



Characterization of odor emission from alternating aerobic and anoxic activated sludge systems using real-time total reduced sulfur analyzer



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HIGHLIGHTS

- Odorous volatile sulfurs emitted from AAA system characterized.
- VSC peaks right after start of aeration for AAA system observed.
- More sulfur emission during air-on period than air-off observed.
- Effect of dimethyl sulfoxide in influent on sulfur generation studied.
- Odor control schemes for both air on and off periods suggested.

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ABSTRACT

Anaerobic biodegradation of sulfur-containing compounds always generates volatile sulfur compounds (VSCs) including H₂S, methyl mercaptan, and dimethyl sulfide (DMS). VSC emissions from wastewater treatment plants (WWTPs) result in odor complaints from people living nearby. To control odor-causing compounds in WWTPs, it is important to know the odor emission quantity particularly with continuous monitoring. Since modified activated sludge processes always include anaerobic, anoxic and aerobic conditions for nutrient removal, odor emission from these different environmental settings is expected.

In this study, continuous monitoring of VSCs from the headspace of an alternating aerobic and anoxic (AAA) activated sludge process via total reduced sulfur (TRS) analyzer was performed. There is clear pattern of the initial TRS peak immediately after the initiation of the aeration in the AAA system and TRS concentration begins to drop through the remaining air-on cycle. On the other hand, during the air-off period, TRS concentrations increase with time. In particular, a clear inflection point in the TRS profile could be observed after complete removal of nitrate during air-off, meaning more VSCs formation. Since the highest odor emission occurs after the initiation of aeration, the future control of exhausted air should only deal with air collected during the initial aeration period (e.g., 30 min), a similar concept for the treatment of first flush in combined sewer overflow. In addition, application of a control scheme to initiate aeration immediately after denitrification is completed during air-off should be beneficial in reducing odor emission.

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1. Introduction

The odor-causing gaseous compounds are produced and emitted in wastewater treatment plants (WWTPs) from each step of the treatment process. The emitted odors from WWTPs, in particular from sludge handling processes, have become a significant source of environmental annoyance, since odor-related complaints from communities surrounding WWTPs have been constantly increasing during the last decades (Karageorgos et al., 2010; Choi

et al., 2012). The cost for controlling odor is expensive, exemplified by the fact that Philadelphia had spent USD 2.5 million a year to minimize the effect of the odor on neighboring community (Cheng et al., 2009).

Main odorous compounds generated include volatile sulfur compounds (VSCs), reduced nitrogen compounds and volatile fatty acids in WWTPs (Wang et al., 2012). Among them, VSCs such as H₂S, methyl mercaptan, dimethyl sulfide (DMS), and dimethyl disulfide are known as main odorous compounds due to their extremely low odor threshold levels (e.g., H₂S 0.7 ppbv and DMS 0.3 ppbv; Devai and DeLaune, 1999; Lehtinen and Veijanen, 2011). Unfortunately, the generation of VSCs is unavoidable due to various anaerobic

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conditions encountered in WWTPs where inorganic sulfate and sulfur-containing organic compounds are transformed to H_2S and other reduced sulfur compounds, e.g., DMS. Compound to the problem is the fact that as urbanization accelerates, WWTPs are located closer to the residential areas (Karageorgos et al., 2010), resulting in increasing number of odor complaints as in the case of Metropolitan Seoul, Korea (Choi et al., 2012).

Each of different treatment unit processes in WWTPs may release different odorants (Easter et al., 2005). A potential odor source would be the aeration basins due to its stripping effect on previously accumulated reducing sulfur compounds present in the influent as well as in the return activated sludge (RAS). There have been many studies regarding VSC emission from aeration tanks (CDM, 2003; Cheng et al., 2005; Kim et al., 2006; Wu et al., 2006; Beghi et al., 2012). For example, DMS emitted from aeration basins with aqueous concentration varying from 5 to $1260 \mu\text{g L}^{-1}$ was found to be responsible for odor problem (Cheng et al., 2005). In fact, significant odor problems from VSCs (e.g., DMS) have been encountered in well aerated activated sludge tanks in Philadelphia WWTP since 1980s (Glindemann et al., 2005) and in the residential area near an industrial science park in Taiwan (Wu et al., 2006). The presence of 200 ppbv H_2S and 8 ppbv DMS was also reported in aeration tanks of Concord WWTP (Amirhor et al., 2006). Thus, unlike layman's wisdom that odor generation only occurs under anaerobic conditions, aerobic conditions in aeration basins also release odorants.

