ABSTRACT

A short review is given on the many industrial uses of DMSO, to demonstrate the likelihood that residues from these industrial applications may be discharged into the sewer and are fed with sewage into municipal waste water treatment plants. Laboratory data show that concentrations of DMSO as low as 1 to 10 mg/L in bottled anoxic activated sludge can cause dimethyl sulfide DMS concentrations four orders of magnitude above odor threshold. The productivity of the DMSO reduction to DMS by anoxic activated sludge from three different WWTP is in the range of 29 to 73 µg g\(^{-1}\) h\(^{-1}\) (µg DMS g\(^{-1}\) VSS h\(^{-1}\)). An aerobic acclimation period of five days for activated sludge reduced DMS formation significantly. A new interpretation of historical field data allows the conclusion that the decade old sporadic “canned corn” odor problem of the North East municipal WWTP (“NEWPCP”) of Philadelphia is likely caused by intermittently peaking industrial DMSO sewer discharge and lacking acclimation of the activated sludge to the treatment of DMSO and DMS. Sewage authorities are recommended to have waste water samples analyzed for DMSO and DMS if they have problems with “rotten cabbage” or “canned corn” odor and believe that the DMSO odor mechanism may apply. A source control of DMSO may then allow for mitigation of the odor using existing treatment technology, for example by achieving acclimation of activated sludge to the treatment of DMSO and DMS.

KEYWORDS

Dimethylsulfoxide, DMSO, dimethylsulfide, DMS, odor, sewage, municipal waste water

BACKGROUND

One odor attributed to municipal waste water plants that is resisting normal H\(_2\)S control strategies can be described as “cabbage” or “canned corn” like (Porter et al., 2004). This odor could be attributed to the compound Dimethylsulfide (DMS), which has an air odor threshold in the order of 0.001 mg/m\(^3\).

Natural cycling of DMS and formation from DMSO: DMS can be produced biologically through the reduction of dimethylsulfoxide (DMSO) by many microorganisms (Alef and Kleiner, 1989; Andreae, 1980; Drotar at al. 1987). It has been shown that microorganisms found in sewage sludge form DMS under anoxic and anaerobic conditions (Zindler and Brock, 1978; Griebler, 1997; Sklorz and Binert, 1994, Rajbhandari et al., 1995). These experiments did “flood” sewage sludge bacteria with high concentrations of DMSO (up to 30 mass %) to measure biological activity and thus did not investigate the odor potential of low mg/L additions of DMSO as they might occur in
sewage. The redox potential of DMSO at pH 7 of 160 mV (Wood, 1981) is lower compared to that of nitrate respiration, but higher compared to that of sulfate reduction. No significant natural biological production of DMSO in sewers and waste water treatment has been reported. However, DMSO waste residues from industrial sources could be an important source of DMSO for the engineered waste water environment.

DMSO is also a man-made chemical used by industries and for consumer goods: DMSO (CAS number 67-68-5) is a very good industrial solvent, which itself does not evaporate from water and has almost no odor. DMSO has no significant health effect (an OSHA PEL limit has not been established). The annual production of DMSO amounts to about 50,000 metric tons annually (Vignes, 2000). Consumers use DMSO in household chemicals and pharmaceuticals.

The chemistry of dimethylsulfoxide (manufacturing, analysis, properties and uses by industries, consumers, medicine and pharmacology) has been reviewed by Martin and Hauthal (Martin and Hauthal, 1975).

DMSO use by industries comprises the following applications with examples: Stripping paints; coatings or inks (Lallier, 1995); printing inks component (Tabayashi et al., 1991); general solvent for biocides (Rajini et al., 1989); reaction solvent for biocide production (Bayer et al., 1982); reaction solvent for biocide production (Akieda et al., 1992); solvent for herbicides (Wilson and Fleischfresser, 1977; Katritzky et al., 1987); cleaning of printed circuit boards and semiconductors (Matsumoto, 1992a); polymerization reactor cleaning (Maeda and Sato, 1992); cleaning of diesel and fuel injectors (Wolski et al., 1983); degreaser (Matsumoto, 1992b); cleaner for graffiti (Leys, 1994); extraction solvent (Choffe et al., 1966); and many more applications. This short review may demonstrate it is probable that residues of these applications may be discharged into the sewer and are fed with sewage into municipal waste water treatment plants.

