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Aeration tank odour by dimethyl sulphoxide (DMSO) waste in sewage

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Abstract Sewage plants can experience dimethyl sulphide (DMS) odour problems by at least one mg/L dimethylsulphoxide (DMSO) waste residue in plant influent, through a DMSO/DMS reduction mechanism. This bench-scale batch study simulates in bottles the role of poor aeration in wastewater treatment on the DMSO/DMS and sulphate/H_2S reduction. The study compares headspace concentrations of sulphide odorants developed by activated sludge (closed bottles, half full) after six hours under anoxic versus anaerobic conditions, with 0 versus 2 mg/L DMSO addition. Anoxic sludge (0.1 – 2 mg/L dissolved oxygen, DO) with DMSO resulted in about 50 ppmv DMS and no other sulphide, while DMSO-free sludge was free of detectable sulphides. Anaerobic sludge (no measurable DO to the point of sulphate reduction) with DMSO resulted in 22/4/37 ppmv of H_2S/methanethiol (MT)/DMS, while DMSO-free sludge resulted in 44/8/2 ppmv of H_2S/MT/DMS. It is concluded that common "anoxic" aeration tank zones with measurable DO in bulk water but immeasurable DO inside sludge flocs (nitrate reducing) experience DMSO reduction to DMS that is oxidation resistant and becomes the most important odorant. Under anaerobic conditions, H_2S from sulphate reduction becomes an additional important odorant. A strategy is developed that allows operators to determine from the quantity of different sulphides whether the DMSO/DMS mechanism is important at their wastewater plant.

Keywords Aeration basins; dimethylsulphide; dimethylsulphoxide; odour; wastewater treatment

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Introduction

Dimethyl sulphoxide (DMSO, CAS number 67-68-5) is a widely used industrial solvent and pharmaceutical (Martin and Hauthal, 1975), which has unlimited solubility in water, almost no odour, and has no significant health effects. This compound is also linked to the natural sulphur-cycle and is produced by many microorganisms (Zinder and Brock, 1978; Alef and Kleiner, 1989; Sklorz and Binert, 1994; Griebler, 1997) including those microbial communities found in sewage and activated sludge. DMSO can be biochemically reduced by microorganisms to dimethyl sulphide (DMS) which has a strong "rotten cabbage" or "canned corn" odour. The necessary redox potential at pH 7 is 160 mV (Wood, 1981), which is somewhat lower than the level for nitrate reduction (see equation 1, "anoxic" conditions), but significantly higher than the redox level for sulphate reduction ("anaerobic" conditions).

$$(CH_3)_2SO + 2e^- + 2H^+ = (CH_3)_2S + H_2O \quad (160\,mV, \quad \text{"anoxic"}) \qquad (1)$$

The annual global industrial production of DMSO of about 50,000 metric tons could result in a significant DMS odour-forming potential, assuming that the DMSO is incompletely recycled and inappropriately disposed into sewage plants where equation (1) applies. Only specifically designed industrial wastewater treatment units (Park *et al.*, 2001) are able to eliminate concentrated industrial DMSO waste (in the order of 1000 mg/L DMSO) completely (complete degradation under fully oxic treatment conditions). It is likely that not all

industrial users recycle DMSO or eliminate DMSO waste completely. No legal regulation is in place that forces DMSO users to limit or to report sewer disposal of DMSO to their local sewage plant. Currently, municipal waste water authorities do not have protocols that explicitly deal with potential municipal wastewater odours caused by DMSO that is entering their wastewater collection and treatment systems through residential commercial and/or industrial discharges.

Glindemann *et al.* (2006a) demonstrated that DMSO waste disposal by a single industrial source into the municipal sewer can explain "canned corn" or "rotten cabbage" odour events as produced in a wastewater plant by the odorant DMS (Burlingame, 1999; Porter *et al.*, 2004, see Figure 1; Cheng *et al.*, 2005) from the aeration system of a conventional municipal wastewater treatment (specifically, the city of Philadelphia's North East Water Pollution Control Plant (NEWPCP)). The critical DMSO residue concentration in sewage plant influent was found to be as low as 1 mg/L. Figure 1 is adapted from these studies and shows specifically that DMS was by far the most abundant sulphide in headspace bottle samples; however, the specific odour intensities of H_2S and MT (their inverse odour detection thresholds) are significantly higher. The role of DMS in contributing to overall "pure" canned corn odour of wastewater becomes clearer in Figure 2 where DMS occurs "pure" under anoxic treatment conditions and DMSO; however, DMS occurs mixed with much H_2S and MT under anaerobic conditions.