In addition, domestic WWTPs also receive wastewater from various sources which may contain a number of odorants and odor-causing precursors such as volatile organic compounds and sulfur-containing compounds (Glindemann et al., 2007; Cheng et al., 2009; Lei et al., 2010). These precursors are transformed to VSCs while wastewater is being treated. For example, dimethyl sulfoxide (DMSO), which is used commonly in photo-electronics, semi-conductor (Hwang et al., 2007) and thin-film transistor liquid crystal industries (Lei et al., 2010; Fukushima et al., 2013; Wu et al., 2014) is discharged into a WWTP and can cause "canned corn-like" nuisance odor in the form of DMS as the case of Philadelphia's Northeast WWTP (Glindemann et al., 2005; Cheng et al., 2007). This is due to the fact that 95% of about 150 tested strains of microorganisms (prokaryotes, eukaryotes, aerobes and anaerobes) are able to carry out the 2-electron transfer of DMSO reduction to DMS (Alef and Kleiner, 1989).

A variety of modified activated sludge processes used nowadays all provide anaerobic, anoxic and aerobic conditions for biological nutrient removal and these different conditions may also favor odor generation. For example, under anoxic conditions with measurable dissolved oxygen (DO) in bulk water but undetected DO inside sludge flocs, the microbial reduction of DMSO to DMS can occur (Glindemann et al., 2007; Bamforth, 2014). Even under high DO conditions in the aeration tank, average DMS concentration of $250 \mu\text{g L}^{-1}$ was found (Cheng et al., 2005). The presence of DMS in aeration tanks is due to the fact that DMSO can be reduced via 2-electron transfer to DMS as mentioned before. Also DMSO can be used as a terminal electron acceptor and eventually reduced to DMS (Zinder and Brock, 1978) in the presence or absence of O_2 (Griebler and Slezak, 2001). All the studies reported in the literature have focused on sporadic manual sampling and odor analysis to quantitate odorants level in headspace of in the mixed liquor of a bioreactor. Continuous monitoring of a bioreactor has not been performed to investigate odor emission characteristics of the reactor under different operating conditions.

Consequently, the present study was undertaken to monitor VSC emission from an alternating aerobic and anoxic (AAA) system by using a real-time total reduced sulfur (TRS) analyzer. The VSC emissions during both air-on and air-off periods in an AAA system were monitored. In addition, in order to assess the impact of sulfur

contents in the feed on the odor emission from the AAA system over time, 30 mg L^{-1} DMSO was added into the feed of the AAA system and headspace TRS and DMS were monitored.

To the best of our knowledge, this is the first attempt to continuously monitor TRS profiles during air-on and air-off period in an AAA system.

2. Materials and methods

2.1. Experimental set-up

A lab-scale AAA system consisted of a reactor (4 L), a settling basin (3.8 L) and a feed tank (40 L) for supplying feed to the AAA system (Fig. 1). The content in the feed basin, stored for about 3-d feeding for deliberately providing anaerobic conditions, was gently stirred to maintain wastewater composition homogeneous. The feed tank was covered to minimize loss of odorants generated during the storage.

The AAA system was operated in a cyclic mode of 2 h air-on and 2 h air-off. During air-on cycles, air was supplied to the bioreactor at the rate of 800 mL min^{-1} ; the range of the DO in the system was measured from 2 to 3 mg L^{-1} . It was hypothesized that the accumulated sulfide compounds from feed as well as from RAS could be stripped out of the mixed liquor in the beginning of the air-on cycle. During air-off cycles, the content of the reactor was mixed with a motor-driven stirrer. The hydraulic retention time (HRT) and solids retention time (SRT) of the system were maintained at 8 h and 15 d, respectively. The SRT was controlled by wasting appropriate amount of MLSS ($2000\text{--}3000 \text{ mg L}^{-1}$) from the reactor. The RAS was recycled to the head of the AAA basin at 100% of the influent flow rate. The upper part of the AAA reactor was sealed with a cover while the gas in the headspace was continuously withdrawn at 620 mL min^{-1} to a real-time TRS analyzer. A vent was made in the cover to allow fresh air to flow into the head space during the air-off, and to allow air emission through the surface of the bioreactor to flow out. Additional gas samples were also collected from the headspace for gas chromatographic analysis of DMS. System pH and ORP were continuously monitored using ORP (Mettler Toledo Type Pt4805-5c-DPAS-K8S/325, Woburn, Massachusetts) and pH probes (Mettler Toledo Type HA405-DXK-S8/225) installed on the bioreactor. The pH and ORP signals were transferred to a PC using a data acquisition and control program (LabView 8.0, NI-Korea, Seoul, Korea).

2.2. Sample preparation and analysis

2.2.1. Wastewater samples

Wastewater used in this study was collected from the primary effluent of a local WWTP. Once the wastewater was delivered (twice a week) to the laboratory, COD, TN, and TP were analyzed according to the Standard Methods (APHA, 2005). NH_4^+ , NO_3^- , SO_4^{2-} , and PO_4^{3-} were analyzed using Dionex ion chromatography (ICS-90, USA). S^{2-} was measured according to the Standard Methods (APHA, 2005). The same water quality parameters were analyzed for the effluent from the system.

