INFICON

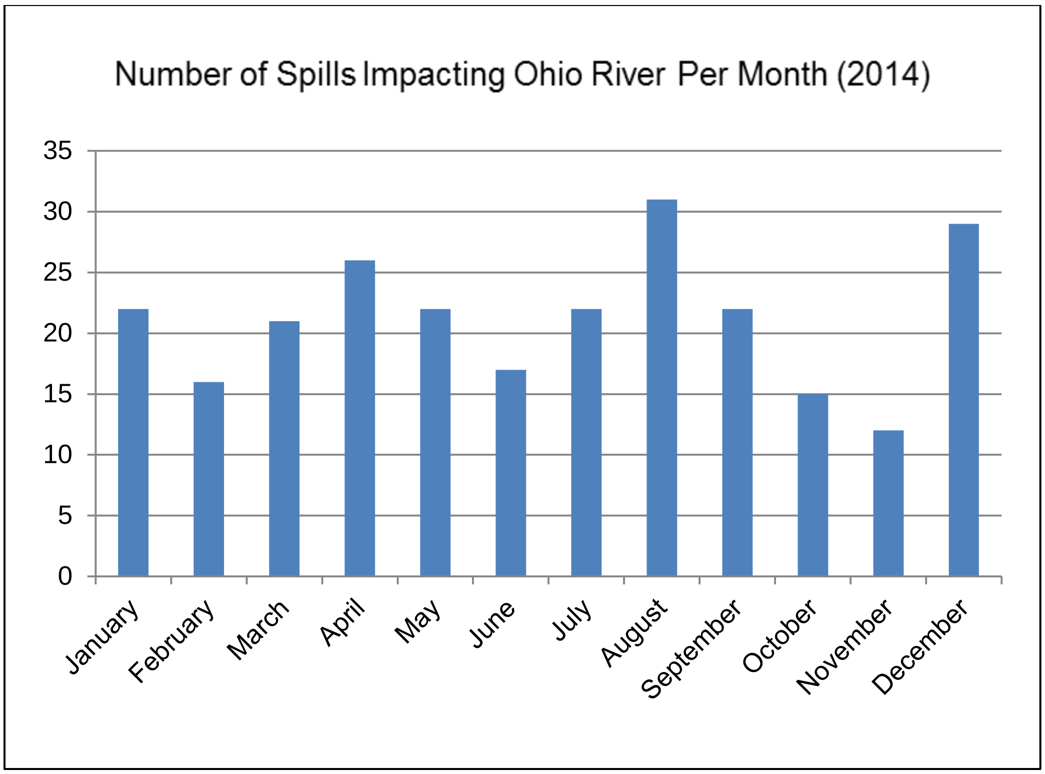
Protect Drinking Water with Continuous, Unattended Monitoring

A WHITE PAPER ON VOLATILE ORGANIC COMPOUND SAMPLING USING CMS5000 MONITORING SYSTEM

Introduction

In January 2014, an estimated 10,000 gallons of 4-Methylcyclohexanemethanol (MCHM), an industrial chemical used to process coal, spilled into the Elk River in West Virginia, USA[1]. The spill occurred upstream of the Kanawha County municipal water intake system, contaminating the water supply of nearly 300,000 people. Large scale chemical spills such as this have drawn attention to the importance of safeguarding water supplies, especially near municipal water system intake locations. While the Elk River spill drew headlines due to its size and scope; many less noteworthy industrial spills occur regularly along rivers and lakes. In 2014, the National Response Center (NRC) recorded an average of five spills per week in water systems around the nation. On the Ohio River an average of 20 spills per month were recorded. (See Figure 1.) These spills included gasoline, diesel, cyclohexane, and styrene[2].

Figure 1: ORSANCO recorded spills



http://www.orsanco.org/images/stories/files/emergencyResponseProgram/cincinnatidatarequest%20jan%202013%20-%20dec%202015.xls

Ohio River Valley Water Sanitation Commission (ORSANCO)

ORSANCO was formed in 1948 to monitor and control pollution in the Ohio River Valley[3]. They monitor many biological and chemical markers indicative of water quality. After a spill of carbon tetrachloride in 1977, the Organics Detection System (ODS) was created in 1978 to ensure future spills would be detected and identified then immediately notify officials to coordinate emergency response activities[4]. A system was devised where daily samples were collected by operators to monitor volatile organic compounds (VOCs) in surface waters. ORSANCO was eventually able to implement an automated system which provided continuous VOC data.

