CHAPTER 4.0

ODOR- AND CORROSION-CAUSING COMPOUNDS

4.1 Overview

Knowing the chemical composition of malodorous gas mixtures, the contribution of individual odorants to odor thresholds and intensity, and the mechanisms by which odorants are generated in sewers is key to developing optimal odor-monitoring and -control strategies. This chapter describes advances in identifying malodorous compounds emitted from sewers, biological mechanisms for odorous and corrosive chemical formation in sewers, and emerging measurement methods. Though over 60 papers were reviewed for this assessment, only a small fraction contributed new knowledge related to the subjects under consideration. Those papers are referenced where applicable throughout this chapter.

The knowledge base of odorous chemicals from sewers has not expanded appreciably during the past decade or more. Far more work related to odors from wastewater treatment processes appears to have been completed and will be referenced in this chapter where appropriate (for example, emerging odor measurement methods). The database related to chemicals that compose the mixtures of malodorous gases emitted from sewers is sparse and has limited advances toward understanding the specific chemical components that should be controlled to avoid odorous emissions from sewers. The knowledge base associated with corrosive gases is focused entirely on hydrogen sulfide. Hydrogen sulfide formation mechanisms, corrosion mechanisms, and prevention strategies are described in Chapter 9. A shorter summary of factors affecting hydrogen sulfide formation and release in sewers is provided in this chapter.

4.2 Malodorous Compounds Associated with Municipal Wastewater

Malodorous compounds are often characterized as small, hydrophobic, volatile molecules that contain one or two functional groups composed in part of oxygen, sulfur, or nitrogen. Several general classes of malodorous compounds that may be relevant to odors associated with sewers are listed in Table 4-1.

Table 4-1. Odorous Compounds Associated with Untreated Wastewater

Class of Compound	Relevant Examples
Inorganic gases	Ammonia, hydrogen sulfide
Mercaptans	(Allyl, amyl, benzyl, crotyl, ethyl, methyl, propyl) mercaptans
Other organic S	Dimethyl sulfide, diphenyl sulfide, thiocresol, thiophenol
Amines	(Dibutyl, diisopropyl, dimethyl, ethyl, methyl, triethyl) amines
Diamines	Cadaverine (1,5-pentanediamine), putrescine (butanediamine)
Other organic N	Indole, pyridine, skatole
Volatile fatty acids	(Acetic, propionic, butyric, isovaleric) acids

The compounds listed in Table 4-1 have a wide range of characteristic odors. For example, hydrogen sulfide is characterized by rotten-egg odors, but several of the mercaptans cause odors characterized as decaying cabbage or vegetables, and other organic sulfur-containing compounds span a wide spectrum of odor characteristics, ranging from "skunk-like" to "garlic-like." Several amines are characterized by "fishy" odors. The two diamines are often characterized simply as "putrid." Two of the three other organic nitrogen-containing compounds (indole and skatole) are characterized as having strong fecal odors. Existing knowledge does not allow for accurately predicting the characteristic odors of various mixtures of these compounds. However, hydrogen sulfide, with its characteristic rotten-egg smell, is widely assumed to be the most prevalent malodorous and corrosive compound in the wastewater collection system. Additional details related to corrosion mechanisms are described in Section 4.4. The remainder of this section focuses on odorous gases.

Sato et al. (2001, 2002) completed two separate studies that taken together support the generally accepted belief that most odorous compounds emitted from sewers form during transport and are not appreciably discharged directly to municipal sewer systems. Sato et al. (2002) identified and quantified odorous gases associated with freshly excreted human feces. Toilet headspace samples were collected immediately after human defecation. The concentrations of malodorous compounds were generally low: 5–26 ppb for hydrogen sulfide, 2–15 ppb for methyl mercaptan, less than 100 ppb for ammonia, and approximately 10 ppb for volatile fatty acids (VFAs). Interestingly, concentrations of VFAs, particularly acetic acid, were five orders of magnitude higher for subjects with diarrhea than for normally healthy subjects. This implies that direct discharges of VFAs may be significant during flu season, but additional research would be needed to quantify the contribution of such discharges.

Sato et al. (2001) also collected wastewater (human waste) samples from a storage tank at a community wastewater treatment plant (it was not stated but is assumed that the wastewater was sampled prior to treatment and is representative of end-of-sewer samples). Liquid samples were transferred to the gas phase through purging with helium and were analyzed by gas chromatography with mass spectrometry (GC/MS) (nonsulfur compounds) or gas chromatography with flame photometric detection (GC/FPD) (sulfur species). Approximately 90 percent of the malodorous compounds on a gas phase molar basis were C2 to C5 VFAs. Acetic acid was the dominant VFA (up to 120 ppm), followed by propionic acid (up to 27 ppm). Sulfur-containing compounds were dominated by hydrogen sulfide (up to 50 ppm) and methyl mercaptan (up to 1.1 ppm). Nitrogen-containing compounds were dominated by ammonia (up to 34 ppm) and trimethylamine (up to1.2 ppm). Pyridine, pyrrole, indole, and skatole were also detected. Dichlorobenzene, a common deodorizer used in household toilets, was also detected.

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It is clear that most malodorous compounds associated with municipal sewers actually form during transport. Biological transformations that lead to the formation of VFAs and other odorants associated with sewers are described in Section 4.3.

4.3   Odorous Gas Formation Mechanisms

Sewer collection systems offer a variety of environments for microorganisms to perform a wide range of microbial transformation processes. This variability is induced by the large flow fluctuations typically observed in most sewer networks, causing changes to the dissolved oxygen (DO) availability in the collection system and promoting erosion or deposition of sewer sediments and erosion and growth of biofilms. Aerobic conditions are often observed in partially filled gravity sewers, whereas anaerobic conditions occur generally in pressure sewers and full-flowing gravity sewers (Hvitved-Jacobsen and Volertsen, 2001) as well as inside some sewer biofilms and sediments. Because of the low level of nitrate concentrations in most wastewaters, anoxic conditions are generally not significant in sewers (Hvitved-Jacobsen, 2002).

