



Managing emissions

— In oil and gas facilities



Refinement of crude oil into the products and fuels we depend on is incredibly complex. Harmful and highly-regulated volatile organic compound (VOC) emissions often pollute the air near these sites. But it's not just air quality refineries need to preserve. Some refining stages require water—either fresh water in direct contact with crude oil or reused water to cool products after heat-intensive processes. Either way, water pollution is the result.

Habitats, wildlife, water quality and people are put in jeopardy if this wastewater is dumped into the environment without treatment. To comply with environmental statutes, facilities must either fully treat

this wastewater or treat it enough to safely comingle with outside wastewater destined for municipal treatment.

But every facility is unique. An off-the-shelf VOC emission treatment solution won't cut it. Specific problems call for specific solutions. Developing that solution requires a deeper understanding of sources of VOCs in wastewater streams and the methods used to collect and analyze VOC samples.

Only then can a truly effective treatment solution be developed.

We cover it all in this resource.

Common VOC sources in oil refinery wastewater treatment

Many of the processes that turn crude oil into various usable products require water. Below, we describe common processes that result in water pollution.



Desalting

This early-stage process removes brine from crude oil. The brine can cause corrosion of refining equipment if it's not addressed. The process starts by injecting fresh water into the crude oil. This water mixes with the brine in the oil, decreasing the overall concentration of salt via dilution.

Then, the oil is dehydrated and sent on for further refinement. Due to its contact with the crude oil, the briny water is also impacted with VOCs that must be treated.

Fluid catalytic cracking

[This late-stage refinement](#) occurs in the production of gasoline, butane, propane and other "lighter" fuels. It's a chemical reaction meant to break crude oil's larger molecules into smaller ones.

The catalyst is typically made up of powdered silica and alumina. It's fluidized using hot vapor and then mixed with crude oil under high heat, causing the long-

chain crude molecules to “crack” into smaller ones. Because each of the desired fuels that result from fluid catalytic cracking has a different boiling point, the fuels vaporize one by one and are collected. They’re then separately re-condensed using cooling water that must be treated if it’s polluted during the process.

Steam stripping also occurs during fluid catalytic cracking to recover remnant product from the spent catalyst. This also results in polluted water that must be treated.

Hydrocracking

This process combines the fluid catalytic cracking process with hydrogen to produce cleaner-burning gasolines, diesel fuel and jet fuel. Again, the long-chain crude oil molecules are cracked into smaller molecules. Hydrogen is added because it increases the yield of the desired short-chain molecules.

Catalytic hydrodesulfurizing

Crude oil and natural gas typically contain sulfur, which is heavily regulated around the world. Catalytic hydrocracking is integral to the production of ultra-low sulfur diesel fuel and fuels used in aviation, maritime and power generation applications. In addition, removing sulfur is important because even in small concentrations it can poison the catalyst metals used in catalytic reforming (which is described below).

Crude is vaporized under high pressure and high heat and then sent to a reactor where it meets the catalyst (usually aluminum-based with additive cobalt and molybdenum). Then, pressure is reduced and the vaporized materials pass through a gas separator. Off-gases (including hydrogen sulfide, H_2S) are sent away for treatment and recycling. The resulting materials include methane, ethane, butane and propane in addition to the low-sulfur fuel product. As with other refining processes, reused water is used in the cooling process.

Catalytic reforming

This process is characterized by the restructuring of low-octane hydrocarbon molecules to create a blending stock used to make higher-octane products. Input petroleum naphthas are combined with hydrogen-rich gases at high temperature and pressure so that they vaporize. The mixture separates during catalysis (the catalyst is usually a silica or silica-alumina base with platinum or rhenium additives) into useful byproducts like propane, butane or benzene in addition to the desired high-octane reformate used in blending stocks. As before, reused water is used to cool the materials after catalysis.

Complementing your refinery wastewater treatment

As noted in the examples above, water is used in a variety of refining processes. The extent of refinery wastewater treatment depends on the extent to which water is polluted by VOCs or other compounds.

Fresh water is necessary for processes that call for direct contact with crude oil or oil derivatives, but water purity is not an issue in cooling or re-condensing stages. Refinery wastewater treatment is as much about recycling water for reuse as it is cleaning it up enough for compliant discharge into the environment.