Waste management of DMSO: Although industrial applications of the expensive chemical DMSO typically include recycling after use, this process leaves some residues that cannot be fully recycled. Furthermore, DMSO is also part of numerous consumer products, which are not expected to be recycled. Residues of recycling are either eliminated by industrial waste treatment or believed to be disposed into sewers and the general environment. Industries that cause these DMSO emissions are not subject to reporting requirements of section 313 or Title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986 and 40 CFR Part 372. As a result, no “threshold” quantity of DMSO emission is defined to guide DMSO users as to whether they have to report any DMSO discharge to the EPA or to communicate with waste water authorities.

Industrial waste treatment methods (Park et al., 2001; Lee et al., 2004) have been developed to eliminate concentrated DMSO waste water (1000 mg/L DMSO) and to prevent odor problems resulting from DMSO waste in municipal waste water plants. Park et al. (2001) claim that a continuous flow of 800 mg/L DMSO in industrial waste water can be degraded by activated sludge with no odor formed. The bacterial degradation pathway of DMSO comprises subsequently the sulfur chemical products DMS, methylmercaptan (methanethiol), H₂S, and H₂SO₄ as a final product.

Information on sewer odor by industrial DMSO discharge: It is of note that a mysterious odor haunted a German town in a late summer/fall season (reported in a German newspaper in 1996). Alarmed by the public debate and complaints, a chemical company realized that it caused the odor problem by DMSO disposal from manufacturing operations of a local plant. After the plant
increased the discharge of DMSO significantly above six (6) kg/h, odorous sulphur compounds (not specified) were produced by microorganisms in the sewer, from which point the odor moved into populated city areas. The odor problem was eventually solved through separate transport of the waste directly to a WWTP, though it is not clear if the odor had truly disappeared or simply moved from the sewer to the remote WWTP where it was less annoying to citizens. It is remarkable to note that the chemical plant, although the actual cause of the odor, did nothing wrong, because it had been using DMSO as a solvent in compliance with state-of-the-art disposal guidelines. DMSO was recycled after the production cycle, and only diluted waste products were discharged into the sewer. It is further interesting to note that the chemical company had previously sought and received an allowance to discharge DMSO to the sewer. The laboratories of the local sewer department had previously performed aerobic batch tests to show that DMSO is degraded and would not affect the biological functions of general waste water treatment. But the laboratory protocol did not comprise a test for odor from DMSO/DMS under sewer conditions (Wachtl, 1995). It can be assumed that the most important odorous compound in the sewer was DMS from DMSO reduction. This case study demonstrates that both the industry discharging DMSO and the local sewer department were lacking sufficient knowledge to prevent the DMSO-related sewer odor.

*Actual environmental odor problems at* municipal waste water plants resulting from DMSO waste residues are not reported in the literature. Neither literature nor protocols are available to sewer authorities to explicitly prepare them to deal with municipal waste water odor by industrial waste streams of DMSO residues (Figure 1) that cannot be recycled by the industry or which authorities believe are not important enough to be eliminated. Current treatment protocols would only take notice of DMSO if doing so would increase the necessary treatment capacity significantly.

**Figure 1** - The “known” of industrial DMSO waste treatment versus the “unknown” of DMSO affecting municipal waste water treatment

The goal of this work is to show that DMSO disposal could be an underestimated cause of odor for sewers, municipal waste water treatment plants, and the environment (Figure 1, lower part). This
work combines laboratory experiments and the new interpretation of historical field-data to show that very small concentrations of DMSO in municipal waste water can cause significant amounts of odorous DMS.

**METHODOLOGY**

Bench-scale experiments in the laboratory were designed to determine the ability of activated sludge of different WWTP to produce significant quantities of the odorant DMS from low mg/L concentrations of DMSO in waste water. The experimental approach is batch fermentation of sludge with added DMSO in closed bottles and analysis of the resulting headspace gases for odorants.

*Materials for bench-scale experiments:* DMSO, Na$_2$S, and Na-mercaptopoate, HCl (Merck, Darmstadt, Germany). Compressed nitrogen (Messer-Griesheim, Essen). Chemical color test tubes type dimethylsulfide 1a, Draeger Mercaptan 0.5/a, Draeger H$_2$S 0.5a) (Draeger Company, Luebeck). The batch-incubation containers used were PET plastic beverage bottles obtained from a grocery store. These bottles have been earlier tested to be sufficiently airtight and chemically inert (Higgins, 2005).

*Sample description of sludge for bench-scale experiments:* Return activated sludge (RAS) was chosen as biologically active sludge because it is more stable in its composition and metabolism, compared to other types of sludge (faecal substance, primary sludge, aeration tank mixed liquor and digested sludge have all been found to perform the DMSO/DMS reaction, results not shown). The RAS is liquid sediment of the secondary sedimentor as it was taken from the return path. The sludge samples named A, B and C originate from three municipal WWTPs without a measurable DMSO inflow. The microscopically determined microbial composition of the samples is typical of municipal waste water treatment.