Problem

ORSANCO integrated VOC monitoring into the water treatment plant infrastructure of the Ohio River, the main source of drinking water for more than 5 million people[5]. ORSANCO monitors the raw water influent at 16 locations along the river for VOCs. They monitor 30 known toxic VOCs that are representative of spills that may occur based on the industries that operate along the river. (See Table 1.) If a spill resulting in significant levels of VOCs occurs in the river, ORSANCO alerts state and federal agencies and downstream water utilities to effectively respond to the situation and mitigate the risk.

Table 1: Ohio River monitoring compound list

Peak #	Compound	CAS #	R.T.
1	Trichlorofluoromethane	75-69-4	2:35
2	Bromomethane	74-83-9	3:03
3	1,1-Dichloroethylene	75-35-4	3:03
4	Methylene Chloride	75-09-2	3:33
5	trans-1,2-Dichloroethylene	156-60-5	3:51
6	Acrylonitrile	107-13-1	3:51
7	1,1-Dichloroethane	75-34-3	4:23
8	Chloroform	67-66-3	5:49
9	1,1,1-Trichloroethane	71-55-6	6:10
10	Carbon tetrachloride	56-23-5	6:30
11	1,2-Dichloroethane	107-06-2	6:54
12	Benzene	71-43-2	6:54
13	Trichloroethylene	79-01-6	8:18
14	1,2-Dichloropropane	78-87-5	8:48
15	Bromodichloromethane	75-27-4	9:28
16	cis-1,3-Dichloropropylene	10061-01-5	10:39
17	Toluene	108-88-3	11:33
18	trans-1,3-Dichloropropylene	10061-02-6	12:12
19	1,1,2-Trichloroethane	79-00-5	12:43
20	Tetrachloroethylene	127-18-4	13:06
21	Dibromochloromethane	124-48-1	13:50
22	Chlorobenzene	108-90-7	15:42
23	Ethylbenzene	100-41-4	16:06
24	1-Chloro-2-fluorobenzene*	348-51-6	16:35
25	Styrene	100-42-5	17:31
26	Bromoform	75-25-2	17:54
27	1,1,2,2-Tetrachloroethane	79-34-5	19:09
28	1,3-Dichlorobenzene	541-73-1	21:08
29	1,4-Dichlorobenzene	106-46-7	21:20
30	1,2-Dichlorobenzene	95-50-1	22:04
31	Hexachlorobutadiene	87-68-3	26:06

* Internal standard

Early water monitoring efforts by ORSANCO employed manual sample collection techniques and the transfer of those samples to a benchtop gas chromatograph (GC) for analysis. (See Figure 2.) This approach is not only cumbersome and time consuming, but may compromise the sample integrity as well. ORSANCO investigated options for automated sampling systems designed to collect samples at timed intervals. Automatic sampling offered the advantage of more regular and frequent sample collection than that of manual sample collection.

Figure 2: Benchtop gas chromatograph with purge and trap sampling system and automatic sample collector[4]