BioAir Solutions is an industry leader in eliminating emissions that impact oil refinery wastewater. Our multi-step treatments include the installation of an integrated system that starts with [degasification](#) of wastewater. It's followed by biological (and sometimes also physicochemical) treatment of polluted airstreams that result from degasification.

We discuss the way such a system works in a later section. But before the right treatment can be specified, an accurate accounting of the VOCs impacting a site must be taken.

Testing methods for VOCs

These compounds pose a double-edged threat: Not only can [VOC emissions](#) cause nuisance complaints from nearby residential areas encroaching on industrial sites, they're also heavily-regulated pollutants known to harm people, wildlife and the environment.

Accordingly, the U.S. Environmental Protection Agency has worked alongside industry leaders to develop VOC testing methods that identify and quantify emissions. The emission [assessments](#) we provide are a critical early step toward developing a solution that reduces or eliminates these harmful emissions.



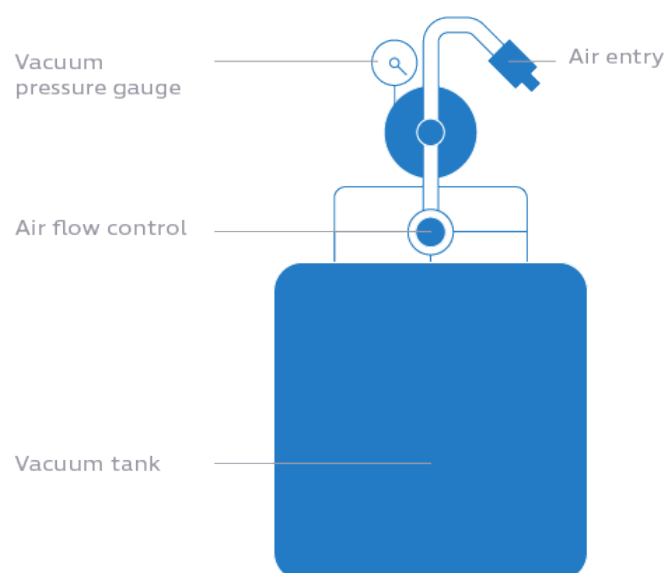
VOC testing methods TO-15, TO-17 and ASTM D5504

The EPA's [Method TO-15](#) outlines proper VOC testing by collecting air in a specially-prepared stainless steel vacuum canister. Air is drawn into the canister through a flow controller for as little as an hour or as long as two days. Then, the canister is sent for laboratory analysis. Collection of air samples using VOC testing method TO-15 is shown in [this video](#).

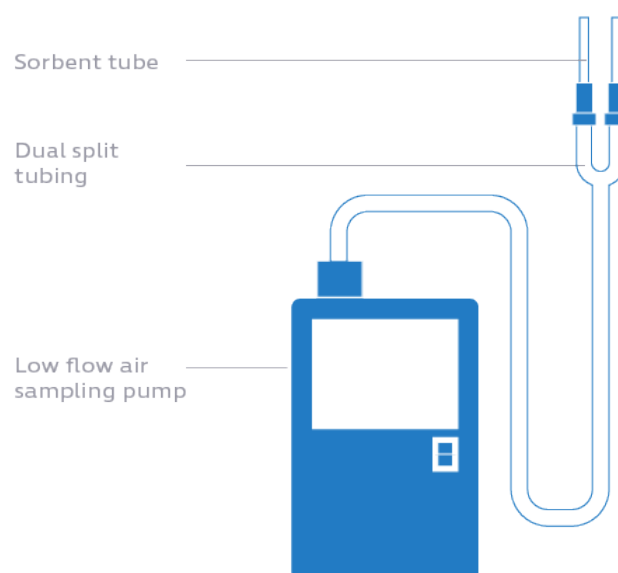


See the TO-15 testing method in action.

TO-15



TO-17



[Method TO-17](#) differs in that air samples are collected through sorbent tubes instead of canisters. The sorbent traps VOCs as air passes through the tube. Prior to analysis, the sample is freed from the sorbent via thermal desorption. A TO-17 test kit is shown in [this video](#).



Watch to learn more about TO-17.

Reduced organic sulfur compounds (ROSCs) commonly accompany volatile hydrocarbons as emissions from oil & gas processing facilities. Unfortunately, most conventional VOC testing methods don't accurately detect sulfur compounds. In response, the [ASTM D5504](#) testing method provides for the collection of air samples in inert plastic bags. Then, those samples are analyzed by sulfur chemiluminescence detectors (SCDs). Sulfur chemiluminescence detection is described in a later section.