Aerobic and anoxic microbial degradation of wastewater do not generally contribute significantly to the generation of odorous compounds in collection systems (Hvitved-Jacobsen and Volertsen, 2001). As such, this section focuses on anaerobic heterotrophic microbial processes that are involved in the generation of the odorous substances typically associated with sewer odor complaints.

Figure 4-1 shows the main anaerobic mechanisms related to carbon transformation in sewers: anaerobic hydrolysis, fermentation, methanogenesis, and sulfate reduction.

Anaerobic hydrolysis is an important precursor to the other anaerobic processes involving the transformation of large, complex organic molecules into smaller, simpler molecules that can be directly utilized by other microorganisms as a substrate. Hydrolysis directly provides the substrate for fermentation and sulfate reduction and indirectly provides substrate for both methanogenesis and sulfate reduction (via fermentation as an intermediate process). The organic products of anaerobic hydrolysis generally do not contribute directly to odor emissions from sewers, with the exception of the hydrolysis of organic sulfur-containing compounds by bacteria such as *Proteus spp.*, *Bacteroides spp.*, and *Clostridium spp.*, resulting in the production of hydrogen sulfide, organic sulfides, and disulfides (Hvitved-Jacobsen and Volertsen, 2001). However, in sewer systems without significant accumulation of sediments, fermentation and sulfate reduction are the dominant odor production pathways (Hvitved-Jacobsen, 2002).

Microbial fermentation involves the transformation of organic products (that is, readily biodegradable substrate) from anaerobic hydrolysis into fermentation products such as low-molecular-weight organic products and carbon dioxide. These organic products generally include a wide range of VFAs and volatile organic compounds (VOCs), which can contribute to the overall odor emissions potential from a sewer system (Hvitved-Jacobsen, 2002).
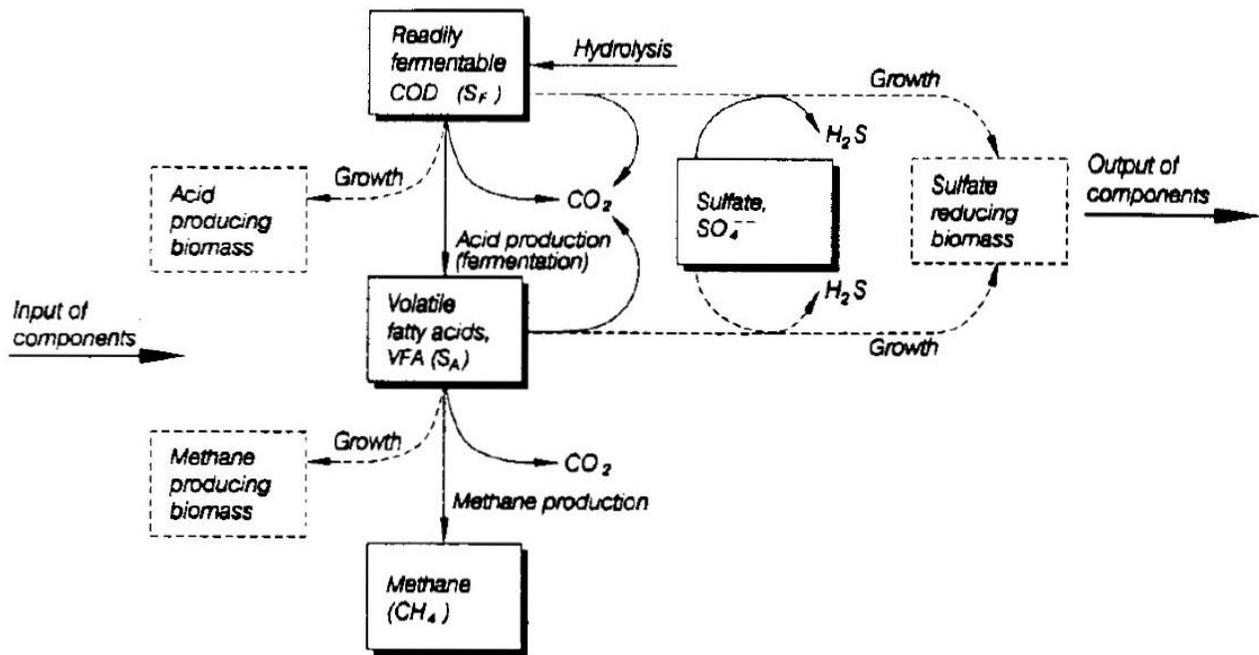
Figure 4-1. Anaerobic Carbon Transformations in Sewer Systems (Reproduced from hvitved-jacobsen, 2002)

Fermentation products can be used by both methanogenic and sulfate-reducing bacteria (SRB) as a substrate (Hvitved-Jacobsen and Volertsen, 2001); however, methanogens compete with SRB within biofilms and sediments. Typically, methanogenesis occurs only in areas where sulfate does not penetrate into the biofilms and sediments, and it is therefore regarded as a minor anaerobic process leading to odor formation (Hvitved-Jacobsen, 2002); sulfate reduction, on the other hand, contributes significantly to the production of hydrogen sulfide and is one of the key microbial processes involved in the generations of odorous and corrosive compounds in sewers.

4.3.1 Fermentation

Fermentation processes can occur in all of the major parts of the sewer system (in sediment, biofilms, and bulk wastewater), provided that a suitable anaerobic environment is present (Hvitved-Jacobsen, 2002). Short-chain organic molecules are produced during fermentation through oxidation and reduction reactions that use organic matter as both the electron donor and acceptor. In general, VFAs are generated through the fermentation of carbohydrates (for example, starch), whereas other sulfur-containing compounds, such as mercaptans, are generated through the fermentation of proteins (Hvitved-Jacobsen, 2002).

