benzene: 10-30 ppb	Yes	$15,000 - $50,000	Commercially Available
	Cavity-Enhanced Spectroscopy	Methane, Benzene	Continuous or semi-continuous	Yes	Methane: 1-10 ppb Benzene: 0.1-30 ppb	Yes	$40,000 - $150,000	Commercially Available
Chromatography	Mass Spectrometry	Benzene, Methane, NMOC	Semi-continuous	Yes	Methane: < 1 ppm Benzene: < 10 ppb NMOC: < 50 ppb	Yes, if carrier gas included. Handheld units may have higher detection limits than	$20,000 - $60,000	Commercially Available

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[43] A study based on SF_6 measurements (a tracer gas) reports this detection limit in mg/m^2 across the measurement plane between the detector and the sun. See “EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux” at https://www3.epa.gov/ttnemc01/guidlnd/gd-052.pdf.

Table 2: High-level Summary of Sensor Technologies

Sensor Categories	Monitoring Technologies	Compound Classes	Sampling rate	Simultaneous Detection of Multiple Compounds?	General Limit of Detection	Remote capability	Cost Range	Degree of Market Penetration
						bench-top units.		
Ionization	Photoionization Detector (PID)	Benzene	Continuous	Yes	Benzene: 2-100 ppb NMOC: 0.05-200 ppm	Yes	$1,000-$10,000	Widespread use
	Flame Ionization Detector (FID)	Benzene, NMOC, Methane	Continuous	Yes	Methane: 1-10 ppm Benzene: 10-100 ppb NMOC: 50-500 ppb	Yes	$5,000-$50,000	Widespread use
Reactive	Pellistor	Methane	Continuous	No	Methane: 100-1,000 ppm	Yes	Under $1,000	Commercially Available
	Electrochemical	Methane, Total VOC	Continuous	No	Methane: ~100 ppm Total VOC: 100-1,000 ppb	Yes	Under $1,000	Commercially Available
	Metal Oxide Semiconductor	Methane, Total VOC	Continuous	No	Methane: 10-100 ppm Total VOC: 1-10 ppm	Yes	Under $1,000	Commercially Available

Table 3: Key for the Color-Coding in Table 2

Cost[5]	Under $1,000	$1,000-$50,000	Over $50,000
Commercially Available?	Available for purchase in larger quantities/from multiple vendors	Available but limited quantities/limited vendors/prototype	Not commercially available, only used in research
Precision/Resolution[1]			
BTEX	< 10 ppb	10-100 ppb	> 100 ppb
Methane	< 1 ppm	1-10 ppm	> 10 ppm
NMOC	< 50 ppb	50 - 500 ppb	> 500 ppb

Notes

1. Resolution bins are based on typical background concentrations of the pollutants listed.

2. "In 2002 the estimated statewide ambient concentration of benzene was approximately 0.6 ppb (~2 µg/m3) (CARB, 2004). Statewide the annual average benzene concentration has decreased from ~2.5 ppb in 1990 to ~0.5 ppb in 2007 (CARB, 2009)." From: https://oehha.ca.gov/media/downloads/crnr/benzenerelsjune2014.pdf

3. Methane background concentrations from: https://www.epa.gov/climate-indicators/climate-change-indicators-atmospheric-concentrations-greenhouse-gases

4. TVOC background concentrations were estimated from the following sources:
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1247565/
http://lib.ugent.be/fulltxt/RUG01/002/166/567/RUG01-002166567_2014_0001_AC.pdf
https://www.aiha.org/government-affairs/PositionStatements/VOC%20White%20Paper.pdf

5. Equipment costs represent the capital expense of the equipment, operating costs are not included. Depending on the manufacturer, some costs may be lower than the prices listed if large quantity orders are placed.

Costs presented in Table 2 are estimated capital costs of the monitoring technology. In many cases, it is possible that cost per unit could be lower than the range presented in the table if a large order is placed to reduce manufacturing costs. Additional costs are needed for operation and maintenance of monitoring technologies or networks. These costs, not presented in the table, can vary depending on the reliability and robustness of the technology, or the sophistication of operating the technology. Operation and maintenance costs may cover a large range, falling anywhere between a few thousand dollars and upwards of $500,000 annually, depending on the technology and application, and the scale of the network. Moving forward, advancements in technology and manufacturing practices help will drive down capital costs and advancements in data analytics, cloud computing, and data management strategies will help drive down operating costs.

6. DETAILED REVIEWS OF AVAILABLE AND EMERGING TECHNOLOGIES

This report aims to evaluate the capabilities of emerging technologies for use in upstream oil and gas ambient air monitoring and leak detection and identify methane, benzene, or NMOC within those emissions. Particularly, focus in this analysis is placed on mid and low range cost technologies that are seeing rapid advancements in capabilities and reduced costs, as well as technologies that provide additional advantages by leveraging the power of cloud-computing and data analytics to get a better picture of air pollution and dispersion. This review is not intended to evaluate technologies capable of estimating emission rates or flux, rather, it is intended to focus on technologies capable of detecting leaks, helping prevent leaks, and/or providing useful information to communities regarding levels of pollution and exposure.

6.1 Mobile Platforms

Emerging technologies continue to experience reductions in size and power consumption, making them more suitable for mobile and aerial deployments. When the term mobile is used here, it refers to a unit that can be motor vehicle mounted or used in a fixed wing an airplane or helicopter. Miniaturized mobile units can be hand held or deployed in an Unmanned Autonomous Vehicle (UAV or drone). Many mobile approaches to methane and VOC monitoring already exist and are commonly used, such as a LI-COR 770, the Picarro Methane surveyor, the National Physical Laboratory Differential Absorption Lidar (DIAL) mobile laboratory, or mobile solar occultation flux (SOF). Emerging technologies, which are often more rugged and durable than more costly equipment, can also be used in mobile approaches.

For the purpose of this report, technology is reviewed based on performance capabilities and specifications in stationary applications. The attribute of a “mobile” technology is a function of the deployment, not of the technology itself. Certain parameters or specifications of a technology may make it better suited for mobile platforms or deployment, such as size, fragility, and response time, but whether it is “mobile” is independent of the technology itself. Here, we describe important criteria to be considered when deploying a technology as a mobile platform and provide some example of mobile-based technologies.

The important parameters to consider for mobile deployments depend on the type of approach. Here, we consider two types of deployments: (1) mobile approaches in a car or van and (2) mobile approaches mounting on a UAV or drone. Airplane deployments are not evaluated due to the high cost of such applications.

For mobile monitoring in a driven car or van, weight and power requirements are not as important. These types of deployments require fast response times and low detection limits since the vehicle can be moving at fairly high speeds (normal driving speeds greater than 25 miles per hour) and is limited in proximity to sources based on roadway availability and terrain. Drone-based mobile approaches have the advantage of being able to get very close to sources, so detection limits may not need to be as low. They are, however, limited in size, weight and power requirements. Fast response times are also necessary for drone-based monitoring.

