A guide to sulfur gas emissions from wetlands and disposal basins: implications for salinity management

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# Table of Contents

1. **The issue** .......................................................................................................................... 1  
2. **What’s emitted and how badly can it smell?** ............................................................... 1  
   2.1. Hydrogen sulfide ........................................................................................................... 3  
   2.2. VOSC ........................................................................................................................... 3  
   2.3. Sulfur dioxide ................................................................................................................ 3  
3. **Key biogeochemical processes** .................................................................................... 7  
   3.1. Under wet conditions – Inorganic S cycle .................................................................... 7  
      3.1.1. Diurnal O₂ cycle ..................................................................................................... 7  
      3.1.2. Density stratification ............................................................................................ 7  
      3.1.3. pH ....................................................................................................................... 8  
      3.1.4. Ebullition ............................................................................................................. 8  
   3.2. Under wet conditions – Organic S cycle ....................................................................... 8  
   3.3. Change in S cycling when wetlands are drying ............................................................ 8  
      3.3.1. Inorganic S gas emission ....................................................................................... 8  
      3.3.2. VOSC .................................................................................................................. 9  
4. **Knowledge needs to better manage the odour problem** ............................................. 11  
5. **Concluding remarks** ...................................................................................................... 11  
6. **Further reading** ............................................................................................................ 12
1. The issue

In areas with irrigated agriculture, excess drainage waters are often stored in disposal basins to avoid returning saline waters to riverways. An unexpected environmental concern associated with disposal basins is that some of them emit foul odours when water levels are lowered or attempts are made to dry them. For example, this phenomenon is commonly observed in saline wetlands and disposal basins of Lower River Murray floodplains (Fig. 1). The emission of foul odours can result in the loss of aesthetic, recreational and tourism values associated with nearby areas and are thought to represent a potential health risk.

The causes and mechanisms of foul odour generation from disposal basins are not known but are almost certainly associated with the cycle of sulfur (S) in these environments. Sulfur is a widespread compound in the environment and a very common salt (as sulfates, $\text{SO}_4^{2-}$) in disposal basins. However, unlike other common salts such as sodium chloride, $\text{SO}_4^{2-}$ salts are biologically reactive and can be transformed into a variety of inorganic compounds (such as pyrite – $\text{FeS}_2$) and organic compounds such as proteins ($\text{S}$ is a key building block of the amino acids in proteins).

The purpose of this review is to provide a layperson’s guide on the possible causes and mechanisms of foul odour generation due to the biological and chemical transformations of sulfur compounds in disposal basins. The review has been spurred by numerous requests to the authors from wetland managers over several years to explain this problem in simple terms. The assessment was made primarily based on overseas literature because there is almost no information available on S gas emissions from Australian wetlands. Therefore, many of the mechanisms that will be proposed here should be viewed as testable hypotheses that will require validation with field and laboratory studies. The review will be divided into three broad topics:

- What kind of S gas can be emitted from wetlands and their basic properties;
- Proposed mechanisms for how these gases are generated, with an emphasis on changes when wetlands are dried;
- An outline of knowledge needs for the effective management of the problem.

2. What’s emitted and how badly can it smell?

Sulfur gases are both foul smelling and noxious. There is evidence from overseas studies that wetlands emit a range of sulfur gases and they vary according to factors such as salinity, wetting–drying regime, soil type and diurnal cycles. Three main types of S gases can be emitted by wetlands: hydrogen sulfide ($\text{H}_2\text{S}$), volatile organic sulfur compounds (VOSC) and sulfur dioxide ($\text{SO}_2$). These differ in the way they are produced (Table 1) and their odour characteristics, smell threshold and toxicity (Table 2). The human nose can detect some of these compounds at very low concentrations.
Figure 1: Foul smell events can decrease the aesthetic values associated with wetlands and could also be a community health concern (Barmera, South Australia). Murray Pioneer, 14 February 2003.
2.1. Hydrogen sulfide

The rotten-egg smell. Hydrogen sulfide is produced by microorganisms in the water columns and sediments of wetlands by the process of sulfate reduction (Fig. 2). Essentially, sulfate-reducing microorganisms can use SO$_4^{2-}$ instead of oxygen to respire, producing H$_2$S as an end-product. Most wetland sediments will be anoxic (without oxygen) at depth because bacteria use the oxygen to respire when feeding on (i.e., decomposing) the organic matter that accumulates on the bottom of the wetland. This means they will be at least some sulfate reduction occurring. While a number of factors control the rates of sulfate reduction, rates tend to be higher in saline wetlands because more sulfate is available.