The specific fermentative pathways and products will be highly dependent on the substrates and microorganisms present (Hvitved-Jacobsen, 2002), but they can include many of the typical odorous substances—ammonia, amines, alcohols, aldehydes, ketones, VFAs, and organic sulfides such as ethyl mercaptan, dimethyl sulfide, methyl disulfide, and hydrogen sulfide (Hvitved-Jacobsen and Volertsen, 2001). As well as producing odorous compounds during fermentation, VFA creation can lead to a reduction in the pH of the wastewater, which in turn promotes the further release of organic sulfides and hydrogen sulfide into the sewer atmosphere (Hvitved-Jacobsen and Volertsen, 2001), thereby potentially exacerbating the odor problems caused by SRB.

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4.3.2 Sulfate Reduction

SRB are anaerobes and as such are relatively slow growing owing to the low energy yield of the sulfur reduction process. SRB will typically be washed out of the bulk wastewater; thus the majority of the sulfate reduction process occurs in sewer sediments and biofilms—sewer slime—where the bacteria are protected from the shear forces associated with the flow (Hvitved-Jacobsen, 2002). Some sulfate reduction can occur in the bulk wastewater flow because of biofilm entrainment; however, this is generally negligible compared to the processes occurring in the sediment and biofilms (Hvitved-Jacobsen, 2002). Generally, sulfate reduction in biofilms is the dominant sulfide formation mechanism in pressure sewers, whereas sulfate reduction in biofilms and sediments is important in gravity sewers (Hvitved-Jacobsen, 2002).

Some common species of SRB are *Desulfovibrio spp.* and *Desulfotamaculum spp.* (Hvitved-Jacobsen, 2002). Ito et al. (2002) studied the speciation and metabolism of SRB present in an oxic–anoxic sewer biofilm using fluorescent in situ hybridization combined with microautoradiography. SRB were observed to be a small fraction (4.8 percent) of the total cells present in the biofilm, with 70 percent of these identified as belonging to the Desulfovibionaceae family, and the remaining 30 percent to the Desulfobacteriaceae family. Further observation showed that less than 50 percent of the total SRB from the Desulfovibionaceae family was identified as *Desulfobulbus spp.* and *Desulfovibrio spp.* Less than 7 percent of the Desulfobacteriaceae family species were identified as *Desulfonema spp.*, suggesting that many species of SRB could not be identified with the probes used in the study. It was also demonstrated that SRB are able to adapt to rapidly changing environments (in terms of oxygen availability), with a percentage of the Desulfobulbus cells having the ability to utilize propionate with oxygen or nitrate as the electron acceptor (9 and 27 percent, respectively), and more than 40 percent of Desulfobulbus cells being able to utilize acetate under anoxic conditions (Ito et al., 2002).

The mechanism of sulfate reduction involves sulfate being reduced to hydrogen sulfide directly using organic carbon as a terminal electron donor according to the following generalized reaction pathway (Hvitved-Jacobsen, 2002):

$$SO_4^{2-} + \text{organic carbon} \rightarrow HCO_3^- + H_2S \qquad (4.3.2\text{-}1)$$

Depending on the substrate and type of bacteria present, low-molecular-weight organics such as acetate can be formed instead of bicarbonate (or carbon dioxide) (Hvitved-Jacobsen, 2002). The concentrations and availability of both sulfate and suitable organic carbon substrate are key aspects that control the type and kinetics of sulfide formation. The hydrogen sulfide formed via reaction 4.3.2-1 is not only one of the dominant odorous chemicals in sewers but also the primary source of sewer corrosion. The role of hydrogen sulfide as a source of sewer corrosion is summarized in Section 4.4, and additional details are provided in Chapter 9.

The amount of sulfate present in a collection system (and hence available for reduction and sulfide production) is dependent on the sulfate content of the raw wastewater (inorganic sulfates and sulfonates). This can also be influenced by groundwater hardness, potable-water treatment methods, and industrial sources (Hvitved-Jacobsen and Volertsen, 2001). When dealing with industrial inputs to collection systems, it is important to consider that other oxidized sulfur compounds, such as thiosulfate and sulfite, may be used as sulfur sources by SRB (Nielsen, 1991). Typically, raw municipal wastewater has sulfate concentrations greater than 5 to 15 g S/m^3, which for thin biofilms will not be the limiting condition for sulfide formation

(Hvitved-Jacobsen, 2002). However, for thicker biofilms or biofilm-covered sediments, the increased resistance to sulfate transfer can result in sulfate-limited conditions that may enable methanogenesis to occur, as noted by Vollertsen and Hvitved-Jacobsen (2000), who observed methane-containing gas cavities inside incubated beds of sewer sediments.

SRB use short-chain organic molecules (typically fermentation products such as alcohols, lactate, pyruvate, and some aromatics) as substrates. The biodegradability and suitability of the substrate is an important parameter affecting the sulfate reduction rate; for example, Hvitved-Jacobsen (2002) notes that enhanced sulfate reduction could occur in sewer systems accepting food-processing waste (which provides a more concentrated supply of readily biodegradable organic matter) or in sewer systems in areas where the organic substrate concentrations have been increased because of water shortages or water reuse. The form of exposure to organic substrates can also affect sulfate reduction; experiments conducted by Norsker et al. (1994) with laboratory-scale biofilm reactors indicated that pulse dosing of organic substrates (similar to concentration variations often found in sewers) increases the organic substrate availability to SRB and hence the sulfate reduction kinetics.

In addition to the sulfate and organic carbon concentrations, temperature and DO concentration impact the formation of sulfides. Wastewater pH is generally not a significant influence on sulfide production because SRB can exist between pH 5.5 and pH 9 and are not inhibited below pH 10 (Hvitved-Jacobsen, 2002). However, it is important to note that pH does have an important influence on the sulfide species equilibrium in the bulk wastewater and will affect the release of compounds into the sewer atmosphere (Hvitved-Jacobsen, 2002). Temperature can have a strong effect on sulfate reduction kinetics, with a temperature dependency coefficient of 1.13 being reported, although this coefficient is reduced (on the order of 1.03) for biofilms or sediments where substrate diffusion is the limiting condition (Hvitved-Jacobsen, 2002). Also, adaptation in lower- or higher-temperature climates may reduce the apparent temperature dependency (Hvitved-Jacobsen, 2002).