One example of a car-based approach is Entanglement Technologies' AROMA Analyzer, a mobile monitoring platform that can detect toxic compounds such as benzene and trichloroethylene. After Hurricane Harvey hit the Houston, Texas area in late August, 2017, a community near a Valero Energy refinery complained of strong odors. Entanglement Technologies thereafter conducted monitoring in the community adjacent to the refinery using the AROMA Analyzer and found, in some locations, instantaneous benzene levels as high as 77 ppb and 90 ppb.[44]

In another example, in Erie, Colorado, odors wafting from an oil and gas drilling rig were impacting a neighboring community. Traditional odor sampling failed to detect odors in excess of Colorado regulations or pinpoint any specific source within the operation. Crestone, the drilling company, thereafter hired Scentroid, a monitoring technology provider that supplies drone-based flying-laboratory monitoring equipment among other things, to conduct odor sampling. Based on their monitoring, Scentroid uncovered that mud clinging to the drilling pipe allowed odors to draft high into the air and pass over sound walls constructed at the site, allowing odors from that mud to waft much farther.[45]

Another example of a UAV sensor deployment is the UC Merced Mechatronics, Embedded Systems and Automation (MESA) and National Aeronautics and Space Administration (NASA's) Jet Propulsion Laboratory (JPL) miniature methane gas sensor. Researchers have successfully conducted flight tests of a small unmanned aerial system equipped with NASA's open path laser spectrometer (OPLS) sensor at various distances from methane-emitting gas sources. The ability of the OPLS sensor to detect methane in parts per billion by volume, as opposed to the parts-per-million sensors that are commercially available, could help more accurately pinpoint small methane leaks. Additional flight testing will feature a fixed-wing UAV, which can fly for longer durations and across longer distances. This is a capability necessary for monitoring natural gas transmission pipeline systems, which are often hundreds of miles long and possibly located in rural or remote areas.[46]

6.2 Sensor Technologies

The different sensors that are evaluated below have been grouped according to cost. Sensors that fall into the mid-range cost include all of the optical absorption spectroscopy sensors, with the exception of the handheld GC sensor. Sensors that fall into the low-cost group include photoionization, NDIR, electrochemical, semiconductor and thermal conductivity sensors. Despite the low cost of photoionization and electrochemical sensors, a relatively low limit of detection (LOD) can be achieved using these commercially available sensors for certain pollutants and applications. Additionally, although low cost sensors have higher LODs than more costly optical absorption spectroscopy techniques, they can be useful for detecting events of high concentrations,

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[44] The Texas Tribune, 2017. *EPA won't release benzene levels collected post-Harvey; private tests show elevated levels.* Available at: https://www.texastribune.org/2017/09/14/epa-wont-release-benzene-levels-collected-after-harvey-private-monitor/

[45] Denver Business Journal, 2017. Tackling odor problems in the oil fields is complicated. Available at: https://www.bizjournals.com/denver/news/2017/09/11/tackling-odor-problems-in-the-oil-fields-is.html

[46] UC Merced – University News, 2016. NASA, UC Merced Successfully Test Miniature Methane Sensor. Available at: http://www.ucmerced.edu/news/2016/nasa-uc-merced-successfully-test-miniature-methane-sensor

spotting trends in time series data, and providing comparisons between other sensors within a network to tease out spatial variations.

Several low and mid-range cost monitoring technologies are reviewed in detail below. Reviews discuss advantages and disadvantages of each of the technologies as well as best uses/applications for these technologies. Descriptive tables within each review summarize parameters that are important to consider in deployments near upstream oil and gas operations: cost, detection limit, accuracy, path length, scalability, and whether the technology is real-time, remote-capable, and portable/mobile-capable. Tables also list some example manufacturers, provide quotes from selected manufacturers, and provide a condensed summary of the predicted future of that technology.

6.2.1 Mid-range Cost

6.2.1.1 Open Path Fourier Transform Infrared Spectroscopy (OP-FTIR)

FTIR is a (laser or IR lamp-based) technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas, detected along a path length established by the user. An FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range, allowing an FTIR spectrometer to measure concentrations of multiple pollutants simultaneously. Computer processing is required to turn the raw data (light absorption for each mirror position) into the desired result (light absorption for each wavelength). The processing required uses a common algorithm called the Fourier transform (hence the name "Fourier-transform spectroscopy").

FTIR spectrometers are most suitable for remote applications, but are not simple to operate and require an experienced operator to ensure proper usage and valid results. Tables 4 and 5 list some specifications of FTIR spectrometers as well as strengths and limitations of the technology. Despite the powerful capability of being able to monitor for a long list of compounds simultaneously over an open path, FTIR is less sensitive to some compounds, such as benzene, than other technologies within the same price range. This makes FTIR an excellent tool for monitoring programs at exploration & production sites, particularly for monitoring along a fenceline. However, this technology only gives a view of what is crossing the line of sight, averages the concentrations over its path length, and may be less effective at capturing a plume rising over a fenceline or other spatial variations occurring within a site or community. For example, it cannot differentiate a narrow high-concentration plume from a diffuse low-concentration plume.

Table 4: Open-path FTIR Specifications

Parameter	OP-FTIR
Cost	~$75,000 - $120,000
Detection Limit	Benzene: ~30-100 ppb Methane: ~15-60 ppb NMOC: ~1-100 ppb
Accuracy	~2-25 ppb
Real-time?	Yes
Remote Capable?	Yes
Capable of being portable/mobile?	Yes
Simultaneous compound detection?	Yes
Path Length	~200-1000m
Scalability	Commercially available but with limited availability; not intended for large number deployment
Example Manufacturers	ABB/Bomem, Cerex Monitoring Solutions, IMACC Instruments, Kassay FSI, MIDAC Corporation, Ruker Optics, Spectrex Inc.
The future?	OP-FTIR is an extremely powerful monitoring tool, capable of detecting a wide range of compounds simultaneously. For its price, the benzene limit of detect is quite high. This technology will continue to be used, primarily for fenceline approaches, or episodic/exploratory studies where the pollutants of concern are not well known. Moving forward, it is possible that other, lower cost technologies, may begin to be used for some applications that currently rely on OP-FTIR.