Another mechanism to produce H$_2$S is also a familiar one – the decomposition of organic matter rich in organic S, like eggs.

H$_2$S is a toxic gas. It can cause illnesses from chronic exposure at low concentrations (irritations of airways, etc) and can be lethal at higher concentrations.

2.2. VOSC

A wide variety of volatile organic sulfur gases occur in the environment and many give pleasant tastes and flavours to foods. However, several also have very unpleasant odours. Some VOSC gases even play a role in climate regulation. (VOSC emissions from oceans contribute to cloud formation. More clouds mean more light is reflected back into space, thus reducing the warming effect of solar radiation.) VOSCs can be produced by a wide variety of mechanisms including: decomposition of organic matter; releases by algae; in marine, estuarine and salt marsh environments, the degradation of dimethylsulfoniopropionate (DMSP) an organic osmolyte (a substance that is part of an organism’s salt balance); and as detoxification by-products when organisms are exposed to H$_2$S. Foul smells associated with VOSCs are also a problem in waste treatment plants, pulp mills and aqueducts.

How badly some VOSCs smell is a subjective judgement. However, just as wine, beer, water, etc, have “expert tasting panels”, there are also similar panels to determine the odour characteristics of VOSCs. However, an important feature of VOSCs is that the human nose can detect some of them at very low concentrations (Table 2).

There is some evidence that naturally saline wetlands and marshes tend to emit more VOSCs than their freshwater counterparts, but the reasons for this are not clear.

2.3. Sulfur dioxide

When previously anoxic sediments are exposed to oxygen, sulfur dioxide (SO$_2$) can be produced during the oxidation of sulfides (e.g., pyrite) by oxygen (Fig. 2). This process can also be catalysed by another group of microorganisms, the “sulfide oxidisers”. SO$_2$ has an acrid smell and can have adverse health effects following chronic exposure. Large quantities of SO$_2$ are also emitted by fossil fuel burning and it is a key ingredient for the formation of smog in cities.

Foul smells in wetlands can be a combination of H$_2$S, VOSCs and SO$_2$. Like good wine each wetland will have its own “bouquet” according to the type and quantity of gases emitted.
Table 1. Some common sulfur gases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Main origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulfide</td>
<td>Reduction of sulfate</td>
</tr>
<tr>
<td></td>
<td>Decomposition of sulfur containing compounds in organic matter e.g.</td>
</tr>
<tr>
<td>H₂S</td>
<td><img src="image1" alt="L-Cysteine" /></td>
</tr>
<tr>
<td></td>
<td><img src="image2" alt="L-Methionine" /></td>
</tr>
<tr>
<td>Carbonyl sulfide</td>
<td>Reaction of hydrogen sulfide with organic matter e.g.</td>
</tr>
<tr>
<td>COS</td>
<td><img src="image3" alt="Reaction" /></td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>Reaction of hydrogen sulfide/decomposition of organic matter (see above).</td>
</tr>
<tr>
<td>CS₂</td>
<td><img src="image4" alt="Interconversion" /></td>
</tr>
<tr>
<td>Methanethiol (MT)</td>
<td>Reaction of hydrogen sulfide with organic matter</td>
</tr>
<tr>
<td>CH₃SH</td>
<td>Decomposition of sulfur containing compounds in organic matter</td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td>Reaction of hydrogen sulfide with organic matter</td>
</tr>
<tr>
<td>(DMS) (CH₃)₂S</td>
<td>Decomposition of sulfur containing compounds in organic matter e.g.:</td>
</tr>
<tr>
<td></td>
<td><img src="image5" alt="Oxidation of Methanethiol" /></td>
</tr>
<tr>
<td>Dimethyl disulfide</td>
<td>Oxidation of Methanethiol</td>
</tr>
<tr>
<td>(DMDS) (CH₃)₂S₂</td>
<td>![Oxidation of pyrite (FeS₂)]</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>Oxidation of pyrite (FeS₂)</td>
</tr>
<tr>
<td>SO₂</td>
<td><img src="image6" alt="Oxidation" /></td>
</tr>
</tbody>
</table>

*Interconversion of these two compounds in the soil and atmosphere:

COS + H₂O ⇌ CO₂ + H₂S

CS₂ + OH⁻ ⇌ COS + HS⁻
Table 2. Smell description and the range in odour thresholds and health effect thresholds for common sulfur gases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hedonic index (nature of smell)</th>
<th>Odour detection threshold in ppt(v)</th>
<th>The threshold concentration (ppm(v) &amp; ppt(v)) below which most people will experience no appreciable risk of health effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulfide</td>
<td>rotten eggs</td>
<td>0.1–270 (1)</td>
<td>10 ppm or 10,000,000 ppt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 (2)</td>
<td></td>
</tr>
<tr>
<td>Carbonyl sulfide</td>
<td>sulfide</td>
<td>250 (1)</td>
<td>1.25 ppm or 1,250,000 ppt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100,000 (2)</td>
<td></td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>medicinal/sulfur, vegetable sulfide, aromatic</td>
<td>8,100 (2)</td>
<td>10 ppm or 10,000,000 ppt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9,620 (3)</td>
<td></td>
</tr>
<tr>
<td>Methanethiol (methyl mercaptan)</td>
<td>garlic/putrid</td>
<td>0.0003–38 (1)</td>
<td>0.5 ppm or 500,000 ppt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>900–8,510 (3)</td>
<td></td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td>stench decayed vegetables</td>
<td>0.3–160 (1)</td>
<td>50 ppm or 50,000,000 ppt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,000 (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>600 – 401,000 (3)</td>
<td></td>
</tr>
<tr>
<td>Dimethyl disulfide</td>
<td>putrid, decayed vegetable, putrification, foul</td>
<td>1.1–610 (1)</td>
<td>0.0035 ppm or 3,500 ppt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100–3,610 (3)</td>
<td></td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>pungent/irritating</td>
<td>2,700,000 (2)</td>
<td>0.3 ppm or 300,000 ppt</td>
</tr>
</tbody>
</table>

Source – Chemwatch Material Safety Data Sheet (Revision No: 2 CD2006/2) **NB: CSIRO does not warrant these values as “safe” exposure levels and they must be regarded as indicative and for comparison purposes only. DO NOT rely on the values in the table above to make decisions about what is or is not a safe exposure.** Determining the appropriate limits to apply to toxic gas exposure depends on many variables. For example, safe exposure concentrations for the general population will often be set at different concentrations from those for occupation exposure as workers exposed to toxic substances have workplace programs to monitor exposure and health, such as those exposed to organophosphate insecticides. Exposure limits, toxicology, “safe levels” and the way toxicity data is converted into standards or limits for airborne concentrations are complex subjects and beyond the scope of this document. Health effect threshold concentrations are quoted in ppm and have been converted to ppt for comparison with the odour threshold values, note that ppm (v) = parts per million by volume and ppt(v) = parts per trillion by volume so that ppt = ppm x 1,000,000.

(1) Animal nutrition studies, (2) Chemical engineering, (3) Bio-industry (composting, waste water treatment).
Figure 2: Major chemical transformations during the reduction of sulfate, the oxidation of sulfides, and the decomposition of organic matter.
3. Key biogeochemical processes

It has been observed that disposal basins emit foul smells mainly when they are drying. In the following, we will review in more details the main chemical reactions that occur when saline wetlands are “wet” and the ones that may be occurring when they are “drying”. As few studies have been conducted on the emission of S gases in Australian wetlands – the mechanisms proposed here are hypotheses that will require confirmation using laboratory and field studies.

3.1. Under wet conditions – Inorganic S cycle

There are two key features of the sulfur cycle under wet conditions: 1) the accumulation of sulfides and organic-S in the sediments and 2) the trapping of S gases emitted from the sediments by the water column. For simplicity, we will review these processes in detail by first looking at the inorganic component of the sulfur cycle.

In most wetlands, the decomposition of organic matter in the sediments consumes much oxygen and anoxic conditions prevail within a few millimetres below the sediment-water interface. Under such anoxic conditions, *dissimilatory sulfate reduction* occurs and H$_2$S is produced as an end-product (Fig. 2). Much of the H$_2$S produced in the sediments will react with Fe and other metals to form sulfide minerals, but some H$_2$S can also escape to the water column by diffusion from the sediments. However, most of the H$_2$S diffusing from sediments to the water column will rapidly react with O$_2$ (eventually producing sulfate) and thus not reach the atmosphere (Fig. 3).