https://archive.epa.gov/emergencies/content/fss/web/pdf/schulte.pdf

Solution

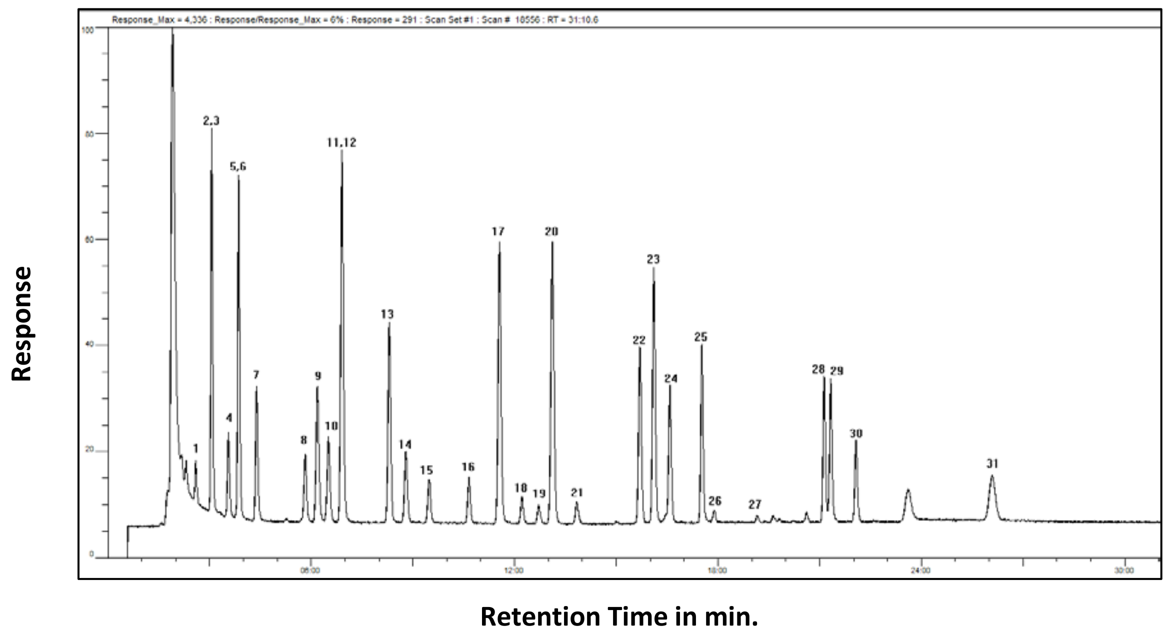
ORSANCO installed the INFICON CMS5000 Monitoring System at select locations on the Ohio River, for automated, unattended monitoring of VOCs in the Ohio River. (See Figure 3 and 7.) The CMS5000 Monitoring System is a self-contained system utilizing GC technology for continuous, unattended, remote monitoring of air or water. It rapidly analyzes VOCs in water using a modified EPA purge and trap concentrator protocol. No sample preparation is required. The state-of-art SituProbe™ purges VOCs from a continuous water stream, collects them on a Tri-Bed carbon concentrator, and then desorbs them to the GC for analysis. The Micro Argon Ionization Detector (MAID) provides sensitive detection of organic compounds having an ionization potential of 11.7 eV or below. CMS5000 has:

- low consumable load
- argon tank lasts approximately 4-6 months
- toluene permeation tube has an 6-8 year lifespan
- MAID detector source has a 96 year half-life

Figure 3: CMS5000 installed at ORSANCO site in Midland, Pennsylvania, USA

A water source can be piped directly into the CMS5000 flow vessel, continuously providing water samples to the instrument. ORSANCO customized the flow system design to allow for grab samples; and allow calibration and verification standards to be easily introduced. The compact wall mounted design of the CMS5000 allows for easy integration into pre-existing water treatment infrastructures. CMS5000 is capable of detecting all of the ORSANCO compounds of interest with a detection limit of 1 ppb or less. (See Figure 4.)

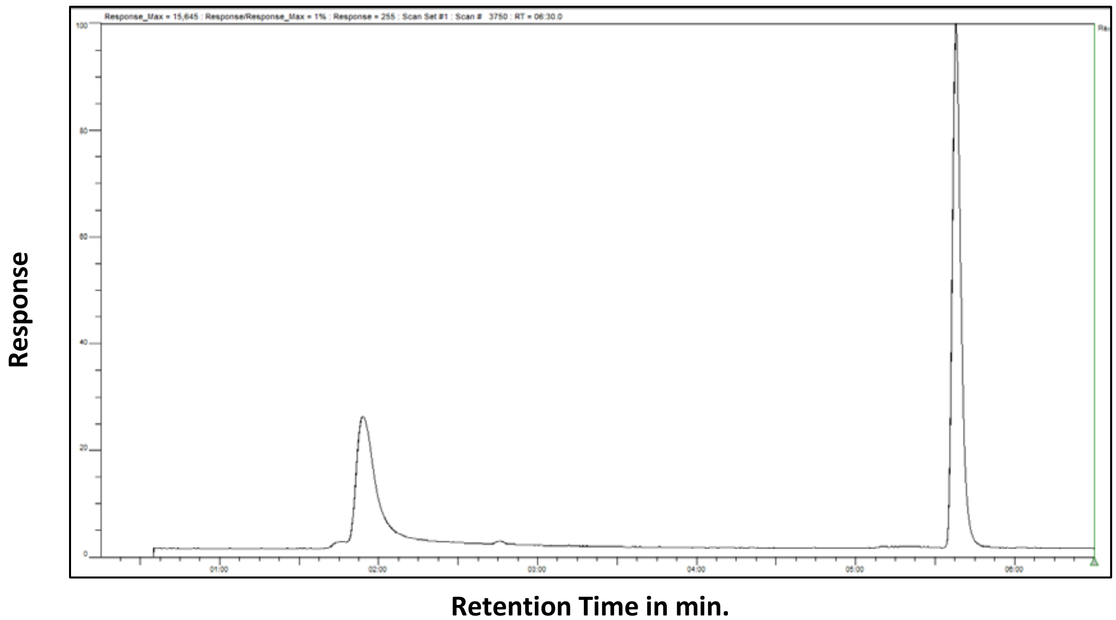
Figure 4: ORSANCO 1 ppb calibration standard