Table 5: Advantages and Disadvantages of Open-Path FTIR

Advantages	Disadvantages
Many compounds are infrared active and absorb IR light (meaning many can be detected, and analyzed simultaneously)	IR detectors need cooling to operate. Liquid nitrogen used for detector cooling must be refilled and maintained regularly (~weekly)
Remote-capable	Gas-phase water spectral interference as well as CO and CO2 interference
Real-time	Field implementation and data collection requires highly experience personnel
Equipment is fairly rugged and portable	Infrared beam has limited range and may not be sensitive enough to meet ambient data quality objectives. Maximum path length is on the order of 400-500 meters.
	High cost

In 1997, in response to chemical releases into the neighboring community, Contra Costa County required the installation of a fenceline monitoring system at the Tosco Oil Refinery in Rodeo, CA, USA (now owned by Phillips 66). An OP-FTIR fenceline monitoring system consists of two OP-FTIR configurations deployed along the north and south fencelines of the facility. The one-way optical path of the north fence line is 930 meters long and the south path is 955 meters. The systems are set to monitor on a frequency of every five minutes and to sound an alarm if concentrations of some 26 target compounds exceed pre-set concentration levels parts per million /meter (ppm/m level). A monthly report evaluates system performance and summarizes the chemicals detected, their concentrations, and the system detection limit for them. The system contains a spectral library of over 300 chemicals. Electronic preservation of the collected monitoring spectra allows the spectra from any monitoring period to be re-examined for the presence of other-than-target chemicals. Overall, these systems appear useful for early warning and evaluation of high-level releases (along with the constituents of the release) and provides information to the community about routine operation, but is not adequate for determining emissions flux during normal operations.

6.2.1.2 Tunable Diode Laser Absorption Spectroscopy (TDLAS)

TDLAS is a technique for measuring the concentration of a specific species, such as methane, in a gaseous mixture using tunable diode lasers and laser absorption spectrometry. The advantage of TDLAS over other techniques for concentration measurement is its ability to achieve very low detection limits (of the order of parts per billion [ppb]), however, unlike FTIR, TDLAS is tuned to detect one specific compound at a time.

One of the historic disadvantages of absorption spectroscopy as well as laser absorption spectroscopy in general is that it relies on a measurement of a small change of a signal on top of a large background. In addition, noise introduced by the light source or the optical system typically increase the detection limits of the technique. In general, absorption spectroscopy is seldom used in its simplest mode of operation, and new design uses appear to have overcome many of the common problems of the past.

With recent advancements, two ways to improve the capability of TDLAS have emerged; one is to reduce the noise in the signal, the other is to increase the absorption. The former can be achieved by the use of a modulation technique, whereas the latter can be obtained by placing the gas inside a cavity in which the light passes through the sample several times, thus increasing the interaction length. This can be obtained by placing the species inside a cavity in which the light bounces back and forth many times, whereby the interaction length can be increased considerably. This has led to a group of techniques denoted as cavity-enhanced absorption spectroscopy (CEAS, see Section 6.1.3 below). An example of where the cavity is outside the laser is the use of a multi-pass cell, which can provide an enhanced interaction length of up to ~2 orders of magnitude. Multi-pass cells are commonly used in TDLAS technologies.

There has been a dramatic influx of TDLAS technologies on the market over the past few years, and these technologies continue to drop in price while achieving low limits of detection and enhanced precision. To help commercialize these types of advances, the EDF launched it Methane Detectors Challenge in 2014. The two highest performing sensors of that challenge were both TDLAS sensors. Tables 6 and 7 list specifications of TDLAS as well as strengths and limitations of the technology.

Table 6: Tunable Diode Laser Absorption Spectrometry Specifications

Parameter	Tunable Diode Laser Absorption Spectrometry
Cost	~$15,000 - $65,000
Detection Limit*	Benzene: ~10-30 ppb Methane: ~0.5-1 ppm *Detection limit is dependent on path length but is shown for a typical path lengths here.
Accuracy	Benzene: ~1-10 ppb Methane: ~100 ppb
Real-time?	Yes
Remote Capable?	Yes
Capable of being portable/mobile?	Yes
Simultaneous compound detection?	Yes
Path Length	~10-1000m
Scalability	Commercially available but with limited availability; not intended for large number deployment

Table 6: Tunable Diode Laser Absorption Spectrometry Specifications

Parameter	Tunable Diode Laser Absorption Spectrometry
Example Manufacturers	Aeris Technologies Inc., Axetris, Boreal Laser, GAZOMAT, Indrio Technologies, Norsk Elektro Optikk, OPSIS AB, PKL Technologies, PSI Physical Sciences, Quanta3, Senscient, SENSIT, Simtronics group, Unisearch Associates Inc.
Quotes from Manufacturers	"*Indrio's advanced laser-based sensors, freshly out of a research lab at Stanford, marks the next big epoch in accurate monitoring of pollutants in air. Over the next few years we will work tirelessly to scale up our operations and make it accessible to a large market. The power of advanced laser-based sensing will reach mass market and revolutionize how air pollution is monitored and controlled.*" - Ritobrata Sur, Indrio Technologies "*The disruptive combination of high performance, small size, low weight and power consumption of Aeris sensors will enable effective, low cost natural gas leak detection solutions in fixed, mobile, and handheld applications from the wellhead to the burner tip.*" - James J. Scherer, Aeris Technologies, Inc.
The future?	Continuous monitoring in the upstream production environment requires breaking the cost barrier and TDLAS technology is beginning to offer better value, with prices dropping, detection becoming more sensitive, and offering the advantage of open path sensing to reduce the number of sensors needed.

Table 7: Advantages and Disadvantages of TDLAS

Advantages	Disadvantages
High spectral resolution minimizes interference from other gases	Only one compound is detected per laser, fewer measurable compounds, and limited sensitivity
24/7 remote monitoring	Limited to quantitation of compounds with overtone absorbencies in the near- and mid-IR range
Rapid response time - typically 1 second	Susceptible to blocked beams and dust/objects interfering with signal
Long measurement path length, up to 1 km	
Real-time	
Economical compared to alternative technologies with similar capabilities	

Some examples of current uses of TDLAS technology include fenceline monitoring for refineries (both Chevron and Phillips 66 refineries in the Bay Area use open path TDLAS monitors for detecting hydrogen sulfide[47]) or methane monitoring at natural gas storage facilities (Pacific Gas and Electric has tested a TDLAS sensor at one of its storage facilities in northern California[48]).

Considering the current rate of advancement of this technology, TDLAS displays significant promise as a technology for monitoring in the E&P sector. IBM Research published their "5 in 5" predictions of five innovations that they believe will help change our lives within 5 years. IBM predicted that in 5 years, new, affordable sensing technologies deployed near natural gas extraction wells, around storage facilities, and along distribution pipelines will enable the industry to pinpoint invisible leaks in real-time.[49] IBM scientists and engineers made cheap, compact, silicon-chip-based tunable diode lasers and photodetectors.[50] Each 5- by 5-mm sensor should cost about $300, says team leader Hendrik F. Hamann.[51] IBM can fabricate the sensors on silicon wafers using the same technology for putting transistors on a computer chip, which should drastically reduce manufacturing costs and be easy to scale up. Wireless sensors, placed around a well pad, will send data to cloud-based computers. On the basis of the methane reading combined with weather data, IBM is predicting that the software will pinpoint the location of the leak and quantify it. This is a perfect example of how emerging monitoring technologies coupled with cloud-based sensor networking and data analytics can bring a rise of new solutions that help reduce pollution, waste, and the likelihood of catastrophic events.