It is of interest to know why the "anoxic" DMSO/DMS mechanism took place in an aeration tank system that is generally thought to be "oxic". A wastewater treatment plant (WWTP) aeration tank is primarily an oxygen-rich environment (oxic zones), but the local oxygen concentration will be smaller in poorly aerated zones and in sludge sediment on the bottom or walls of the aeration tank. In addition, oxygen is depleted in sludge flocs by bacterial consumption, while the surrounding bulk water phase of the sludge is still oxic. The plant design comprises intentionally weakly aerated "selector zones" and non-aerated sludge thickeners. The oxygen concentration around a specific bacterial floc is alternating over time, due to the flow and recycling of sludge as return activated sludge (RAS) between differently aerated zones.

Using the language of wastewater science of aeration treatment, "anoxic" and "anaerobic" conditions are *different*, as outlined for the purpose of this paper:

- The term anoxic or anoxic zones will refer to sludge conditions where nitrate reduction typically provides the oxygen source in bacterial sludge flocs (because

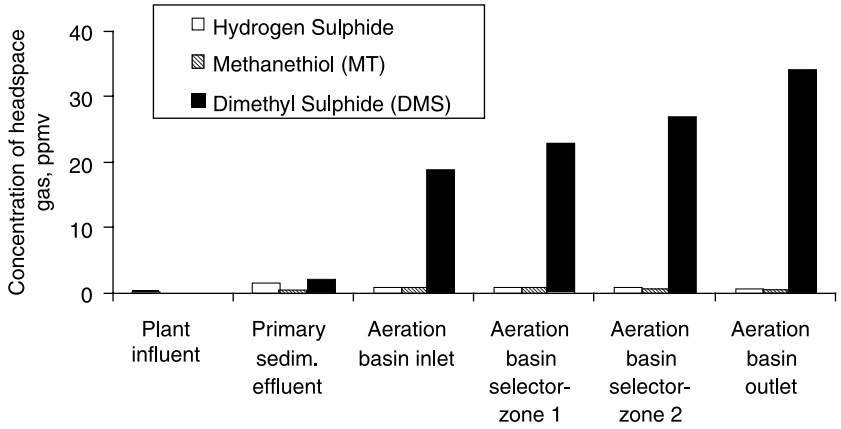

Figure 1 Volatile sulphur odorants of municipal NEWPCP plant influent mixed with RAS sludge in bottles. Digest of historical data (Porter *et al.*, 2004, Table 2)

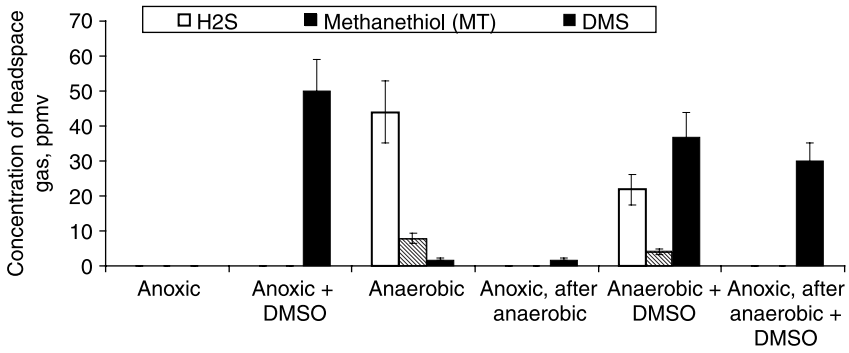

Figure 2 Typical volatile sulphide odorant "fingerprints" of activated sludge under conditions of different DMSO and oxygen supply. Headspace concentration in triplicate bottles incubated for six hours at 22 °C

dissolved oxygen is depleted inside dense flocs, therefore "anoxic"), but 0.1–2 mg/L DO is measurable in the bulk water phase to prevent sulphate reduction to H_2S, respectively to oxidise any H_2S. Since DMSO reduction is akin to nitrate reduction in many aspects (redox potential, enzymes), the detection of actual DMSO reduction (in the absence of H_2S formation) would indicate actual anoxic conditions. A condition of 0.1–2 mg/L DO is sometimes referred to as "hypoxic water", i.e. a condition of low but measurable oxygen concentration.