In sewer systems, oxygen consumption can occur rapidly. Hvitved-Jacobsen (2002) suggests that if the bulk wastewater DO concentration is maintained above 0.2 to 0.5 g O_2/m^3, sulfide emissions to the sewer atmosphere should not be significant. The objective is not to avoid sulfide formation (in the sewer biofilm) but to keep the bulk sulfide at a low-concentration level in order to control odor problems. Norsker et al. (1994) demonstrated that the variations in DO conditions under which the biofilms are established can also have a strong influence on the sulfate reduction potential. Although biofilms grown at all oxygen levels had the potential to produce sulfide, those grown at very low DO concentrations had the greatest sulfide production potential (Norsker et al., 1994).

4.4   Hydrogen Sulfide as a Corrosive Gas

Hydrogen sulfide causes direct corrosion of metals such as iron, zinc, copper, lead, and cadmium. More importantly, hydrogen sulfide forms sulfuric acid, which can cause major damage to wastewater facilities, including the crown of concrete sewer pipes.

Corrosion of wastewater pipelines is caused primarily by microbially induced corrosion (MIC). This is a complex process involving many active organisms that are not fully understood. There are two distinct phases of MIC: The first is the conversion of ubiquitous sulfate in the wastewater to sulfide, some of which is released as gaseous hydrogen sulfide; the second is the conversion of hydrogen sulfide to sulfuric acid, which attacks susceptible pipeline materials.

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As described in Section 4.3, the bacteria producing sulfide are generally considered strict anaerobes and, consequently, live beneath the water surface in gravity sewers and on the pipe walls in force mains. The bacteria may also thrive in sludge and grit deposits found along the bottom of sewer pipes. In order to produce sulfide compounds, the bacteria require a source of sulfur and a food supply. Sulfate, generally abundant in wastewater, is the common sulfur source. However, other forms of sulfur such as organic sulfur from animal wastes can also be reduced to sulfide. Dissolved organic material prevalent in the wastewater provides an ample food supply for bacteria to flourish. The sulfate reaction in a wastewater collection system can be defined in accordance with Equation 4.3.2-1. The overall sulfide and sulfuric acid formation mechanisms are illustrated in Figure 4-2.

Figure 4-2. Overall Corrosion Mechanism in Wastewater Pipelines (From ASCE, 1989)

Sulfate and nutrients diffuse into a biofilm that grows on the submerged wetted walls of sewer pipes. There, the sulfate is reduced to sulfide, primarily through the action of anaerobic SRB. The hydrogen sulfide then diffuses out of the biofilm and into the wastewater, where it dissociates primarily between hydrogen sulfide (H_2S) and bi-sulfide (HS^-). The uncharged

hydrogen sulfide can be released to the overlying sewer atmosphere, absorbed to water films on the sewer pipe, and oxidized to sulfuric acid.

4.4.1 Rate of Sulfide Production

The rate of sulfide production is dependent upon environmental conditions in the slime layer. The following wastewater conditions are the most critical parameters impacting the rate of sulfide production:

- *Concentration of organic material and nutrients.* These materials diffuse into the slime layer and are consumed by the SRB.

- *Sulfate concentration.* Sulfate and organic matter will be used by the SRB in the ratio of approximately 2:1, depending upon the relative concentrations of each.

- *Dissolved oxygen.* DO is critical in determining whether anaerobic or aerobic bacteria will dominate the breakdown of organic material in the wastewater. If the DO concentration is in excess of 1.0 mg/L, aerobic bacteria will likely dominate the activity, particularly on the outer layers of an attached biofilm. Consequently, increased DO will reduce the production of sulfide by limiting the food reaching the anaerobic bacteria.

- *pH.* The pH determines the proportions of HS^- and H_2S found in the wastewater and directly influences the amount of hydrogen sulfide gas available for release into the atmosphere.

- *Temperature.* Each degree Celsius increase in temperature represents a 7 percent increase in the biological activity of the SRB (up to 30°C).

- *Wastewater velocity.* Velocity of the wastewater in the sewer influences the thickness of the slime layer and deposition rates for organic material.

- *Surface area.* The flow depth influences the free water surface and determines the submerged pipe surface in which the slime layer may form.

- *Detention time.* This is particularly important in force mains, submerged sewers, and sewers with little DO present. As the detention time increases, more oxygen is consumed, oxidation-reduction potential (ORP) decreases, and organic material becomes more solubilized, a condition that favors the SRB.

4.4.2 Solubility of Hydrogen Sulfide Gas in Wastewater

Dissolved hydrogen sulfide gas dissociates in water as follows:

$$H_2S \Leftrightarrow HS^- + H^+ \tag{4.4.2-1}$$

The equilibrium constant K_{H2S} is for this dissociation defined as:

$$[HS^-] \times [H+]/[H_2S] = K_{H2S} = 1.12 \times 10^{-7} \text{ at } 25°C \tag{4.4.2-2}$$

where [HS-], [H+], and [H_2S] denote the molar concentrations of the respective constituents. Consequently, if hydrogen ions are present in the wastewater, the concentration of dissolved hydrogen sulfide gas must increase as bacteria produce sulfides so the chemical equilibrium of the above dissociation reaction is maintained. The production of hydrogen sulfide is highly sensitive to the concentration of hydrogen ions (i.e., pH). A reduction of the wastewater pH indicates increased hydrogen ions in the wastewater and causes an increase in dissolved

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hydrogen sulfide gas concentration. Conversely, increasing the pH causes a reduction of the dissolved hydrogen sulfide gas concentration.

A second dissociation from HS$^-$ to S^{2-} can occur; however, generally, S^{2-} only exists at pH levels greater than 12, which is well above the normal wastewater pH range.

Because hydrogen sulfide gas is relatively insoluble in water, its solubility can be described by Henry's Law as follows:

$$X_{H2S} = K_{H2S}P_{H2S} \tag{4.4.2-3}$$

where X_{H2S} = mole fraction of dissolved hydrogen sulfide at equilibrium in the liquid phase (moles H$_2$S/moles liquid), K_{H2S} = Henry's law constant for hydrogen sulfide gas at a given temperature (moles/liter H$_2$S/atm H$_2$S), and P^*_{H2S} = partial pressure of hydrogen sulfide gas at equilibrium in the atmosphere (atm).