6.2.1.3 Cavity-Enhanced Absorption Spectroscopy/Cavity Ring Down Spectroscopy

One mechanism used to improve the sensitivity of laser absorption spectroscopy is to increase the path length. This can be done by placing the species inside a cavity in which the light bounces back and forth many times, whereby the interaction length can be increased considerably. This has led to a group of techniques denoted as CEAS. Multi-pass cells, described previously in Section 6.1.2, are one way to increase the path length. Whereas the multi-pass cells typically can provide an enhanced interaction length of up to ~2 orders of magnitude, resonant cavities can provide a much larger path length enhancement, up to ~10^4 to 10^5 with high reflecting mirrors with reflectivities of ~99.99–99.999%. In CRDS the absorbance is assessed by comparing the cavity decay times of a short light pulse as it "leaks out" of the cavity on and off-resonance, respectively. Other variations of CEAS include off-axis integrated cavity output spectroscopy (OA-ICOS), continuous wave cavity enhanced absorption spectrometry (cw-CRDS), and optical feedback cavity enhanced absorption spectroscopy (OF-CEAS).

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[47] http://www.fenceline.org/

[48] Optics.org, 2016. Laser methane sensor installed at California gas storage facility. Available at: http://optics.org/news/7/12/17

[49] IBM Research: 5 in 5. "Smart sensors will detect environmental pollution at the speed of light." Available at: http://research.ibm.com/5-in-5/environmental-pollutants/

[50] Zhang, Eric J., et al. "Silicon photonic on-chip trace-gas spectroscopy of methane." Lasers and Electro-Optics (CLEO), 2016 Conference on. IEEE, 2016.

[51] Chemical & Engineering New, American Chemical Society, 2017. "Looking for methane leaks." Available at: https://cen.acs.org/articles/95/i35/Looking-methane-leaks.html

Table 8: Cavity Ring Down Spectroscopy Specifications

Parameter	CRDS
Cost	~$40,000 - $120,000
Detection Limit	Benzene: ~0.1-30 ppb Methane: ~1-10 ppb
Accuracy	Benzene: ~0.1-1 ppb Methane: ~0.1-1 ppb
Real-time?	Yes
Remote Capable?	Yes
Capable of being portable/mobile?	Yes
Simultaneous compound detection?	Yes
Path Length	~200-1000m, inside the cavity
Scalability	Commercially available but with limited availability; not intended for large number deployment
Example Manufacturers	Entanglement Technologies Inc., Los Gatos Research (ICOS), Picarro Inc., Tiger Optics
Quotes from Manufacturers	"*In the past five years, Picarro has developed and commercialized methane detection hardware (CRDS-based) and analytical solutions for emissions quantification and asset management for energy companies involved in natural gas production, transmission and distribution. Particularly in states where emissions are being regulated, we are providing solutions to the industry so that compliance with regulations can be demonstrated and quantified.*" - Aaron Van Pelt, Picarro "*The AROMA analyzer, while currently only conducting speciated BTEX, TCE, and 1,2-cDCE analyses will quickly grow in capability to include the PAMS compounds and will provide a 1-second response time, non-speciated measurement mode for broad area surveys.*" - Tony Miller, Entanglement Technologies

Table 8: Cavity Ring Down Spectroscopy Specifications

Parameter	CRDS
The future?	CRDS is one of the leading extractive methane monitoring technologies on the market, particularly for mobile applications. This highly sensitive technology has potential for a strong future as new technologies emerge being capable of detecting very low levels of hydrocarbons with the selectivity to quantify specific toxic compounds, such as benzene.

Table 9: Advantages and Disadvantages of CRDS

Advantages	Disadvantages
User friendly, minimal maintenance needed after servicing or calibration (infrequent calibration needed), no consumables	May need to apply sample filtering components to avoid interferences
Greatly increases sensitivity with much longer effective path lengths. Insensitive to vibrations during measurements.	Key components needed for this type of instrumentation typically drive up the cost
Easy field deployment	Multiple species detection is difficult
Remote and mobile-capable	Limited to the laser spectral range available

One of the more well-known CRDS technologies is the Picarro, often used to survey for natural gas leaks using their mobile car-mounted “Surveyor” monitoring platform. Another example is the Entanglement Technologies AROMA analyzer, a mobile approach to real-time monitoring of VOCs that are hazardous air pollutants, such as benzene and trichloroethylene. The fast-response, high selectivity, and low detection limits of CRDS technologies make it very well suited to mobile approaches looking for detailed spatial resolution.

6.2.1.4 Handheld Gas Chromatographs

GC is commonly applied in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. Handheld GCs combine micro columns with a variety of conventional detectors to reduce the size and weight of bench top instruments to offer a GC for portable use. Traditionally, grab or passive air samples are collected in the field and later analyzed by a gas chromatograph in a laboratory. Now, handheld micro GCs are capable of detecting BTEX compounds and other VOCs in near real-time in the field. The most common detectors used in conjunction with handheld

GCs are PID, flame ionization detectors (FID), or metal oxide semiconductor detectors (MOS). The detectors themselves, described later in this document, are capable of monitoring for total VOCs. The advantages of the handheld GC is that it can analyze for specific individual VOC compounds. Tables 10 and 11 list specifications of handheld GCs as well as strengths and limitations of the technology.

Table 10: Handheld Gas Chromatograph Specifications

Parameter	Handheld Gas Chromatograph
Cost	~$5,000-$25,000
Detection Limit	Benzene: ~1-1000 ppb NMOC: ~1-100 ppb
Accuracy	Benzene: ~0.1-10 ppb NMOC: ~0.1-10 ppb
Real-time?	Near real-time, not continuous
Remote Capable?	Yes, depending on the needs of a carrier gas
Capable of being portable/mobile?	Yes
Simultaneous compound detection?	Yes
Path Length	N/A; could be artificially made
Scalability	Most common portable GC detectors are widely available making this technology easily scalable
Example Manufacturers	Agilent, Defiant Technologies, Femtoscan, Inficon, PerkinElmer Torion, Vernier Mini GC
The future?	Few low-cost solutions exist that are capable of speciating to detect specific VOC compounds. As GCs continue to decrease in price and size, they may be the future of quantifying community exposures to hazardous air pollutants in near real-time.