- The term anaerobic or anaerobic zones will refer to sludge conditions where commonly both oxygen and nitrates have been consumed and the activated sludge bacteria will reduce other compounds such as sulphates and sulphites into H_2S. H_2S can be subsequently methylated to methanethiol (MT) and DMS (Lomans *et al.*, 1997; Higgins *et al.*, 2006). If DMSO is added, it would be reduced to DMS. Under these conditions both the DMSO and the sulphate reduction mechanism are valid, and DMS is generated by both mechanisms.

The work outlined in this paper had the following objectives:

- Demonstrate that the "anoxic" DMSO/DMS mechanism is possible under conditions of measurable dissolved oxygen (0.1–2 mg/L DO) in the bulk water phase of activated sludge and at DMSO concentrations as low as 2 mg/L.
- Demonstrate that the DMSO/DMS mechanism can exist in combination with common sulphide forming mechanisms (sulphate reduction, etc.) under anaerobic conditions.

Methods

Approach

The influence of the supply of oxygen and of DMSO on sulphide odorant formation by sludge flocs in an aeration tank is efficiently simulated by bench-scale incubation of the sludge in bottles and headspace measurement. The bottle incubation and headspace method is reliable and sensitive (Glindemann *et al.*, 2006a,b) and was consistently used in this work. Return activated sludge (RAS) that consists of volatile suspended solids (VSS) = 3.9 g/L and contains 110 mg/L added sulphate was used for the sludge floc bench-scale experiments. The sludge was not acclimated to eliminate DMSO, in order to match scenarios where DMSO enters the sewer as intermittent large industrial discharges and activated sludge cannot adapt sufficiently to the chemical. This sludge best matches a typical aeration tank process.

Sludge floc bench-scale experiments – odour emissions determinations under anoxic and anaerobic conditions with and without DMSO

Samples of 500 mL sludge were incubated without shaking for six hours at 22 °C in the dark in triplicate gas tight plastic PET beverage bottles (1,000 mL, i.e. 500 mL headspace gas volume) under different conditions (anoxic, anaerobic) with, and without 2 mg/L DMSO added. The amount of DMSO added was determined based on the influent data provided and collected at the Philadelphia NEWPCP plant (Glindemann *et al.*, 2006a). The bottles were not shaken in order to limit (but not to suppress) oxygen transport from the gas phase into the liquid phase, similar to an aeration tank where mixing shear (turbulence) is low. All sludge samples were stripped in the incubation bottles with GC-grade nitrogen before incubation until initial odorants and oxygen were removed, following methods established by Glindemann *et al.* (2006b) and Higgins *et al.* (2006).

For bench-scale testing purposes the following parameters were established to reflect typical aeration conditions in aeration tanks:

- *Anoxic* conditions were produced by reducing the initial oxygen concentration in sample headspace gas to 5% oxygen in the gas phase (that is, initially 2 mg/L DO in the liquid phase). This prevented anaerobic conditions by keeping DO levels above the 0.1 mg/L limit in the course of six hours of incubation, and also limited the oxygen available to the bacterial sludge flocs, and best matches anoxic conditions that would be seen in an aeration tank.
- *Anaerobic* conditions were generated by simply closing the deaerated bottles, to match similar conditions of oxygen depletion in sludge floc sediment.
- *Anoxic after anaerobic* conditions (alternating oxygen conditions) were produced by reusing the previous anaerobic samples after analysis, by adding 5% oxygen into the bottle headspace, vigorously shaking for 10 minutes and immediately analysing the sample for sulphides. It was intended to explore the elimination effect of oxygen (approximately 2 mg/L DO) on sulphides formed during the previous anaerobic period.

Chemical analysis of the essential volatile sulphide odorants H_2S, MT and DMS in headspace gas was conducted after the incubation by use of chemical test tubes (Draeger, Germany, see Glindemann *et al.*, 2006b), detection limit 1 ppmv, in the bottle headspace gas.