Regardless of the VOC testing method used, the next step is analysis of the sample.

GAS CHROMATOGRAPHY AND MASS SPECTROMETRY (GC/MS)

Gas chromatography is a physiochemical separation technique, while mass spectrometry analyzes compounds via ionization. Each provides complementary information during VOC testing. To get the most comprehensive profile of the VOCs emitted from a site, the two methods are coupled together.

There's rarely only one compound in an air sample. Usually, several VOCs are emitted from a facility. A gas chromatograph separates compounds in an air sample so

that individual identification of compounds can be made by analytical detectors such as mass spectrometers (MS) or sulfur chemiluminescence detectors (SCDs).

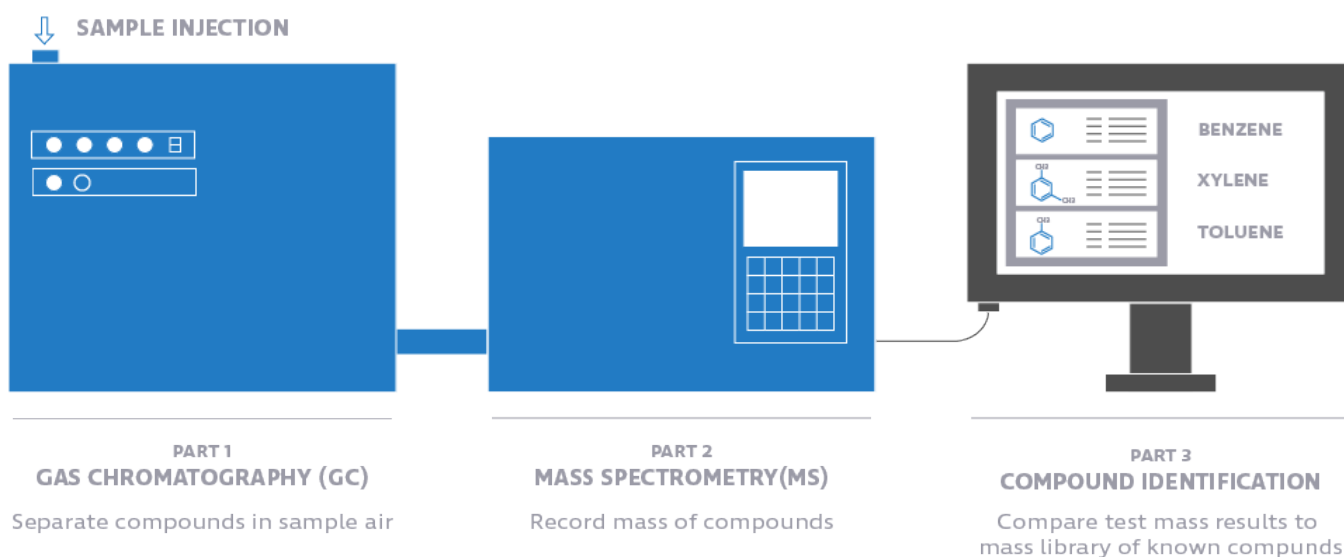
A mass spectrometer sends ionized atoms from the collected compounds through a sensitive filter that records their amounts and masses. Scientists then compare the data gathered from the mass spectrometer against a list of known compounds based on their mass, identifying both VOCs and ROSCs as well as determining their concentration. [Watch this video](#) to better visualize how GC/MS works.



See how GC/MS works.

GAS CHROMATOGRAPHY AND SULFUR CHEMILUMINESCENCE DETECTION (GC/SCD)

Sulfur chemiluminescence is a detection method that quantifies sulfur concentration by recording the amount of light given off during a chemical reaction. Like mass spectrometry, sulfur chemiluminescence detectors are commonly coupled to gas chromatographs and analyze emission streams containing ROSCs through a two-stage process.



The first stage is the introduction of a sulfur-containing sample plus hydrogen (H_2) and ambient air into a reaction furnace under vacuum to generate sulfur monoxide (SO). In the second stage, the sulfur monoxide is carried to a reaction chamber where it reacts with supplied ozone (O_3). The result of that reaction is sulfur dioxide (SO_2) and UV light.