*Method of anoxic incubation in bottles:* The sludge sample and DMSO were poured into incubation bottles with a hole in the plastic cap to allow intermediate gas sampling and re-sealing with clear tape. The sample was than purged with 20 liter of nitrogen per liter of sludge, to remove any initial volatile sulfur compounds and oxygen. Air (21% oxygen) was than added to the nitrogen headspace to set the initial oxygen concentration to 5%. It has been found that the presence of this small amount of oxygen in the bottle headspace gas was successful to prevent H$_2$S and methanethiol formation by sulfate reduction and biomass breakdown. On the other hand, oxygen was found to be quickly depleted in the liquid phase, to the point of anoxic conditions favorable for DMSO reduction. The bottles were then incubated for up to 72 hours standing up-right at room temperature (22°C) and were periodically very gently shaken so that biomass flocks could mix with water but still did settle and were anoxic. The oxygen consumption in the bottles was checked with a dissolved-oxygen electrode for qualitative purposes until oxygen concentrations were undetectable in the liquid phase of sludge after about 15 to 45 minutes.

*Experiment 1, variation of DMSO concentration:* RAS A (500 mL) in four 4 different 1000 mL bottles was amended with four different concentrations (0, 1, 2, 10 mg/L) of DMSO and incubated for 24 hours. The concentration of DMS, mercaptan and H$_2$S in headspace gas was analyzed after an interval of 0.1, 2, 4, 6, 12, and 24 h.

*Experiment 2, variation of sludge from different WWTP:* A volume of 500 mL of each of the sludge A, B and C types from three different WWTP and 2 mg/L of DMSO were incubated for 72 hours in
The concentration of DMS, mercaptan and H₂S in headspace gas was analyzed after an interval of 0.1, 2, 4, 6, 12, 24 and 72 h.

**Controls:** Parallel control experiments were also prepared with no DMSO added, and with heat sterilized liquid sludge samples and DMSO added. Parallel control experiments were also prepared, the first had no DMSO added and the second was heat sterilized with DMSO added.

**Experiment 3, Influence of sludge acclimation time on DMSO elimination:**
This experiment included 20 days of aerobic sludge acclimation to DMSO and DMS and odor measurement after intermediate extra DMSO addition and a two hour anoxic period on day 0, 5, 10, 15, and 20 (Figure 4). This simple semi-continuous feed design was chosen because of the lack of a continuous bench-scale fermenter. Return activated sludge (500 ml) was poured into a bottle (1000 ml) and aerated. DMSO (2 µl/L) was added immediately and at intervals of six hours for a total aerobic acclimation period of five days. The bottle’s contents were then removed into a bucket and the sludge flocks were washed five times with five liters of tap water to remove remaining amounts of DMSO, and the flocks were regained by sedimentation. Then, the sludge sediment was again placed into the bottle, DMSO (10 µl/L) was added and the sludge was aerated for a DMSO-degradation period of six hours (similar to the aeration period in an aeration-tank process). After this period, the aeration was stopped, dissolved oxygen was stripped out, and the bottle was incubated for an anoxic DMSO-reduction period of two hours (similar to the anoxic sedimentation period in a secondary settler), and the headspace gas was measured for DMS and odor using dilution-olfactometry. This sludge sample was then used for three more subsequent five day periods of aerobic acclimation and subsequent aerobic/anoxic odor-tests. The data of “day 0” represent the control experiment without acclimation; where DMSO was added, the bottle was incubated under anoxic conditions for two hours and the odor-test was executed without previous acclimation.

**Methods of analysis of headspace gas samples for volatile sulfur odorants and for odor:** DMS, mercaptan and H₂S were measured through the use of small homemade chemical color test tubes, which reduced the necessary gas sample volume according to the availability of sample gas in the bottles. To prepare these test tubes, the packing material from Draeger test tubes (type Dimethylsulfide 1a, Mercaptan 0.5/a, H₂S 0.5a, where the numbers mean detection limit in ppmv) was removed, fractionated, and refilled into glass tubes of 2 mm inner diameter. These test tubes were validated by comparison with the results of the original commercial Draeger tubes. H₂S and mercaptan gas standards were produced from Na₂S and Na-mercaptanoate by addition of 1 N HCl. The test tube method has also been validated by comparison with gas chromatography and comparison with certified gas standards of H₂S, mercaptan and dimethylsulfide (methodical publication in preparation). The detection limits were according to the specification of the original Draeger tubes. The precision was about 5% at a level of 10 ppmv.