Under most conditions in the sewer, the actual partial pressure of hydrogen sulfide in the sewer headspace (P_{H2S}) is low relative to the saturation partial pressure (P^*_{H2S}). Thus, there is a hydrogen sulfide gradient from the surface of wastewater to the overlying sewer atmospheres and consequential driving force for emissions of H$_2$S from wastewater to sewer air. Bacteria continuously produce sulfides that are converted to hydrogen sulfide, which is released to the atmosphere, where it can cause corrosion and odor and safety problems.

4.4.3 Corrosion of Sewer Walls

Once sulfides are produced in the wastewater as the result of sulfate reduction, hydrogen sulfide gas will be released into the atmosphere. The hydrogen sulfide gas is oxidized on the pipe surface above the water line as described by the following equation:

$$H_2S + O_2 \xrightarrow{\text{bacteria}} H_2SO_4 \tag{4.4.3-1}$$

Oxidizing bacteria, such as *Thiobacillus concretivorous*, *Thiobacillus neapolitanus*, *Thiobacillus ferro-oxidans*, or *Thiobacillus thioxidans*, are aerobic and thrive in low-pH environments. To grow, they require a source of sulfur (H$_2$S), a moist surface (the pipe walls above the water surface), and a carbon source (CO$_2$). The surface pH of new concrete pipe is generally in the range of 11 to 13. Cement contains calcium hydroxide which neutralizes the acids and inhibits formation of oxidizing bacteria when the concrete is new. However, as the pipe ages, the neutralizing capacity of the pipe is consumed, the surface pH drops, and the sulfuric acid–producing bacteria become dominant. In active corrosion areas, the surface pH can drop below 2.0. As sulfides are formed and sulfuric acid is produced, calcium hydroxide is converted to calcium carbonate (gypsum), which is easily eroded by wastewater.

4.5 Odor-Sampling and Analysis Methods

The previous subsections involved the nature of malodorous and corrosive compounds associated with sewers and the biological transformation mechanisms that can lead to their formation. Methods for sampling and analyzing malodorous compounds and mixtures are considered in this subsection.

Odor-sampling methods can be divided into three broad classifications: (1) human sensory evaluations, that is, perceptions of odor thresholds, concentrations, and pleasantness by odor panelists; (2) measurement of chemical-specific surrogates for odor, for example, hydrogen

sulfide; and (3) measurements of nonspecific odor fingerprints or profiles, for example, "electronic nose" systems. Each of these approaches is described below.

4.5.1 Sensory Evaluations

Conventional measurements of odor involve human sensory evaluations (Figure 4-3). An olfactometer (Figure 4-4) is typically employed to quantify odor detectability by using sequentially decreasing dilutions-to-threshold (D/T) values and presenting the results as odor units (OUs) or threshold odor numbers (TONs). Odor intensities may also be measured by subjective comparisons to a reference chemical such as n-butanol. While these methods are frequently employed to assess odors associated with wastewater, there have been few studies reported for sewers. Furthermore, sensory evaluation methods in the present have been limited, owing to uncertainties related to large differences in sensitivities to odors among odor panelists, and the aging of samples between sample collection and employment of an odor panel (McGinley and McGinley, 1997; Walsh, 1996); however, more-recent standardizations of panelists' selection and olfactory-operating protocols using the European CEN standard for dilution olfactometry have significantly improved the repeatability of olfactory determinations. Figure 4-5 shows the ratio of maximum to minimum odor concentrations observed by members of the same odor panel for the same gas mixture. The majority of ratios are between 1 and 3 with, as expected, greater variations at low odor concentrations.

| (a) | (b) |

Figure 4-3. Olfactory Evaluation of Odor Samples by Panelists (a) Sitting in the Same Room (Courtesy of Silsoe Research, Bedford, UK) and (b) Using an Olfactometer While Isolated from Other Panelists (Courtesy of St. Croix Sensory)

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Figure 4-4. **Example of Olfactometer with Two Sniffing Ports** (Courtesy of Aromatrix, Singapore)
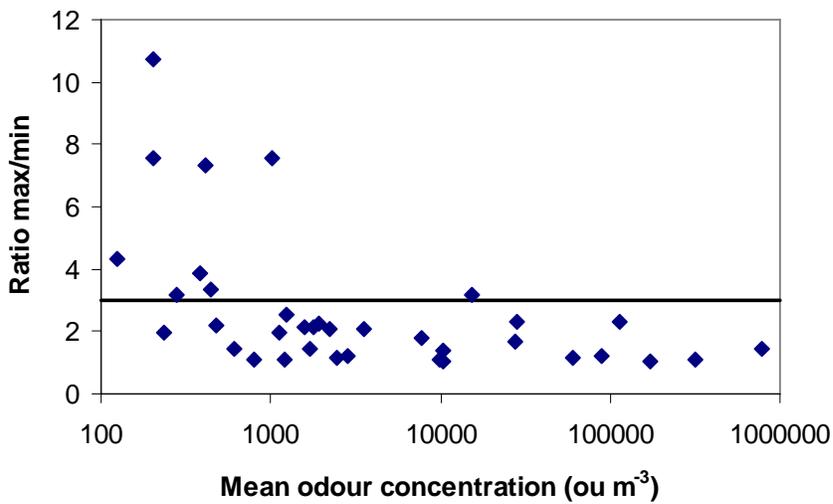

Figure 4-5. **Repeatability of Paired Sewage Odor Samples** (After Gostelow and Parsons, 2000)

There remains significant uncertainty regarding the effects of mixtures of wastewater odorants on the sensory evaluation of related odors, and few papers on this subject have been published over the past decade. Laing et al. (1994) completed a systematic study to assess the effects on human sensory evaluations of chemical mixtures of odors relevant to wastewater treatment facilities. They studied hydrogen sulfide, isovaleric acid, butanethiol, and skatole as well as binary, trinary, and quaternary mixtures of these odorants. The perceived odor intensities of mixtures were greater than any individual components but less than the sum of intensities of individual components. As the number of components in a mixture increased, there was greater

suppression of the effects of individual components. However, the intensity of the most-dominant component was observed to provide a good approximation of the intensity of the mixture. The least frequently suppressed component was observed to be hydrogen sulfide; the most frequently suppressed components, isovaleric acid, and skatole. Importantly, the "unpleasantness" of mixtures was usually greater than individual components of the mixture, and as such, methods or models based on single odorants may significantly underestimate the number of odor complaints.