Sludge floc bench-scale experiment – sulphide formation by long-term breakdown of activated sludge with no oxygen (anaerobic)

This experiment was designed to simulate the production of sulphides during anaerobic periods that were much longer than six hours. In some poorly mixed aeration tanks, sludge flocs could be present and decay over multiple days/weeks, depending on how the sludge blanket is managed and removed. RAS (500 mL, VSS 3.9 g/L) was deoxygenated and incubated under nitrogen atmosphere in triplicate bottles (1,000 mL) at 22 °C, and the headspace concentration of volatile sulphides and of methane (as an indicator of methanogenesis) was measured by GC (Glindemann, *et al.*, 2006b) for up to 30 days.

Results and discussion

In these two main bench-scale experiments, the odour generation that occurs in the presence and absence of DMSO in WWTP aeration tank sludge floc was examined. Experiments included examining the role of oxygen concentrations in the aeration tank mixed liquor, which can vary, for the typical sulphides formed via the DMSO and/or sulphate reduction mechanisms.

In the first main bench-scale experiment six aeration tank conditions were examined (Figure 2):

(1) *Anoxic conditions without DMSO:* Sludge flocs did not form detectable sulphide odorants (Figure 2). It is concluded that the common strictly anaerobic sulphide-forming mechanisms, i.e. sulphate reduction to H_2S, protein breakdown to H_2S and MT, and methylation of H_2S to MT and DMS, are inhibited under these conditions, or H_2S and MT, after their formation in anaerobic flocs, are reoxidised in the hypoxic water phase. If typical small amounts (0.1–2 mg/L) of H_2S and MT are carried over to the sludge floc from the upstream WWTP processes, they would be quickly reoxidised in the aeration tank. DMS was not seen or formed during this experiment.

(2) *Anoxic conditions with DMSO added:* Sludge flocs formed DMS as the only detectable volatile sulphur compound. It is an important conclusion that DMSO reduction to DMS is possible in aeration tanks by anoxic sludge flocs in the presence of 0.1–2 mg/L DO in surrounding water phase.

(3) *Anaerobic conditions without DMSO:* Sludge flocs formed significant levels of H_2S that greatly influence the total odour of the headspace sample. Smaller concentrations of MT and DMS were also seen. The significant level of H_2S is an indicator that the sulphate reduction mechanism is the prime odour generation mechanism under these conditions. It is possible that MT and DMS are also products of other mechanisms, such as methylation of H_2S (Lomans *et al.*, 1997), but it is less likely that sulphur-protein breakdown has already started after only six hours, since this formation mechanism requires much more incubation time (as seen in Figure 3).

(4) *Anaerobic conditions with DMSO:*Sludge flocs formed significant concentrations of both H_2S and DMS, but low MT. Since both H_2S and DMS were formed in the presence of DMSO, the only difference from Test 3 is the amount of 2 mg/L DMSO that was added. It is concluded that both sulphate reduction (H_2S as the indicator signal) and DMSO reduction (DMS as the indicator signal) occurred and are important. However, sulphide methylation and sulphur-protein breakdown (MT as the indicator signal) are unimportant mechanisms.

(5) *Anoxic after anaerobic conditions without DMSO:* Sludge flocs formed H_2S, MT and DMS under anaerobic conditions, but when the sample was rendered anoxic, both the H_2S and MT concentrations in the headspace disappeared (they were probably oxidised) and DMS was still present (DMS is relatively inert to oxidation). Under these test conditions, the initial DMS concentration was small, but remained at the same level even after the other reduced sulphur compounds were oxidized, indicating that once DMS is formed it stays in the sample even after re-aeration in

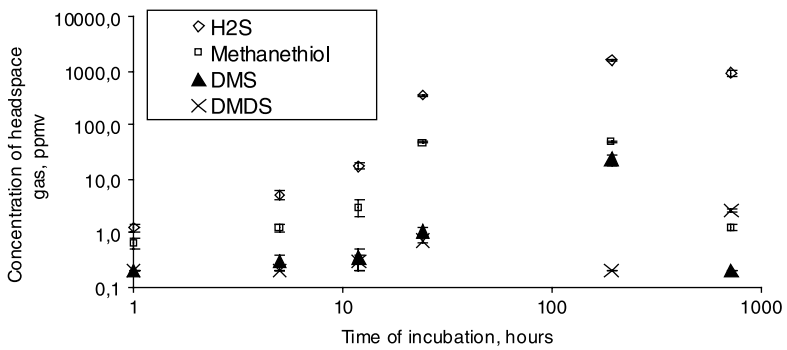

Figure 3 Volatile sulphide odorants of activated sludge (RAS) breaking down anaerobically over a time course of 1, 5, 12, 24, 190 and 720 hours (30 days). No DMSO added. Error bars for incubation in triplicate closed bottles at 22 °C. Methanogenesis started after 8 days (CH_4 data not shown)