Odor measurements were performed by dilution olfactometry with a panel of four trained volunteers. About 50 mL of bottle headspace gas were sampled with a glass syringe and consumed per testing session, and the results are expressed as the dilution factor to detection threshold (DT), respectively European odor units (OU).

**Units, constants, calculation methods:**
Concentrations in water and sludge are mostly presented in mg/L. Concentrations in the headspace gas are presented in ppmv as they were measured with Draeger test tubes. One ppmv of DMS in gas is equal to 2.583 mg/m³ DMS in gas at 22°C. One mg DMSO is equivalent to 12.8 µmol. The water/gas partition coefficient of DMS is 15, which is equivalent to a
Henry law constant of 170 Pa m³/mole at 25 °C, which is a good approximate for application in sewage and sludge (Higgins et al., 2005). The odor threshold of DMS in air was established to be 0.001 mg/m³ or 0.4 ppmv by dilution olfactometry within this work. *The productivities of DMS formation* were approximately calculated from the slopes in Figures 2 and 3 within the initial two hour period (change of headspace concentration per time), multiplication by a factor 15 (the partition coefficient K of DMS for water/air at 22°C), division by the VSS concentration, and conversion of the unit into µg* g⁻¹*h⁻¹ (µg DMS g⁻¹ VSS h⁻¹) for the individual experiments and sludges. This model assumes the amount of DMS produced can be approximated by the amount of DMS in the liquid, which can be estimated from the measured headspace concentration, under assumption of a dynamic liquid-vapor-equilibrium (K = 15).

**RESULTS AND DISCUSSION**

DMS was the only volatile sulfur odorant that could be detected in headspace gas of the DMSO amended samples of experiment 1 and 2. H₂S and mercaptan were undetectable as expected due to the anoxic conditions. H₂S, mercaptan and DMS could not be detected in headspace gas of the controls (with no DMSO added, and with DMSO added to heat sterilized liquid sludge samples). This result can be explained by the anoxic (versus anaerobic) conditions and the short incubation time, which prevented sulfate reduction and protein breakdown as conditions for H₂S and mercaptan formation.

*Experiment 1, variation of DMSO concentration:* A plot of the headspace gas concentration of DMS in incubation bottles with different amounts of DMSO added to return activated sludge is shown in Figure 2. It can be seen that the concentration of DMS is peaking later and at a higher level with increasing DMSO concentration. It is concluded that in actual WWTP conditions, a longer hydraulic detention time is necessary to convert the DMSO load fully into DMS. The *productivities* of DMS formation were approximately calculated from the slopes in the figure within the initial two hour period and yielded in 73, 63, and 52 µg DMS g⁻¹ VSS h⁻¹) for sludge A, B, and C.

**Figure 2: Concentration of DMS in incubation bottles with different amounts of DMSO added to return activated sludge of plant A.** The concentration of DMS can be translated into an odor concentration four orders of magnitude above the odor threshold of DMS (in the order of 1 ppmv).
Experiment 2, variation of sludge from different WWTP: The headspace gas concentration of DMS in the incubation bottles with 2 mg/L DMSO added to return activated sludge from three different plants A, B, and C is shown in Figure 3. It can be concluded that activated sludge of different plants has a similar ability to reduce DMSO to DMS. The subsequent decline of DMS could be attributed to microbial consumption. The productivities of DMS formation were approximately calculated from the slopes in the figure within the initial two hour period, and resulted in 49, 29, and 43 µg DMS g\(^{-1}\) VSS h\(^{-1}\) for sludge A, B, and C.

Figure 3: Concentration of DMS in incubation bottles with 2 mg/L DMSO added to return activated sludge from three different plants A, B, and C

![Graph showing DMS concentration over time for different plants A, B, and C.]