A few other factors could influence whether or not H$_2$S will be emitted from wetlands, including:

- The diurnal wetland O$_2$ cycle.
- Density stratification
- pH
- Ebullition (bubble formation)

3.1.1. Diurnal O$_2$ cycle

It is common for small Australian wetlands to have large fluctuations in O$_2$ concentration over a daily cycle. Oxygen is added to the water column of wetlands by diffusion from the atmosphere and by photosynthesis by plants, algae and some bacteria. In return, O$_2$ is consumed in wetlands by the decomposition of organic matter and aerobic respiration. Because photosynthesis does not occur at night but respiration and decomposition do, there is a tendency for small wetlands to have lower O$_2$ concentrations at night, especially in summer when warm temperatures increase the rates of decomposition and respiration. It can be hypothesised that H$_2$S produced in sediments will be more likely to escape to the atmosphere at night when low O$_2$ concentration in the water column would decrease water column H$_2$S oxidation rates.

3.1.2. Density stratification

Many wetlands have periods when the water column is stratified into layers with different densities because of differences in temperature and salinity. When stratified, there is a tendency for bottom waters to become anoxic and accumulate H$_2$S because O$_2$ consumption rates in sediments can be rapid relative to the rate of diffusion of O$_2$ from the overlying water layer. In shallow wetlands, such stratification is seldom long lasting when it occurs because wind can efficiently mix the water column. However, when wetlands destratify rapidly, it is possible that a pulse of H$_2$S from bottom waters could be rapidly released to the atmosphere.
3.1.3. **pH**

H$_2$S is a “weak acid” and a proportion present in the water column will tend to dissociate into either HS$^-$ or S$^{2-}$ at different pHs. In general, at neutral and alkaline pH, the preferred forms in water will be HS$^-$ and S$^{2-}$ (which are not volatile) while at more acid pHs, H$_2$S becomes favoured. Thus, it should be expected that a higher proportion of the H$_2$S produced in wetland will escape to the atmosphere when wetlands are acidic.

3.1.4. **Ebullition**

Diffusion is not the only process that can transfer H$_2$S produced in sediments to the water column. When water becomes supersaturated with a given gas (or set of gases), bubbles will tend to form. Bubble formation in unconsolidated sediments at the sediment–water interface is especially common in summer, when decomposition rates (and the production of CO$_2$, N$_2$, methane and other gases) are higher and the solubility of gases in the warmer water is lower. The formation and release of bubbles in sediments could be an effective mechanism to emit H$_2$S produced in sediments to the atmosphere in some wetlands.

3.2. **Under wet conditions – Organic S cycle**

The organic sulfur cycle in wetlands is not as well known as its inorganic counterpart. Sulfur can be integrated in organic matter by the process of assimilatory SO$_4^{2-}$ reduction (Fig. 2). This occurs when algae and bacteria consume sulfate and convert it to protein-sulfur within their cells. Organic sulfur accumulates on the bottom wetlands when plants and animals die. Because decomposition rates are slower under anoxic conditions, there is tendency for organic matter (and organic-S) to slowly accumulate in wetland sediments.

VOCS will be produced in wetland water and sediments when wet, particularly by releases from algae and decomposition in the sediments. What specific compounds are produced and at what rates is not known for Australian inland wetlands. It is possible that some of the VOSCs produced will be consumed by bacteria in the water column. How much of the remaining VOSCs will be released to the atmosphere is unknown. What factors control the rates of production and emissions for different compounds is not well known. However, in overseas studies, VOSC emission rates tend to be higher in saline wetlands. In addition, VOSCs emission rates are related to other factors such as temperature, diurnal cycles, degree of sediment wetness and sediment texture. To our knowledge, there has been no study of VOSC emissions from Australian inland wetlands.

3.3. **Change in S cycling when wetlands are drying**

Two key factors could influence the S gas emission rates when wetlands are drying: 1) the exposure of previously anoxic sediments to oxygen and 2) the loss of the overlying water column as a “trap” for S gases emitted from the sediments. The proposed consequences for the changes in these two environmental factors on the inorganic and organic S cycle are outlined below.