the aeration tank. However, the DMS concentration is comparably low to the results from treatments where DMSO was added, and may suggest that the DMSO/DMS reduction mechanism is not important.

(6) *Anoxic after anaerobic conditions with DMSO:* Sludge flocs formed H_2S, MT and DMS under anaerobic conditions, but when the sample was rendered anoxic, both the H_2S and MT concentrations in the headspace disappeared (they were probably oxidised) and DMS was still present (DMS is relatively inert to oxidation). When compared with the DMS signal in the treatments without added DMSO, this sludge floc DMS signal was very large. This means that DMS was primarily generated by the DMSO reduction mechanism with some small contribution due to the sulphate reduction mechanism.

The data in Figure 2 in summary mean that if a wastewater treatment system produces H_2S, and MT in anaerobic zones (which are rare), the H_2S and MT would be subject to fast reoxidation elimination in anoxic zones (that are more common). Therefore, the moderately oxidation-resistant DMS is selectively enriched in anoxic aeration tank zones, and its quantity increases on addition of DMSO to the point were DMS will overpower other sulphide odorants with its "canned corn" or "rotten cabbage" scent. Earlier research on "canned corn" odour that was guided by the common paradigm that anaerobic zones (H_2S and its methylation) are the main objective of odour mitigation, was giving too much weight to H_2S and MT, and disregarded the importance of large DMS signals, that can only be explained by DMSO reduction.

These data allow the conclusion that DMS formation by DMSO can be dominant in odour generation in anoxic and even in anaerobic conditions. If DMSO is present, the resultant DMS is additive to the amount of odorants generated in the sulphate reduction mechanism. Since DMS is resistant to oxidation, unlike the other reduced sulphur compounds, more DMS is present at higher DMSO concentration. Test conditions without added DMSO were found typically to have much lower DMS concentrations than those where DMSO was added. Chemical "fingerprints" (Figure 2) of sulphide odorants in headspace gas of activated sludge can provide hints whether the DMSO reduction mechanism is important or not. This is of use if a canned corn or rotten cabbage odour is being experienced by the surrounding community or plant operator due to the aeration tank.

The second main bench-scale test examined the changing sulphide formation under anaerobic conditions for a period of up to 30 days, with the following results, as shown in Figure 3.

Without the addition of DMSO, the concentration of DMS was found to be very small compared with that of H_2S and of MT. It is hypothesised that H_2S formation by sulphate reduction begins after about five hours of storage, while the subsequent protein breakdown of obligate aerobic bacteria and methylation of H_2S form additional H_2S, MT and small amounts of DMS. After eight days of incubation, the small DMS concentration began to peak, while after 30 days, VOS (volatile organic sulphur) compounds disappeared. It is hypothesised that this rise and subsequent disappearance of DMS is linked to methanogenesis that causes methylation of MT to form DMS, and subsequent demethylation of DMS. This mechanistic hypothesis assumes that breaking down liquid-activated sludge exhibits a similar sulphide cycle as digested biosolids that undergo "solid digestion" (Glindemann *et al.*, 2006b). This hypothesis is also supported by the headspace gas measurement of methane that appeared on day 8 of incubation, while methanogenesis became intense on day 30. The concentration of dimethyl disulphide DMDS (typically a product of oxidation and dimerisation of MT, see Glindemann *et al.*, 2006a) is always small, because of the anaerobic conditions. As indicated in Figure 3, these results imply that anaerobic wastewater treatment zones, without DMSO, would produce only minor