Table 11: Advantages and Disadvantages of Handheld GCs

Advantages	Disadvantages
Can provide speciation of complex VOC mixtures	Not a continuous monitor
Low detection limit	Some unit require a carrier gas
	High cost

PIDs, FIDs, and MOS are most common in handheld GCs because of their small size. Laboratory GCs often use mass spectrometers as the detector, but mass spectrometers are typically the size of an oven or refrigerator. Conventional mass spectrometers separate compounds by giving them an electric charge and passing them through electric and/or magnetic fields depending on the mass/charge ratio. By determining what compounds make up a given sample, these instruments can identify almost any substance. Jeffrey T. Glass' research group from Duke University has developed a specialized mass spectrometer that can detect methane and other volatile organics found in natural gas. This ability should help it distinguish between gas leaking from wells and gas leaking from nearby farms since the two sources would have different chemical signatures. [51] Glass' group has managed to shrink the instrument down to shoe-box size and has used data analytics to maintain high performance. Their work now is focusing on trying coded apertures in different versions of mass spectrometers to determine which would be best for creating scaled down, mobile devices for field use. They are also working to show these devices can detect trace amounts of methane to spot leaks in infrastructure and various explosives to thwart terror attempts.[52]

Large advances are being made in the field of portable GCs. With the advancement of MEMS technology, it is possible future technologies have adequate detection limits and size to make them useful mobile approaches or for compound-speciated continuous or semi-continuous ambient air monitoring. Right now the technology appears to be best suited for field surveys and inspections.

6.2.2 Low Cost

6.2.2.1 Non-dispersive Infrared Sensor (NDIR)

The main components of an NDIR sensor are an infrared source (lamp), a sample chamber or light tube, a light filter and an infrared detector. They are often used to measure combustible gases. The IR light is directed through the sample chamber towards the detector. In parallel there is another chamber with an enclosed reference gas, typically nitrogen. The gas in the sample chamber causes absorption of specific wavelengths, and the attenuation of these wavelengths is measured by the detector to determine the gas concentration. The detector has an optical filter in front of it that eliminates all light except the wavelength that the selected gas molecules can absorb.

NDIR sensors are quite a bit smaller than any of the technologies reviewed so far, and are capable of achieving moderate to low detection limits for methane, as low as 1 ppm. [53] Since NDIR sensor are especially suited to sense infrared absorbing VOCs, it is very well suited for sensing methane. Tables 12 and 13 list specifications of NDIR as well as strengths and limitations of the technology.

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[52] Duke University Pratt School of Engineering News, 2016. "Coding and Computers Help Spot Methane, Explosives." Available at: http://pratt.duke.edu/news/coding-and-computers-help-spot-methane-explosives

[53] Zhu, Zipeng, Yuhui Xu, and Binqing Jiang. "A one ppm NDIR methane gas sensor with single frequency filter denoising algorithm." *Sensors* 12.9 (2012): 12729-12740.

Table 12: Nondispersive Infrared Sensor Specifications

Parameter	NDIR
Cost	~$1,000-$10,000
Detection Limit	Methane: ~1-500 ppm NMOC: ~500-1,000 ppm
Accuracy	Methane: ~1-100 ppm NMOC: ~50-100 ppm
Real-time?	Yes
Remote Capable?	Yes
Capable of being portable/mobile?	Yes
Simultaneous compound detection?	No
Path Length	N/A; could be artificially made
Scalability	This technology has been used for many years and is quite established, making it easily scalable if demand increased
Example Manufacturers	Alphasense, C-Lock Inc, Edinburgh Sensors, Mipex Technology, Scentroid, Winsen, Wuhan Cubic
The future?	NDIR sensors provide a middle-ground between very low cost sensors like electrochemical, metal oxide semiconductor, and pellistors and mid-range cost technologies like tunable diode laser absorption spectrometers. Their high stability, reliability, and longer lifetime than very low-cost sensors make them an excellent option at price points often below $10,000. In the future, advanced data analytics will likely allow for even lower detection limits than currently capable with NDIR sensors.

Table 13: Advantages and Disadvantages of NDIR

Advantages	Disadvantages
Well-suited for methane and other infrared absorbing VOCs	Detection limit is high compared to other optical techniques
High detection accuracy for the cost	Can suffer from spectral interference - particularly from water vapor
Relatively low cost	
High stability and fast response time	
Not affected by hazardous chemical environments, no poisoning effects	

NDIR sensors offer many advantages for detecting methane and other infrared absorbing VOCs.[54] Though limited to detecting specific compounds, NDIR sensors are the middle-ground between very low cost sensors like electrochemical, metal oxide semiconductor, and pellistors and mid-range cost optical technologies like tunable diode laser absorption spectrometers. Their small size, high stability, and fast response time make them well suited for mobile applications, particularly aerial/drone deployments. Since this technology offers advantages from both sides, having the stability, response time, and relatively low detection limit associated with optical techniques but also has the small size and price tag, it is a great option for lower-cost methane monitoring.

6.2.2.2 Photoionization Detector (PID)

PID is a type of gas detector. Typical PIDs measure volatile organic compounds and other gases in concentrations from parts per billion to 10,000 ppm. The photoionization detector is an efficient and inexpensive detector for many gas and vapor analytes. PIDs produce instantaneous readings, operate continuously, and are commonly used as detectors for gas chromatography or as hand-held portable instruments. Hand-held, battery-operated versions are widely used in military, industrial, and confined working facilities for health and safety.

As compounds enter the detector they are bombarded by high-energy UV photons and are ionized when they absorb the UV light, resulting in ejection of electrons and the formation of positively charged ions. The ions produce an electric current, which is the signal output of the detector. The greater the concentration of the component, the more ions are produced, and the greater the current. The current is amplified and displayed on an ammeter or digital concentration display. The heart of the PID is the lamp that emits those UV photons. The photon energy depends on the type of gas used to fill the lamp, and the crystal used as the transmission window. In general higher energy lamps

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[54] NDIR sensors are especially well-suited to detecting methane due to high infrared absorption. Being less sensitive to other infrared absorbing NMOCs coupled with typical low ambient concentrations of NMOCs, NDIR sensors show little utility at this time unless they are being challenged with very high concentrations.

respond to the broadest range of compounds while the lower-energy lamps offer the best selectivity.[55]

PIDs are well suited to detect VOCs with proper ionization potential, such as isobutylene and aromatic hydrocarbons, making it a good candidate for detecting benzene-like compounds, though it is not capable of speciating down to a specific compound without additional sampling efforts. The EPA Office of Research and Development has been working on a low-cost fenceline VOC sensor called the SPod. The SPod is a low cost, solar-powered system that combines wind field and air pollutant concentration measurements made with a PID to detect emission plumes and help locate the source of emissions. The current design works only in "near-fenceline" applications where localized source emission plumes may be present.