Experiment 3, Influence of sludge acclimation time on DMSO elimination:
The peak odor concentration versus acclimation time of activated sludge with added DMSO is shown in Figure 4. It was found that activated sludge requires an aerobic acclimation time of more than one week to reduce DMSO-related DMS and odor in the alternate anoxic state. It is suggested that a prolonged aerobic exposure of the sludge to DMSO could eliminate DMSO more quickly so that intermittent anoxic conditions will meet less DMSO and will form less DMS and therefore less odor. The major odor compound in this experiment was found to be DMS. It is concluded that an acclimation time in the order of 10 to 20 days will allow activated sludge to eliminate DMSO at the 10 mg/l concentration level. It can also be concluded that continuous inflow of DMSO into WWTP might not cause odor problems due to acclimation. However, one event of DMSO inflow in WWTP influent weekly will likely not allow acclimation to occur, which may intermittently result in odor problems.
Discussion and new interpretation of historical DMS data of an odorous aeration tank in light of the DMSO mechanism:
The City of Philadelphia Water Department (PWD) is said to have experienced sporadic problems with off-site odors at its Northeast Water Pollution Control Plant (NE WPCP) for decades. It is important to note that the odor still exists in spite of improved ventilation from process areas, process changes in the aeration basins, and the use of chemical treatment in the Return Activated Sludge (RAS). The predominant odor has been described as that of “canned corn” or “cabbage”, which can be associated with dimethyl sulfide (DMS). Waste water analysis data from literature (Porter et al., 2004) revealed that dimethyl sulfide (DMS) was quickly becoming the major odorant in activated sludge from the aeration basin (Figure 5). On the other hand, the aeration process had kept H2S and methyl mercaptan well under control. The sampling efforts were guided by two primary theories as to how odor is forming at the NE WPCP: Methylation of inorganic sulphide (H2S) by organic solvents in plant influent or breakdown of sludge protein to form methyl sulfides (Porter et al., 2004).

However, these data may be better interpreted by the proposed link between DMSO in waste water influent and “cabbage” odor: The waste water influent may contain DMSO waste, which is reduced to DMS by sludge bacteria. The necessary DMSO concentration in plant influent would need to be in the order of only 1…10 mg/L to generate the DMS levels in the headspace of Figure 5 (compare with previous figures). The PWD laboratories and previous research projects had no guidance to prompt them to add DMSO to the volatile organic compounds (VOC) monitoring program. It is also nearly impossible to detect DMSO accidentally at these low mg/L concentrations, because DMSO can not be extracted from water for liquid VOC analysis, and DMSO can not evaporate from sludge for headspace gas analysis. DMSO/DMS would also explain why methyl mercaptan and H2S were barely detectable in this case study compared to DMS (Figure 5). If sulphate reduction, sulphide methylation, or protein breakdown were important, H2S and methyl mercaptan would be the major products.
A DMSO-source control program has been presented to PWD suggesting that the sporadic “canned corn” aeration tank odor of the NE WPCP plant is dominated by suspected DMSO waste, and action upon this presentation would subsequently help mitigate the odor through control of the DMSO/DMS odor mechanism.

**Figure 5:** Odorous volatile sulphur compounds in bottle headspace gas of plant influent and of RAS sludge of the municipal NE WPCP plant, anoxically incubated for two hours (digest of data taken from Porter et al., 2004, Table 2, averages calculated). The specific odor intensities (or inverse odor detection limits) of the three sulfur compounds H$_2$S, methyl mercaptan and dimethyl sulfide (DMS) are similar. Therefore, DMS is the most important odor compound, which can explain the “canned corn” or “rotten cabbage” odor of the PWD NE plant.

![Graph of volatile organo-sulfur compounds](image)

**CONCLUSIONS**

- Significant gas concentrations of odorous DMS are formed by activated sludge that is not acclimated to DMSO and DMS degradation, on intermittent addition of low mg/L concentrations of DMSO under anoxic conditions.
- “Canned corn” or “rotten cabbage” is the best odor descriptor when DMSO is reduced by sludge and DMS is the dominant odor compound, with much smaller concentrations of H$_2$S and methanethiol.
- The productivity of the DMSO reduction to DMS by anoxic activated sludge from three different WWTP is in the range of 29 to 73 µg*g$^{-1}$*h$^{-1}$ (µg DMS g$^{-1}$ VSS h$^{-1}$).
- An aerobic acclimation period of more than five days of activated sludge suppressed the production of DMS in the laboratory. It is assumed that DMSO and DMS are eliminated by acclimated activated sludge under aerobic conditions, and thus, subsequent anoxic conditions (similar to anoxic conditions in secondary sedimentation that follow on aerobic conditions during aeration) will not produce DMS odor.
- Historical odor and DMS data of the North East municipal WWTP (“NEWPCP”) of Philadelphia allow the conclusion, that the decade old odor problems of the North East municipal WWTP (“NEWPCP”) of Philadelphia are likely caused by intermittently peaking industrial DMSO sewer discharge and lacking acclimation of the activated sludge to the treatment of DMSO and DMS.
- More field-research is necessary to understand the acclimation of municipal WWTP to the treatment of DMSO residues in plant influent.
Sewage authorities are recommended to have waste water samples analyzed for DMSO and DMS, if they have problems with “rotten cabbage” or “canned corn” odor and believe that the DMSO odor mechanism does apply.

REFERENCES