The UV light generated by this reaction is directly proportional to the amount of sulfur in the sample. The light is measured by a photomultiplier tube; that value is then compared against known values.

Crafting your VOC emission solution

VOC testing and analysis tells us which compounds are emitted at a facility as well as each compound's concentration. The next step is to run internal and governmental comparisons. The initial comparison is the analysis of VOC testing at your site against our database from previous jobs. It's a quick way for us to determine the treatability of your challenge. If our database yields no results, our scientists will conduct a thorough literature review to see if your problem can be treated.

The other comparison is the sample VOC concentrations against statutory VOC limits. This is a critical step because not all VOCs are regulated equally. Comparing site sample data to statutory VOC limits will help us further craft the emission [treatment solution](#) perfectly tailored to the challenge at your site.

In the U.S., we comply with the EPA. But as an international company we're well-versed in navigating the global patchwork of environmental regulations.

VOC testing and analysis is a key step to solving an oil and gas facility emission challenge. When our experts are armed with detailed information about the emissions coming from your site, they're empowered to develop the custom treatment solution uniquely tailored to solve your exact problem.

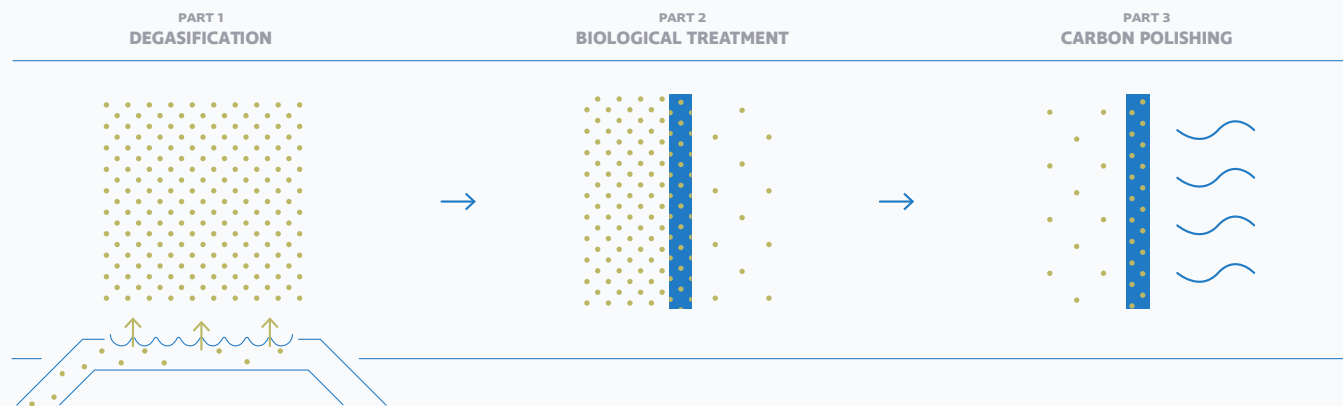
We discuss the ideal treatment methodology below.

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Eliminating VOCs in oil and gas wastewater streams

At oil and gas refining sites around the world, staying compliant with applicable environmental statutes is a two-front battle. Both air and water are polluted by VOCs and other unwanted compounds during refining; both must be treated before they're released into the environment.

In an earlier section, we demonstrated how VOCs impact water used in various refining processes. Here, we discuss the ideal scenario for eliminating these compounds from oil and gas facility wastewater streams.



Stage 1: Degasification

When VOCs and other unwanted compounds dissolve into the water used at various stages of crude oil refinement, the first step in refinery wastewater treatment is to get those compounds out of the water. That's because the most effective elimination of those compounds occurs when they're in the air phase.

Common degasification methods include:

- Pressure reduction, which decreases the solubility of the gases dissolved in water when the pressure of the mixture is reduced.
- Thermal reduction, which reduces solubility of gases in aqueous solutions when the temperature is increased.
- Membrane degasification, in which water with dissolved gases is pumped inside a membrane and the space outside the membrane is vacuated. This causes the gases to leave the water and escape through the membrane.
- Inert gas substitution, where inert gases like helium, argon, nitrogen or ambient air are bubbled into a vigorously stirred solution and substitute the unwanted compounds.

BioAir Solutions' [Rainfall® degasifier](#) is designed to efficiently eliminate compounds impacting oil refinery wastewater. The polluted water is pumped to the top of the degasifier vessel, where it falls downward through random media featuring high surface area and void fraction. This turns the water into very small droplets.