Table 14: Photoionization Detector Specifications

Parameter	PID
Cost	Under $5,000, sensor head $150-400
Detection Limit	Benzene: ~2-100 ppb NMOC: ~0.05-200 ppm
Accuracy	Benzene: ~2-15 ppb NMOC: ~0.1-10 ppm
Real-time?	Yes
Remote Capable?	Yes
Capable of being portable/mobile?	Yes
Simultaneous compound detection?	No
Path Length	N/A; could be artificially made
Scalability	PIDs are widely used and would have no problem with scalability if there were an increase in demand
Example Manufacturers	Aeroqual, Alphasense, Drager, Gray Wolf, Ion Science, Mocon Baseline, RAE Systems
The future?	PIDs have a very promising future for low-cost continuous fenceline or community monitoring of toxics or VOCs. They are a good compromise between less sensitive and less reliable EC or MOS sensors and more expensive mid-range cost technologies. They can be useful for triggering a more precise but inexpensive passive/grab sample with

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[55] RAE Syetems. The PID Handbook, third edition. Available at: http://www.raesystems.com/sites/default/files/content/resources/pid_handbook_1002-02.pdf

Table 14: Photoionization Detector Specifications

Parameter	PID
	a SUMMA canister or can be used to detect leaks and locate at fencelines in real-time for a fraction of the cost of an ORS fenceline system.

Table 15: Advantages and Disadvantages of PIDs

Advantages	Disadvantages
Better sensitivity than other low-cost sensors like electrochemical or metal oxide sensors	More expensive than electrochemical and metal oxide sensors
Small size	Cannot detect methane
Fast response time	Poor detection of small hydrocarbon molecules
Reliable, cost-effective	May produce false positive readings in extremely high humidity conditions
Long lifetime compared to other low cost sensor technologies	

PIDs can also be used to trigger grab samples during episodic events – allowing for more complex analysis by other means. In the past, regulatory agencies for episodic events or releases that negatively impact communities took samples with trained scientists or engineers that have identified proper sampling locations and methods through systematic observations of industrial operations and air impacts. Often times though, episodic events can occur when trained staff are not present and it can be difficult to sample at the proper time. PID sensor therefore can be configured to continuously monitor for total VOCs and trigger a grab sample at the right time when an episodic release causes concentrations to increase within the community. Sampling technologies, such as absorbant cartridges and canister grab samples triggered by PIDs, require minimal technical know-how and little training to operate. These sampling devices could also be distributed in advance to a network of volunteers within communities who are alerted by local PIDs to the presence of compounds from an unplanned release.

PIDs are intrinsically not selective enough for ambient air monitoring. When coupled with other technologies, though, they can provide meaningful data. PIDs can be used as the detector for a gas chromatograph, they can be used in a fenceline monitoring system such as the EPA SPod, or they can be used as a trigger to grab an air sample as the right time. Additionally, devices can include a filtering or absorbing cartridge that eliminates other VOCs in the mixture, allowing for selective sensing of benzene, but the detection limit on this method is around 10 ppm, about one order of magnitude too high for effective ambient air monitoring. Regardless, PIDs appear to be one of the most promising low-cost sensors for VOCs. In the future, multiple sensor arrays coupled with artificial neural network algorithms (or other data analytics techniques) will be considered as feasible candidate sensor systems.

6.2.2.3 Electrochemical (EC)

Electrochemical (EC) sensors rely on an electrochemical reaction with the target analyte present in the sampled air to produce an electrical signal proportional to the contaminant concentration. These sensor are very low-cost, typically priced under $200, and can be priced much lower (for just the sensor, additional costs are needed for processing the signal and storing/communicating the data).

EC sensors are low cost, low power, compact sensors and in general, their response time is about 120 seconds depending on the air temperature. As with PIDs, electrochemical cells are broadband sensors, but with a different profile: PIDs show a better sensitivity than electrochemical cells for VOCs. If one wishes to measure a VOC with electrochemical cells, then it is necessary to optimize the electrochemical sensor to the target VOC. In fact, EC sensors show little selectivity and a limit of detection down to the high ppb range. This type of sensors can be tuned to a specific target gas in many ways.

Most of the EC sensors need humidity to function properly. In fact, certain electrolytes can be damaged by very low humidity, leading to a bias in the measurements. Solid-state material-based sensors (such as MOS) are not so dependent on ambient humidity. Temperature also has an influence on the sensor response, but this interference can be modelled and compensated. EC sensors show long-term stability with drift values between 2% and 15% per year, for example, for the Nemoto and SGX Sensortech devices. Tables 16 and 17 list specifications of EC sensors as well as strengths and limitations of the technology.

Table 16: Electrochemical Sensor Specifications

Parameter	Electrochemical Sensor
Cost	Under $2,000, sensor head $50-200
Detection Limit	NMOC: ~100-1,000 ppb Methane: ~ 100 ppm
Accuracy	NMOC: ~2-100 ppb Methane: ~2-10 ppm
Real-time?	Yes
Remote Capable?	Yes
Capable of being portable/mobile?	Yes
Simultaneous compound detection?	No
Path Length	N/A
Scalability	Manufactured in high volumes; capable of large-scale deployment

Table 16: Electrochemical Sensor Specifications

Parameter	Electrochemical Sensor
Example Manufacturers	Aeroqual, Alphasense, Citytech, Environmental Sensors CO, Figaro, Nemoto, SGX Sensortech, Unitec SRL, United Electric Controls, Winsen
The future?	Electrochemical sensors are becoming more widely available and reliable over time. Extensive efforts are being made by researchers and government agencies to facilitate and communicate responsible use of these sensors that overcome data quality and data interpretation challenges.

Table 17: Advantages and Disadvantages of Electrochemical Sensors

Advantages	Disadvantages
Small	Short lifetime (~1 year)
Real-time	Sensor drift
Low power consumption	Frequent recalibration needed
Low cost	Susceptible to interferences from other gaseous pollutants
More sensitive than metal oxide semiconductor sensors	High limit of detection
	Lacks specificity to toxic compounds of concern, such as BTEX

In general, the main drawback of EC sensors are the lack of sensitivity and/or selectivity (to benzene, for example). Most EC OEM sensors are not able to reach levels lower than 100 ppb of benzene, although a few embedded sensor devices show a sensitivity to few tens of ppb to broadband VOCs.[56] Their limit of detection are two to three orders of magnitude too high for monitoring benzene in ambient air at the desired 1 ppb limit of detection.