3.3.1. **Inorganic S gas emission**

When wetland sediments are exposed to the atmosphere, they will gradually oxidise as oxygen can now penetrate more easily in the sediments. A key inorganic S process under these conditions will be the tendency to oxidise sulfides stored in sediments, producing both sulfuric acid and sulfur dioxide (Fig. 3). The rates at which sulfide oxidation will proceed is dependent on the soil texture (lower in clay compared to sandy sediments) and the frequency of desiccation features (which increase the rates of oxygen diffusion in the sediments), residual moisture, and ambient pH. Thus SO$_2$ as opposed to H$_2$S is the main S gas emitted by the inorganic S cycle when oxygen is present.

There are potentially two mechanisms by which H$_2$S could be emitted from drying wetland sediments. Firstly, because the oxidation of sediments occurs gradually from the sediment surface (Fig. 3), the anoxic conditions suitable for dissimilatory S reduction (and H$_2$S
generation) could persist for significant lengths of time at depth. Some of the H₂S produced within the anoxic zone could then be released to the atmosphere by diffusion or advection (movement of air through pores induced by winds, temperature contrasts, etc), processes that could be aided by the desiccation features that often develop when wetland sediments dry. Likewise, H₂S produced during organic matter decomposition could more easily escape to the atmosphere in the absence of a water cover. In addition, organic matter decomposition rates could increase once sediments are exposed to the atmosphere.

Regardless of whether H₂S or SO₂ is produced or the rates of gas production within sediments change, it is likely that gaseous S emissions increase from drying wetland sediments because some of the gases produced are no longer trapped within the wetland by the water column.

3.3.2. VOSC

VOSC’s are produced by various processes in both oxic (with oxygen) and anoxic wetland sediments (Fig. 3). Here again, there is limited information in the literature to determine whether VOSC emission rates to the atmosphere should increase in drying sediments. It can be speculated that VOSC emission rates will tend to increase in drying wetland sediments because of more rapid decomposition rates of sediment organic matter under oxic conditions and the decreased interception of some VOSCs by the water column. There is also evidence that more VOSC’s are produced in sulfide rich environments. This could occur, for example, when microorganisms produce VOSC’s as a detoxification mechanism against H₂S or by chemical reactions between H₂S and organic matter. As apparently no measurements of VOSC emission from Australian wetlands have been made, it is not possible to predict what VOSC compounds will be emitted and at what rates from Australian wetlands. However, it is likely that foul odour events associated with drying wetland sediments are cause in part by the emission of VOSCs.

Loss of water cover enhances the likelihood of sulfur gases produced in sediments escaping to the atmosphere.
Figure 3: Sulfur cycling in wetlands under wet and drying conditions showing major pathways for sulfur transformations.
4. Knowledge needs to better manage the odour problem.

There has been no study on the forms and the environmental controls on S gas emissions from inland Australian wetlands. Therefore, it is not possible to propose scientifically-defensible management guidelines to minimise foul odour problems during water level management operations in wetlands and disposal basins. A list of critical knowledge needs to better understand the foul odour problem includes:

- To determine what inorganic and organic sulfur gases are emitted from wetlands;
- To understand the environmental factors controlling the rates of emission for the most common foul-smelling gases. Based on the literature, these factors would include sediment texture, organic matter content, sulfide content, water content, salinity, pH, time of day, temperature and the presence or absence of a water column;
- To determine the relative significance of dissimilatory sulfate reduction and organic matter decomposition as sources of H$_2$S emission during wetland drying events.

A number of technical challenges may have to be tackled before some of these questions can be addressed. Instrumentation to measure the concentration of some S gases (H$_2$S and SO$_2$) is readily available. However, many foul odour-generating VOSC’s cannot be readily measured in the field because they occur at very low concentrations (but can still be detected by the human nose). In addition, measuring the rates of emission (“how much is produced per unit area of sediments per unit time”) is logistically more complicated than just measuring the ambient concentration of sulfur gases. In overseas studies, the most widely used method to measure S emission rates from exposed sediments is with incubation chambers. These are either coupled to measuring devices (for gases occurring at higher concentrations) or are used to trap S gases on columns or other media for later analysis in the laboratory. The analytical techniques required to measure S gases at low concentrations are challenging. From our review of the literature, only a handful of laboratories around the world appear to have developed the necessary techniques to measure S gas emissions from wetlands.

5. Concluding remarks

The S cycle and in particular the gaseous components of the S cycle have received limited attention in Australian inland wetlands. Studies overseas should be applied with caution to the Australian context because the environment and management issues associated with S are often different there. As Australian wetland managers must learn to “live with salt”, getting a better understanding of sulfur cycling in inland wetlands should be viewed as a priority.
6. Further reading