Column—DB-624 30 m, 0.32 mm ID, 1.8 µm df, Conc. Fill: 1 min.
GC Temp. Profile—50°C (hold 5 min.) to 90°C at 4C/min., to 180°C at 10°C/min. (hold 30 s) to 50°C at 25°C/min. (hold 1 min. 30 s)

A DB-624 column was selected to separate the compounds of interest, and a 30 minute temperature programmable method was developed. Five point linear fit calibration curves were created using the results from these standards. All calibration curves have a Percent Relative Deviation (%RSD) of 10% or less. The method is calibrated from 1 to 10 ppb. The calibration remains stable over a long period of time, and only requires calibration every 4-6 months. Calibration accuracy is monitored using a check standard method, which samples from an onboard toluene-filled permeation tube. (See Figure 5.)

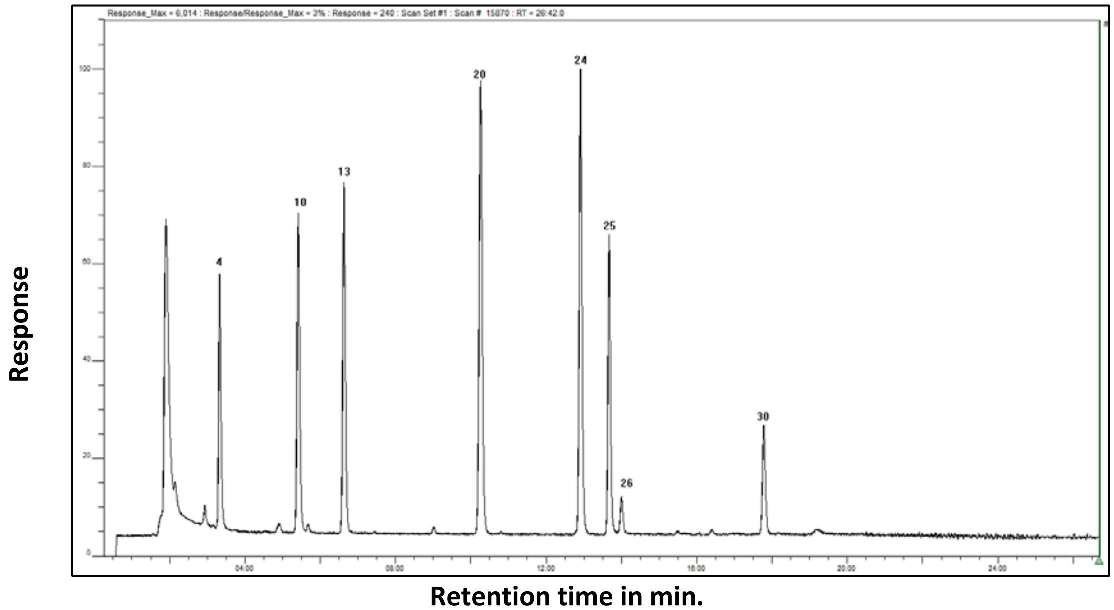
Figure 5: Toluene Check Standard



GC Temp. Profile—50°C (hold 1 min.) to 160°C at 20°C/min.

The toluene permeates at a constant rate, providing a stable concentration for every check standard method run. The toluene check standard response is used to compensate for seasonal water temperature changes and normal detector sensitivity fluctuations. Notable changes in one or more of these parameters may serve as an indication that preventive maintenance is needed to ensure data quality is kept within acceptable limits. As an additional test of calibration accuracy, ORSANCO performs a daily continuing calibration verification (CCV) using a standard that contains a subset of the 30 compounds of interest. (See Figure 6.)