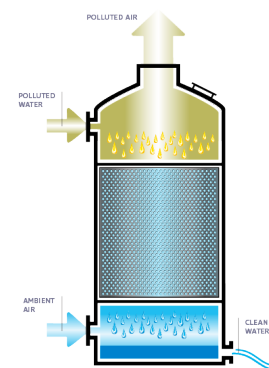
Meanwhile, ambient air is pumped upward through the media. When the air meets the small water droplets, the dissolved gas molecules move from the water phase into the air phase. The treated water is drained safely away.

But refinery wastewater treatment cannot stop here. So far, we've traded one kind of pollution for another. The second and third stages treat the newly-polluted air.

Stage 2: 'Green' biological treatment

As pressure mounts on refineries to enhance the environmental friendliness of their processes, treating polluted air using green methods is an attractive opportunity. [Biological treatment](#) of foul odors is well established. It's not as prevalent in the treatment of oil or gas refinery emissions, but studies have shown biological methods can cost effectively eliminate many VOCs.

The newly-polluted air that results from degasification of refinery wastewater is pumped into a vessel and directed upward through porous media. Inside the media, the air is in contact with small droplets of irrigation water that trickles downward from the top of the vessel and with bacteria and other microorganisms that reside within the media.



See how Rainfall works [here](#).

As pressure mounts on refineries to enhance the environmental friendliness of their processes, treating polluted air using green methods is an attractive opportunity.

The microorganisms are naturally selected based on their ability to metabolize organic compounds. The waste products of that consumption are drained safely away with the downward-trickling water while clean air is released from the top of the vessel.

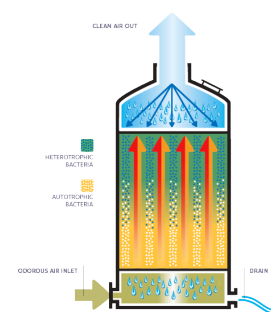
For this stage, BioAir recommends its [EcoFilter® biotrickling filter](#). EcoFilter units feature proprietary EcoBase® structured synthetic media which significantly enhance the conditions inside the treatment vessel. In addition, the design of the EcoFilter supports a greater diversity of biology, which translates to the consumption of a wider range of unwanted compounds.

Stage 3: Adsorptive media polishing for the cleanest possible air (optional)

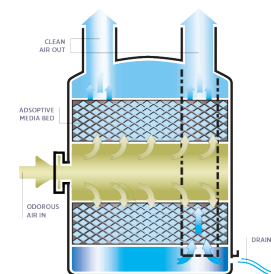
Sending the air treated in Stage 2 through an adsorption filtration unit ensures it is as clean as possible. Adsorption filtration, which may include activated carbon, differs from biological treatment in that it is a physical adsorption process. During this stage, air is forced through a bed of heated or electrically-activated adsorption media. Polluting compounds stick to the adsorbent and clean air is released.

[EcoCarb® adsorption media filters](#) feature porous adsorptive beds that finely disperse air and trap offending compounds over extended service lives. Installing an adsorption media polishing stage after biological treatment creates a best-of-both-worlds scenario:

- End-stage adsorption polishing results in incredibly clean air thanks to the effectiveness of the biological system that precedes it. EcoFilter units routinely exceed 99% removal efficiency on their own.
- Due to the cleanliness of the air entering the polishing stage, adsorption media bed lifetime is extended.
- The one-two punch of the EcoFilter and EcoBed treatment systems result in the cleanest possible air while also substantially reducing overall operating and maintenance costs.



See how EcoFilter works [here](#).



See how EcoCarb works [here](#).



Turnkey refinery wastewater treatment VOC control

The regulations governing natural gas and oil refining operations are strict and getting stricter. The pressure's on for fossil fuel processors to meet stringent statutory regulations while also meeting the needs of today's modern economy.

BioAir Solutions' experts work collaboratively with your team to identify effective, efficient oil refinery wastewater treatment solutions that ensure you stay compliant and that the environment stays clean. We call our process [BioAir Complete®](#), and it combines all [our services](#) into one integrated program that tackles your emissions challenges from beginning to end.

If you want to talk through a specific challenge at your site, [contact us](#) to start a discussion or request a site audit.

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[REQUEST A SITE AUDIT](#)