There may be value in characterizing different wastewaters in terms of their potential to lead to malodorous gases. To measure the odor emission of a liquid wastewater sample, a methodology is needed that relates the emission of odorants to the volume of the respective liquid rather than to the surface area as determined by conventional wind tunnel and emission hood measurements. Two methodologies have been developed to evaluate this potential effect: odor potential (OP) (Hobson, 1995) and odor emission capacity (OEC) (Frechen and Köster, 1998). Both methods involve measuring the odor concentration of air bubbled through a wastewater sample under standardized conditions (Figure 4-6). The air sample is typically collected in an inert container (for example, Tedlar bag, polished stainless steel canister) for conventional sensory evaluations—for example, dilution olfactometry analysis to determine TONs—or determination of specific odorants, such as H_2S. Having applied the OP concept to a range of municipal wastewaters, Hobson (1995) reported TONs ranging over four orders of magnitude for untreated wastewater arriving at a wastewater treatment plant. Such a large range of OP indicates substantial variations in either the septicity or chemical makeup of raw wastewater and clearly shows that there is no such thing as "typical" untreated wastewater. It is important to recognize that the OP method does not account for the potential for a wastewater to form odorants through chemical or biological transformations; that is, it accounts for only a current wastewater state.

Figure 4-6. Odor Emission Capacity Test Reactors

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4.5.2 Studies Involving Hydrogen Sulfide and Other Sulfur Species

Field methods to assess odors associated with wastewater have relied heavily on the measurement of individual odorants (such as hydrogen sulfide concentrations at the fence line of a wastewater treatment plant) using electrochemical sensors (see Figure 4-7). However, there have been few advances in the use of hydrogen sulfide measurements as a means of investigating odor problems, particularly as related to sewers, during the past decade. Several examples are described below; they relate to wastewater treatment plants and other sources, but they may have some application to sewers. As described in Section 4.4, the release of hydrogen sulfide from wastewater is also a major source of corrosion in municipal sewers. As such, methods for measuring hydrogen sulfide gas are also relevant to detecting environments conducive to sewer pipe corrosion.

Figure 4-7. Hydrogen Sulfide Monitor (Jerome 631-x) (Courtesy of Arizona Instruments)

Witherspoon and Barnes (2004) investigated the use of hydrogen sulfide and OU source measurements coupled with a dispersion model to predict odors at the fence line of a municipal wastewater treatment plant. Ambient measurements of hydrogen sulfide and odor D/T values were made (using a field olfactometer) at fence line. Application of a dispersion model significantly overestimated fence line hydrogen sulfide concentrations, but the average ratio of predicted to measured odor concentrations across 20 locations was reasonably good (0.79). Although the specific application involved wastewater treatment processes, the results suggest a possible application to sewers, particularly as related to determination of specific emission sources that might contribute to community odor complaints.

Gostelow and Parsons (2000) gathered previously reported data from odor surveys at 17 wastewater treatment plants to assess the possibility of linking analytical measurements of hydrogen sulfide and sensory evaluations of odor quantified as number of OUs per square meter. All data were obtained for covered treatment processes, both before and after odor control. Correlations between odor concentrations and hydrogen sulfide suggest a power law relationship of the following form:

$$C_{OU} = mC^n_{H2S} \tag{4.5.2-1}$$

where C_{OU} is the odor concentration as measured by sensory evaluation (OU/m^3), C_{H2S} is the hydrogen sulfide concentration (ppm), and m and n are empirical constants. For preliminary treatment prior to odor control (most representative of untreated wastewater in sewers), m was observed to equal 52,555, and n was reported as 0.62. The value of R^2 was only 0.45, indicating that only 45 percent of the variation in odor concentration was explained by variations in hydrogen sulfide. The remainder (55 percent) was explained by other odorants and/or measurement errors. For comparison, values of m and n for aeration tanks were 14,555 and -0.12 ($R^2 = 0.07$), respectively. Values of m and n for sludge storage and handling were 38,902 and 0.64 ($R^2 = 0.69$), respectively. These results are consistent with work by Hobson (1995), who noted that the TONs associated with biogenic odors from wastewater are frequently 5 to 10 times greater than that expected from hydrogen sulfide concentrations. As such, other chemicals clearly play an important role in defining human perception of wastewater-related odors.

Finally, Sye and Chen (2000) described an analytical method to determine a range of sulfur species at parts-per-billion levels in odorous gas mixtures. Sulfur species in air were collected onto an adsorbent (Tenax-GR) with subsequent analysis by thermal desorption, separation by gas chromatography using a fused silica porous-layer open tubular capillary column, and detection by flameless sulfur chemiluminescence (FSC). The use of FSC for detection was concluded to be an excellent alternative to the more common flame photometric detection. Linear responses were observed for sulfur species, including hydrogen sulfide, sulfur dioxide, dimethyl sulfide, dipropyl sulfide, and C1 to C7 speciated thiols. The method was tested for air samples collected above an aerated treatment tank at a petrochemical plant and a hoggery.

4.5.3 Solid Phase Microextraction

Solid phase microextraction (SPME) was first introduced in the early 1990s as a method for concentrating trace chemicals prior to their analysis by chromatographic techniques. It holds promise for the capture of gas phase odorous compounds associated with municipal wastewater with subsequent resolution and quantification at levels of parts per trillion by volume to parts per billion by volume.