The same is true for the current landscape of EC methane sensors, where detection limits are on the order of 100 ppm,[57] one to two orders of magnitude too high for monitoring local air to detect nearby methane leaks. In the future, multi-sensor networks coupled with artificial neural network algorithms may be considered a feasible candidate

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[56] Spinelle, L., Gerboles, M., Kok, G., Persijn, S. and Sauerwald, T., 2017. Review of portable and low-cost sensors for the ambient air monitoring of benzene and other volatile organic compounds. Sensors, 17(7), p.1520.

[57] Sekhar, P.K., Kysar, J., Brosha, E.L. and Kreller, C.R., 2016. Development and testing of an electrochemical methane sensor. Sensors and Actuators B: Chemical, 228, pp.162-167.

sensor system for community or near-fenceline monitoring, but we estimate that this will likely be achieved with MOS-type or PID sensors first. Right now, EC sensors are only ready for deployment in next-to-source applications, such as well head leak detection systems.

Innovative sensor technologies may help overcome some of the limitations that EC sensors currently face. Under the ARPA-E MONITOR program (described in Section 3.1), Palo Alto Research Center (PARC) is developing printed nano-chemical sensor arrays for methane detection. Through advanced data analytics, the sensor system will be trained for high sensitivity and selectivity for components of natural gas and interfering compounds. The goal is to be able to detect methane emissions with a sensitivity of 1 ppm and localize the source of emissions to within 1 meter. By using low-cost printing techniques, the project team's system could offer an affordable alternative to more expensive optical methane detectors on the market today.[58]

6.2.2.4 Metal Oxide Semiconductor (MOS)

MOS sensors rely on a chemical reaction with a metal oxide surface that alters its conductivity or resistivity to provide a measure of contaminant concentration. These sensors are extremely low cost, ranging from $3-50 each per sensor (additional costs are needed for processing the signal and storing/communicating the data).

MOS sensors are usually smaller than EC sensors. They are generally compact, low cost and need higher power than PIDs. They need high temperature for the reactions to take place at a faster rate so a heater is usually incorporated into the sensor. They respond to a wide range of concentrations of the gases: from a few ppb for gases like NO_2[59] to several thousand ppm for other gases. MOS lacks selectivity to measure specific compounds, such as benzene or BTEX compounds. MOS sensors also respond to inorganic gases, so one should not use them to measure low concentrations of other VOCs where gases such as nitric oxide (NO), NO_2 or CO are also present in higher concentrations, as they may interfere with readings, though some sensors have been shown to discriminate between these interfering gases and only pick the target analyte.[60] However, the signal to noise specification provided by the sensor is usually not very clear and none of them have methods to deal with mixtures of VOCs or other pollutants.

Manufacturers typically provide tables of the equivalent gas concentration cross sensitivity to other gases. Response times can be as high as 30-45 minutes[61] but in most cases, their response time is in the range of the few minutes.[62] Like PIDs and EC sensors, MOS sensors do not have specificity to individual organic compounds. Moreover, these sensors do additionally respond to inorganic reducing and oxidizing gases like e.g.,

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[58] https://arpa-e.energy.gov/?q=slick-sheet-project/system-printed-hybrid-intelligent-nano-chemical-sensors-sphincs

[59] Kida T., Nishiyama A., Yuasa M., Shimanoe K., Yamazoe N. Highly sensitive NO2 sensors using lamellar-structured WO3 particles prepared by an acidification method. Sens. Actuators B Chem. 2009;135:568–574. doi: 10.1016/j.snb.2008.09.056.

[60] Fine, G.F., Cavanagh, L.M., Afonja, A. and Binions, R., 2010. Metal oxide semi-conductor gas sensors in environmental monitoring. Sensors, 10(6), pp.5469-5502.

[61] Abbas, M.N., Moustafa, G.A. and Gopel, W., 2001. Multicomponent analysis of some environmentally important gases using semiconductor tin oxide sensors. Analytica chimica acta, 431(2), pp.181-194.

[62] Katulski, R.J., Namieśnik, J., Stefański, J., Sadowski, J., Wardencki, W. and Szymańska, K., 2009. Mobile monitoring system for gaseous air pollution. Metrology and measurement systems, 16(4), pp.667-682.

CO or NOx. To improve selectivity, manufacturers typically incorporate different dopants or filters.

Temperature and humidity are also important interferents of the signal and have to be controlled or measured with precision so they can be extracted and their influence can be modelled. Another issue with this type of sensor is their stability. The response changes over time and the sensors need to be recalibrated more regularly. Information needed to assess these conditions further is difficult to attain because manufactures do not provide much information about the drift or stability. Thus, when using MOS sensors, information about long-term stability, cross-sensitivity to gaseous interfering compounds and humidity sensitivity is also important in order to correct sensor response.

Tables 18 and 19 list specifications of MOS sensors as well as strengths and limitations of the technology.

Table 18: Metal Oxide Semiconductor Specifications

Parameter	Metal Oxide Semiconductor Sensor
Cost	Under $2,000, sensor head $10-100
Detection Limit	NMOC: ~1-10 ppm Methane: ~10-100 ppm
Accuracy	NMOC: ~10-100 ppb Methane: ~1-10 ppm
Real-time?	Yes
Remote Capable?	Yes
Capable of being portable/mobile?	Yes
Simultaneous compound detection?	No
Path Length	N/A; could be artificially made
Scalability	Manufactured in high volumes; capable of large-scale deployment
Example Manufacturers	Aeroqual, AMS, AppliedSensor, Cambridge CMOS Sensors, Figaro, SGX Sensortech, Unitec SRL
The future?	This sensor's limited accuracy prevents it from being used to monitor global methane but it does show potential for other, higher concentration applications, such as monitoring near methane emitters or fencelines. This sensor can distinguish between background and elevated concentrations.

Table 19: Advantages and Disadvantages of Metal Oxide Semiconductor Sensors

Advantages	Disadvantages
Not as sensitive to RH and T as electrochemical sensors	Sensitive to change in RH, T, P; cross-sensitivity
Real-time	High power consumption than EC
Stable	High limit of detection
Low cost	Lacks specificity to toxic compounds of concern, such as BTEX
Small	Non-linear response and long term drift
Longer lifetime than electrochemical (1-2 years)	Can respond to inorganic gases so not well suited to low concentrations of VOCs where gases such as NO, NO2, or CO are present in higher concentrations

MOS sensors are advisable when sensing VOCs that are not measured by PIDs, such as methane or chlorofluorocarbons (CFCs). MOS sensors are lower in cost to PIDs, so if used instead of PIDs to measure total VOCs, it is advisable to use them for detecting large changes in concentrations. Users should take care to field-calibrate these sensors and use data analysis techniques to correct for drift, interference, or temperature/RH dependence. Regardless of sensor flaws, large networks of MOS sensors may be capable of providing detailed information that was cost-prohibitive in the past. Now, a large network (~hundreds of sensors) can be assembled for a similar cost as one traditional ORS technology, in the range of a few hundreds of thousands of dollars.