Figure 6: ORSANCO CCV Standard

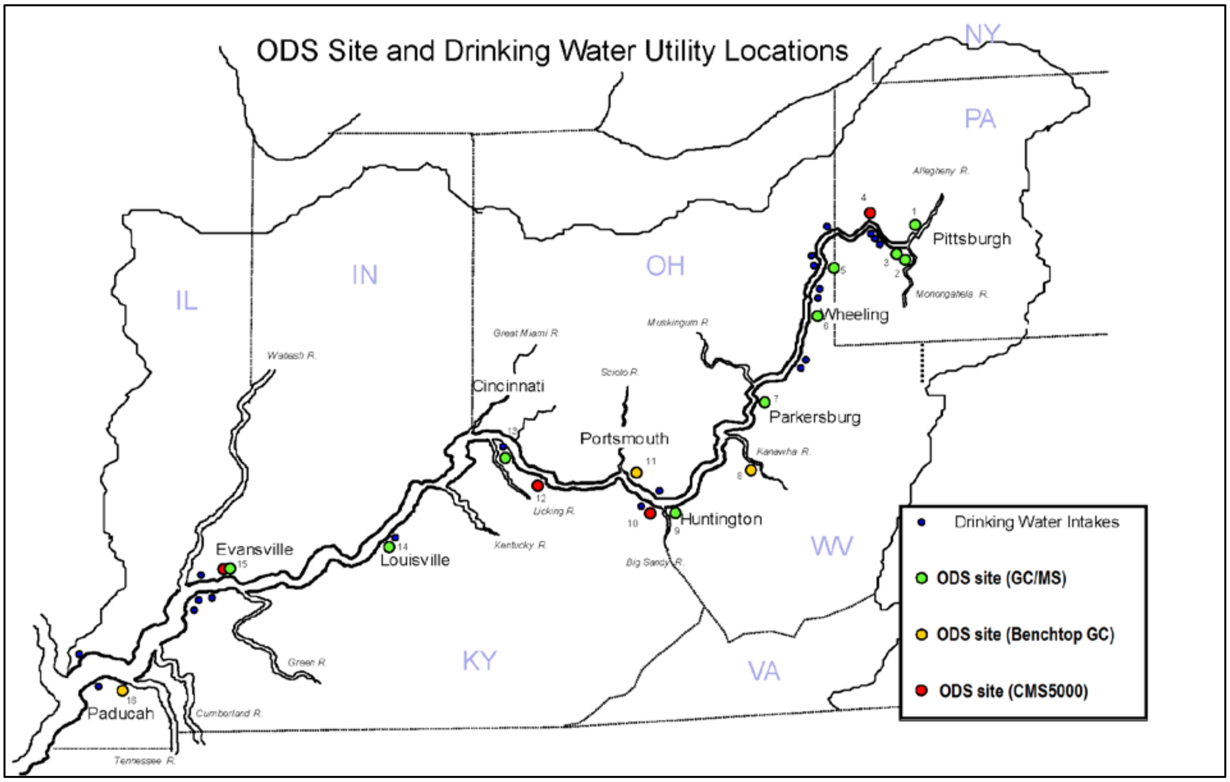


GC Temp. Profile—50°C (hold 5 min.) to 90°C at 4°C/min., to 180°C at 10°C/min. (hold 30 s) to 50°C at 25°C/min. (hold 1 min. 30 s)

Using I/O or Modbus, CMS5000 can be integrated into many existing networks such as SCADA systems. Alternately, CMS5000 can upload data directly to a centralized server. ORSANCO was able to easily establish communication using Modbus protocol.

An automated method sequence controls the instrument to analyze raw water influent every two hours. Each analysis creates a data file, which is saved on both the CMS5000 and an on-site computer. A NEXSENS data logger pulls the data files from the computer and uploads them to a centralized server. If one or more of the compounds of interest exceeds the alarm limit of 2 ppb, the server sends e-mail alerts to ORSANCO personnel. If further confirmation is required, additional samples are collected and analyzed using Gas Chromatograph/Mass Spectrometer (GC/MS). CMS5000 systems were implemented at several points along the Ohio River (See Figure 7.) The ORSANCO Emergency Response Program responds to an alarm based on the concentration level and the toxicity of the detected compound. They will then coordinate with the appropriate government agencies to quickly manage the situation.

Figure 7: Current Organic Detection System (ODS) instrumentation



https://archive.epa.gov/emergencies/content/fss/web/pdf/schulte.pdf

Conclusion

Using a CMS5000 Monitoring System with purge and trap technology to continuously monitor river water at multiple locations is an effective way to detect chemical spills and intercept contaminated water from entering municipal water system intake locations. The stable detector, data integration capability, low consumable load, and onboard check standard methodology all make the CMS5000 Monitoring System the ideal instrument for remote, unattended monitoring.

References

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