SPME involves a sorptive medium (liquid or solid) that is applied as a thin layer over a fused silica fiber. Common coatings include polydimethylsiloxane (PDMS), polyacrylate, and Carboxen. When the coated fiber is placed in a fluid such as air or water, chemicals in the fluid are absorbed into the coating and concentrated prior to analysis by gas chromatography with any of a number of detectors. There are two primary modes associated with the use of SPME fibers: (1) direct sample collection, during which the SPME fiber is exposed directly to the medium of interest (for example, in an air or wastewater stream or sample), and (2) headspace SPME (HS-SPME), in which an SPME fiber is exposed to the gaseous headspace above a liquid or solid sample matrix.

The benefits of SPME for sample collection and preconcentration are numerous and include the ability to

- Concentrate a wide range of analytes

- Use coated fibers in air, water, or wastewater

- Concentrate and analyze trace contaminants that might have otherwise gone undetected with conventional field monitoring or whole-air samples

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- Directly desorb chemicals from an SPME fiber with zero-path injection onto a gas chromatographic column

- Analyze without the use of solvents

The major drawback to SPME is the need to establish chemical-specific partition coefficients between the medium of interest and the fiber coating, and to account for variations in medium temperature, relative humidity, and fluid mechanic conditions around the fiber, each of which might be important variables if samples were collected in the actual headspace of sewers.

The use of SPME for air sampling emerged in the mid- to late 1990s and has been described in numerous papers (for example, Martos and Pawliszyn, 1997). Applications related to sampling sewer gas are sparse. However, several recent studies have focused on the use of SPME for identifying and quantifying odorous gas emissions from various wastewater processes, suggesting its potential use for characterizing low concentrations of odorous chemicals in untreated wastewater, in the headspace of sewers, or downwind of points where sewer odor is released. The latter may be the most relevant application, given that SPME is a technology that is particularly valuable for measuring concentrations of compounds in air at levels of parts per thousand to parts per billion, and such levels are not likely to cause odor complaints when immediately released from sewers. However, higher concentrations can be diluted to parts-per-thousand to parts-per-billion levels downwind of a release point, and being able to effectively identify and quantify an odor fingerprint (chemical composition) downwind of an odor release might be useful for back-calculating the nature and magnitude of release from the source. Several relevant studies are described below.

Kim et al. (2002) used SPME to concentrate odorous chemicals from the headspace of wastewater samples collected from several processes (wastewater influent, thickened sludge, dewatered sludge, and biosolids) at a municipal wastewater treatment plant. A mixed Carboxen-PDMS-coated fiber was used to capture trimethylamine, carbon disulfide, dimethylsulfide, and dimethyldisulfide. A polyacrylate-coated fiber was used to capture propionic and butyric acids. Samples were analyzed by either gas chromatography with mass spectrometry (GC/MS) or gas chromatography with flame ionization detection (GC/FID) (for the carboxylic acids). It was concluded that SPME coupled with GC/FID or GC/MS can be effective for capturing the spectrum of chemicals listed above at low levels of parts per billion. Kim et al. (2002) observed the major reduced sulfur compound in wastewater influent (sewer effluent) to be carbon disulfide.

Huang et al. (2004) employed headspace solid phase microextraction (HS-SPME) coupled with either gas chromatography with nitrogen-phosphorus detection (HS-SPME-GC/NPD) or gas chromatography with mass spectrometry (HS-SPME-GC/MS) to analyze speciated odor components associated with a subsurface-constructed wetland for wastewater treatment. They were able to resolve and quantify a range of VFAs (C2 to C7), volatile alkyl sulfides (dimethylsulfide and dimethyldisulfide), and organic amines (methyl amine, dimethylamine, trimethylamine ethylamine) in wastewater from levels of parts per trillion by volume to parts per billion by volume using PDMS as the SPME coating. It was concluded that for the system tested, removal of propionic acid and isovaleric acid is particularly critical for deodorizing wastewater.

Turkmen et al. (2004) optimized an SPME-GC/MS method for analyzing selected odors known to be generated by digested sludge. The method involved a Carboxen-PDMS-coated fiber

and was used to quantify parts-per-billion levels of sulfurous odor vapors such as dimethylsulfide, dimethyldisulfide, methyl mercaptan, hydrogen sulfide, and carbon disulfide. The authors concluded that dynamic measurements (direct air samples in the field) are suspect unless the fluid mechanic conditions of the calibration standard and field sample are identical. This problem does not exist with static headspace samples, for example, above a wastewater sample. The authors also noted the need to conduct additional research to ascertain possible errors associated with multisorbate competition and to lower detection limits for a range of malodorous chemicals to levels that can be detected by the human nose.

James and Stack (1997) employed both polyacrylate- and PDMS-coated SPME fibers for direct sampling of wastewater and the headspace above wastewater samples. Municipal wastewater, pharmaceutical, and petrochemical discharges were studied. Only direct immersion was used with municipal wastewater. Method detection limits for concentration in wastewater varied between 10 and 170 µg/L, depending on the specific chemical. Thirteen VOCs were identified and quantified for municipal wastewater, including a range of saturated straight-chain VFAs (C2, C3, C4, C6, C12, and C14) and cyclohexane carboxylic acid.

In summary, SPME holds promise for capturing and concentrating a wide range of malodorous compounds associated with wastewater, with subsequent chromatographic analysis to determine concentrations at levels of parts per trillion by volume to parts per billion by volume in air. It can be used for direct sampling in air or in wastewater, or for headspace sampling above a wastewater sample, and has several advantages over more conventional sampling methods. Headspace sampling appears to be the least problematic of these approaches at this time. Additional research is needed, particularly related to the application of SPME for capturing odor-causing compounds associated with untreated wastewater.

4.5.4 Electronic Nose

Electronic nose systems use an array of nonspecific sensors to provide a "fingerprint," or unique profile, of an odor without determining its actual chemical composition. An odor's fingerprint is established by using sensors with varying affinities for odorous gases. Sensor materials can range from conducting polymers to metal oxides and from surface acoustic wave devices to bioenzyme sensors. Conducting-polymer sensors, which are used to measure changes in electrical resistance across polymers, offer the largest range of selectivity and sensitivity to different compounds (Stuetz et al., 1998). The sensor responses can then be further analyzed using pattern recognition techniques (such as multiple-discriminate and principal-component analysis) or neural network algorithms. The choice of analysis technique is dependent on the amount and nature of information available and the type of information required from the analysis (that is, quantitative or qualitative).