Another class of MOS measurement devices consists of e-noses and sensor arrays, which are devices that contain several simple sensors of different types. These arrays use mathematical pattern recognition algorithms in order to compare and recognize gaseous samples. Among the different algorithms used to make the sensor array more specific than each single sensor are smart pattern recognition software are commonly based on neural networks. Sensor arrays are often part of devices called “electronic noses” or “e-noses”. This name is derived from the fact that (part of) their job is to detect odors. Each element in the sensor array responds to a number of different chemicals or classes of chemicals. The individual selectivity of each element is not required as the array of sensors should contain as much chemical diversity as possible. This diversity gives to the e-nose the ability to respond to the largest possible range of analytes. Using a fingerprint method over the collection of sensors, the e-nose is able to classify and identify analyte. E-nose systems are not expected to be readily applicable for accurate quantitative benzene measurement since many of them have another main target application and they are costly. It is reported that cost for an e-nose system ranges from US $20,000 to $100,000 in Europe, the U.S., and Japan.[63,64]

6.2.2.5 Pellistor

A pellistor is a solid-state device used to detect gases which are either combustible or which have a significant difference in thermal conductivity to that of air. The word "pellistor" is a combination of pellet and resistor. The detecting element consist of small "pellets" of catalyst loaded ceramic whose resistance changes in the presence of gas. Many of them require gentle heating in use, so they may be four terminal devices with two connections for a small heating element and two to the sensor itself.

Table 20: Pellistor Specifications

Parameter	Pellistor
Cost	Under $2000, sensor head $50-200
Detection Limit	~1% methane/other combustible gases and vapors
Accuracy	Methane: ~100-1,000 ppm
Real-time?	Yes
Remote Capable?	Yes
Capable of being portable/mobile?	Yes
Simultaneous compound detection?	No
Path Length	N/A; could be artificially made
Scalability	Highly scalable, widely available
Example Manufacturers	Figaro, MICROcel, SGX Sensortech, Sixth Sense, Z.B.P SENSOR GAZ
The future?	While some flammable gas sensing applications are ideally suited to optical gas sensing, with the recent advances in MEMS technology and design, the vast majority of industrial safety applications and instruments will continue to benefit from the tried and tested, low-cost, high performance gas detection provided by pellistors.

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[63] Spinelle, Laurent et al. "Review of Portable and Low-Cost Sensors for the Ambient Air Monitoring of Benzene and Other Volatile Organic Compounds." Sensors (Basel, Switzerland) 17.7 (2017): 1520. PMC. Web. 20 Oct. 2017.

[64] Arshak K., Moore E., Lyons G.M., Harris J., Clifford S. A review of gas sensors employed in electronic nose applications. Sens. Rev. 2004;24:181–198. doi: 10.1108/02602280410525977.

Table 21: Advantages and Disadvantages of Pellistors

Advantages	Disadvantages
Can sense flammable gases that optical infrared sensors cannot, such as hydrogen	Catalyst materials used in the sensor are susceptible to temporary inhibition or permanent poisoning from some gases such as sulfides, silicones, or halides
Newer MEMS-type pellistors overcome power consumption and fragility concerns and are highly manufacturable	Relatively high power consumption needed to maintain the internal temperature of the sensor at the correct temperature
Intrinsically safe	Sensors are fragile and may be susceptible to damage if exposed to significant mechanical shock or impact
Low cost	High limit of detection and low accuracy

Pellistors have been around for many years, and advancements in MEMS-type pellistors are helping them overcome some of the limitations they once suffered from. MEMS-type pellistors consume much less power and are less fragile than traditional pellistors. The introduction of MEMS technology now make small pellistor sensors highly manufacturable. Detection limits are not low enough for exposure monitoring but they continue to be well-suited for flammable gas sensing and safety applications. As the cost of these sensors continue to decrease, they become better candidates for applications outside of industrial safety applications, such as monitoring in homes near oil and gas activities to alert residents of hazardous explosive environments within their basements or crawl spaces.

7. CONCLUSION

Sophisticated monitoring technologies have often been the standard for ambient air monitoring in regulatory enforcement and episodic release scenarios. While there are still many advantages to employing such types of technology, new technology has utility in other types of applications and solutions. With advancements in monitoring and sensing technology that have already been made, and with new advancements demonstrated regularly, the door is open for community and exposure monitoring at lower costs and with more flexible deployment (such as mobile, aerial, or open-path) than previously possible.

The emergence of low-cost sensors is changing the way we think about air quality monitoring. For example, for fenceline methane monitoring, open path TDLAS and other laser absorption technologies with lower detection limits, increased precision, and much lower costs than with more commonly used open path ORS technologies have emerged, and are emerging in increasing numbers. Similarly, for benzene sampling, CRDS and TDLAS technologies have gained, and are continuing to gain better compound specificity with detection limits low enough to be relevant for screening concentrations at health-impact levels. For sampling VOCs generally, traditional technologies like low cost FIDs paired with triggered grab samples offer solutions that pair common place sensing solutions with new techniques for air assessment.

In other contexts, sensors have become inexpensive enough, such as those using MOS, to be able to deploy networks of large quantities of sensors to cover wide areas with high spatial resolution. Granted, while the cost of setting up a large network of low-cost sensors may end up costing the same or more than one sophisticated traditional ORS monitor, sensor networks now have the capability of monitoring many discrete locations at once, such as well heads, fencelines and/or homes, and can provide denser spatial resolution.

Although many advancements have been made in sensing technology, not all low-cost sensors have the accuracy or reliability to monitor for levels of pollutants and low enough detection levels to discern elevations above background. As a result, not all sensors are suitable for measuring concentrations at fencelines, or at significant distances from potential sources of emissions. Many of these sensors, though, are capable of detecting large leaks or significant events of elevated concentrations. For example, for technologies like EC sensors, some technologies are suitable for low-cost on-site leak detection when located near potential sources of emissions and configured appropriately.

In sum, as evidenced by this analysis, the market is changing very rapidly meaning technologies, technology deployment patterns, and data analysis capabilities continue to improve and drop in price. The next big step for this new wave of monitoring technologies is proof-of-concept through field testing that simultaneously delivers data valuable for site emissions characterization and community exposure assessment. One major question about the timeline for this next step lies in whether industry, government and community-led testing will be needed, or both. Similarly, it is unknown whether regulations will emerge that will drive technology deployment.

New sensing technologies are disrupting the air quality monitoring world. Based on the recent trends, we foresee the landscape of air pollutant sensing and air quality monitoring (both in technology development / deployment *and* data analysis) continuing to evolve and improve significantly in the next 5 to 10 years, alongside the coming age of “big data” and the Internet of Things. At the center of this change will be the field use of technology available today and the information and experience leaned from it.

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