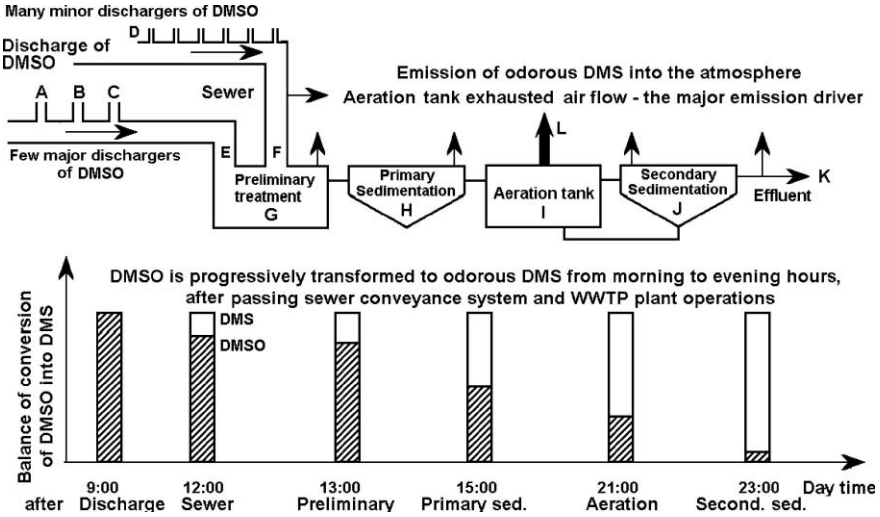

Figure 4 Scheme of DMSO conversion to odorous DMS throughout typical municipal wastewater treatment. Assumption of a single intermittent 9:00 am discharge of DMSO into the sewer, which causes WWTP aeration tank odour at afternoon hours. The DMSO/DMS bars on the time axis of the figure bottom are associated with the WWTP locations on the figure upper part

amounts of DMS compared with H_2S or MT, even after extended periods of anaerobic sludge floc decay. Therefore, a sulphide "fingerprint" with DMS > MT (as in Figure 2, "Anaerobic + DMSO") indicates the DMSO mechanism is important.

It is concluded that activated sludge without DMSO that degrades in closed bottles over a course of 30 days does not exhibit significant DMS formation. This "worst case" scenario of poorly aerated sludge shows that, without DMSO, DMS is unlikely to be formed as a dominating odorant compared with H_2S and MT.

Conclusions

This paper has examined various reduced sulphur compound generation mechanisms, under different oxygen regimes (anoxic and anaerobic conditions) that are present in WWTP aeration tank sludge flocs. Under both anoxic and anaerobic conditions, in the presence of DMSO concentrations of at least 2 mg/L, DMS was shown as the dominant odorant generated by the DMSO reduction mechanism when compared with the sulphate reduction mechanism under oxygen conditions present in a typical WWTP aeration tank. DMS was generated in both mechanisms, but seemed to be generated at a much higher rate and concentration in the DMSO reduction mechanism, when DMSO is present, compared with the sulphated mechanism in aeration tanks.

This paper has described a strategy that will allow operators to evaluate whether a DMSO/DMS reduction odour mechanism has occurred at their wastewater plants, based on if the predominant odorant from the aeration tanks is DMS. This was the case for Philadelphia's NEWPCP, where the wastewater treatment plant operator experienced a persistent "canned corn" odour problem (Porter *et al.*, 2004; Cheng *et al.*, 2005). This strategy led to the discovery of a large discharger of DMSO into their collection and wastewater treatment system (Glindemann *et al.*, 2006a).

Finally, the same anoxic and anaerobic conditions found in the aeration tank, in the presence of DMSO, could occur in the sewer as well as in the treatment stages primary sedimentation, aeration tank and during secondary sedimentation (see scheme in Figure 4). Many sewers are operated in a fashion that allows anoxic and anaerobic conditions to occur, typically due to long gravity and forced main sewer retention times, low

wastewater flow rates, typical BOD loadings and warm wastewater temperatures. Therefore, the DMSO/DMS odour mechanism is not limited to the aeration tank, although, aeration is the most important emission driver of DMS out of the wastewater into the atmosphere.

These results also show that it can be difficult and inefficient to use municipal wastewater treatment plants to eliminate DMSO waste residues in sewage, because the anoxic conditions that favour the DMSO/DMS reduction cannot easily be corrected. Additional measures would have to be taken to make sewage plants able to eliminate DMSO waste safely.

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