The principal components of an electronic nose system are its sample delivery, the sensor array module, and the data analysis module (Figure 4-8). The delivery system is designed to transfer sampled headspace gas from above a sample material to the sensor array chamber in a reproducible manner. This can be achieved by either generating a headspace above a sample and then introducing the sensor arrays to the headspace (static sampling) or pumping the sample headspace from a sample vessel to the sensor array (dynamic sampling). The different performance characteristics of these sample methods have lead to the development of different electronic nose instruments for different fields of application. A number of electronic nose systems are available from commercial manufacturers throughout the world. These systems can

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be classified into three application groups: complex laboratory-based instruments, online systems, and portable devices for field measurements.
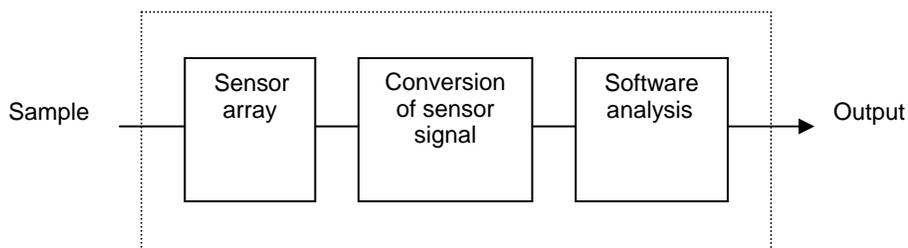

Figure 4-8. Principal Components of an Electronic Nose System

Two recent studies have shown the potential for electronic nose systems for applications related to odors from municipal wastewater. Stuetz et al. (2000) collected wastewater samples over a 5-month period from three locations (inlet works, settling tank effluent, final effluent) at several different municipal wastewater treatment plants. An electronic nose system (an array of 12 polypyrrole-conducting polymers) was used to develop odor profiles from the headspace above wastewater samples. Odor profiles were compared to BOD_5 and OP measurements using canonical correlation analysis. Relatively strong correlations were observed between odor profiles and the wastewater parameters, suggesting an ability of electronic nose systems to detect changes in organic content, and thus odor potential, of wastewater. A particularly strong correlation was observed between BOD_5 and odor profile for raw (untreated) wastewater (from the inlet works), suggesting the possible use of electronic nose systems for monitoring the spatial and temporal odor potential of sewers.

Stuetz et al. (1998) collected Tedlar bag samples from a range of locations at 10 wastewater treatment plants. The contents of bags were analyzed by a dynamic dilution olfactometer to calculate TONs in OUs per square meter. Bag contents were also analyzed to establish odor profiles using an electronic nose system (an array of 12 polypyrrole-conducting polymers). A poor correlation was observed between odor profile and TON when data across all locations were analyzed as a single set. The correlation improved markedly when only data corresponding to TONs less than 4,000 OU/m^3 were analyzed. Furthermore, exceptionally good linear correlations between odor profile and TON were observed when data were grouped into sets for the same treatment works and processes. The linear correlation between odor profile and TON for TONs less than 4,000 OU/m^3 was very good for bag samples collected at inlet works across three wastewater treatment plants, suggesting the possible application of electronic nose systems to predict the TON associated with odors originating from sewers.

The two studies above were summarized by Fenner and Stuetz (1999). Additional applications have included the monitoring of chemical pollutants in wastewater for early warning of process upsets (Bourgeios et al., 2003) and the detection of odor abatement failures (Stuetz and Bourgeios, 2004). The primary benefit of electronic nose technology is that it may eventually provide a means for estimating the effects of malodorous mixtures on human perceptions of odors, and could provide a means for correlating wastewater parameters with fingerprints of malodorous gas mixtures. The primary drawbacks are that the technology does not provide measurements of actual chemicals that compose odors, may not respond at low

concentrations for some chemicals with particularly low odor thresholds, and has not been proven in potential through significant and systematic field studies.

4.6   Major Knowledge and Research Gaps

Microbial transformations play a significant role in the formation and subsequent emission of odorous and corrosive compounds into the sewer atmosphere. Under anaerobic conditions, fermentation processes and sulfate reduction are the dominant mechanisms involved in the production of VFAs and hydrogen sulfide, the latter being a dominant source of both odor and corrosion concerns in sewers. The production of these products is dependent on the wastewater source, types of microorganisms present, and operational conditions. The nature of emitted malodorous compounds (types, amount) affects human detection and response to odors associated with municipal wastewater. Unfortunately, much remains to be learned about the effects of mixtures on odor thresholds and perceptions, and analytical methods have yet to be fully developed for standardizing the effects of malodorous chemical fingerprints.

Major knowledge and research gaps that stem from this review are listed below:

1. Past studies related to the corrosion in sewers have focused entirely on the production and release of hydrogen sulfide and formation of sulfuric acid that leads to corrosion of sewer pipes. Additional research related to whether other biochemical reaction products in sewers lead to corrosion, or enhance the corrosion related to hydrogen sulfide releases, is warranted. More detailed information related to corrosion of sewer pipes is provided in Chapter 9.

2. Fermentation processes and VFA formation remain areas of uncertainty and are worthy of additional basic (laboratory) research.

3. The concept of odor potential should be expanded to include not only the current state of wastewater but also the potential to form odorants following chemical and biological transformations. This necessarily requires greater knowledge of parameters that lead to transformations and the transformation pathways themselves, and thus a need for more laboratory research.

4. Additional field studies are needed to link sensory perceptions of odor complaints—that is, annoyance—with the chemical composition of these odorants.

5. Two promising technologies that might facilitate such efforts include solid phase microextraction for the concentration of trace concentrations of odorous compounds and electronic nose systems. However, each of these technologies requires further laboratory research, and ultimately field evaluations, to optimize using the technology for odors associated with raw (untreated) wastewater.

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