2.2.2. Real-time TRS analyzer

VSCs present in the headspace gas from the AAA system were continuously monitored using a real-time TRS analyzer (M102E, Eco-S&E, Korea). The TRS analyzer can be operated in two different modes; one is for the range less than few ppmv, and the other for the higher range than 1 ppmv. In this study, the analyzer was calibrated with the standard H_2S gas with the R^2 of >0.99 for the range of 0–1000 ppbv, since the TRS concentration was not over the range under normal operation of the AAA system. Therefore, any

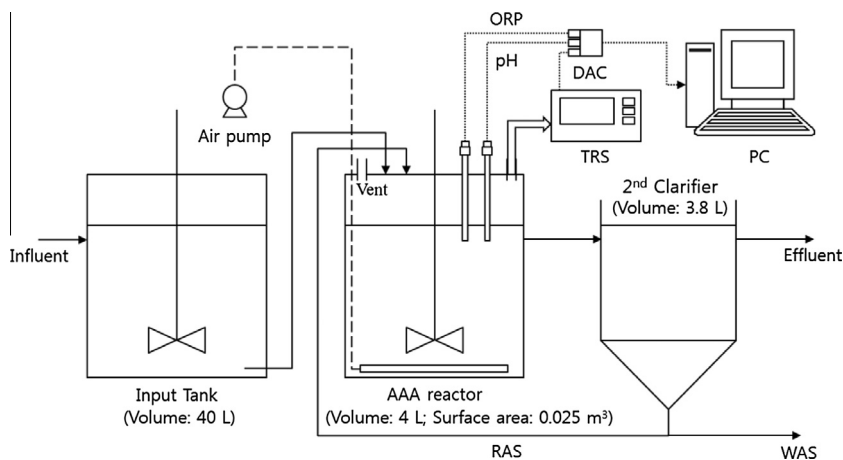


Fig. 1. Schematic diagrams of lab-scale AAA activated sludge system.

signal from the instrument higher than the calibration range was extrapolated to quantitate. In fact, the instrument still showed a good linearity, when it was calibrated for the range up to 30000 ppbv (see Supporting Material (SM), Fig. SM-1).

2.2.3. Impact of DMSO addition on VSC emission from AAA system

Previous studies have clearly indicated that DMSO is the precursor responsible for generating offensive VSC (especially DMS) odor problems. In this study, the DMSO (Bio Basic, Canada) of 30 mg L⁻¹ was added to the feed solution to investigate the impact of influent composition on the VSC emission profile of the AAA system during air-on and -off periods. The continuous DMSO addition lasted for 4.5 cycles in the AAA system.

2.2.4. SPME and GC for DMS analysis

In addition to the measurement of VSCs from the headspace gas of the bioreactor, additional gas sample (at 0.2 L min⁻¹ for 5 min) was taken in a 1-L Tedlar bag for DMS analysis using a SPME followed by the quantification with GC/Mass Selective Detector. The detailed procedures for the analytical method used in this study are shown elsewhere (Kim et al., 2002). The calibration curves for DMS were developed: 0–1000 ppbv and 1–5 ppmv for lower and higher ranges, respectively. Both curves yielded good linearity ($R^2 > 0.99$). The method detection limit was determined as 0.24 ppbv.

3. Results and discussion

3.1. Characteristics of odor emission in AAA system

3.1.1. Wastewater characteristics

Table 1 shows influent and effluent water quality of the lab scale AAA system under normal operation. The COD removal

Table 1
Characteristics of influent and effluent wastewater in the AAA system (unit: mg L⁻¹).

Contents	Influent	Effluent
COD (n = 15)	190 ± 60	28 ± 17
TN (n = 15)	36 ± 6	17 ± 7
NH ₄ ⁺ -N (n = 15)	23 ± 7	2 ± 1.7
NO ₃ ⁻ -N (n = 15)	0.5 ± 0.4	10 ± 5
S ²⁻ -S (n = 15)	8.6 ± 3.9	BDL
SO ₄ ²⁻ -S (n = 13)	26 ± 9	34 ± 6
TP (n = 15)	3.9 ± 1	3.0 ± 0.9
PO ₄ ³⁻ -P (n = 15)	2.3 ± 1.1	2.0 ± 1

*BDL = below detection limit.

efficiency of the system was about 85%. The average NH₄⁺-N concentration of influent and effluent wastewater was 23, and 2 mg L⁻¹, respectively, demonstrating excellent nitrification performance. The influent sulfate-S concentration was about 26 mg L⁻¹ and increased to 34 mg L⁻¹ in the effluent due to oxidation of high sulfide concentration present in the influent. Sulfide concentration was relatively high due to anaerobiosis of stored feed solution.

3.1.2. TRS profile

Typical profiles for TRS emission, measured by the real-time TRS analyzer, are shown in Fig. 2 for 1-wk data. There is a consistent trend of increasing/decreasing TRS concentrations during air on/off period (more discussion later). The TRS concentration peaks which were in fact observed in the beginning of each air-on cycle varied from <20 ppbv up to 400 ppbv probably due to varying septic conditions of feed solution. In particular, lower TRS emissions over several cycles were observed when the feed solution was replaced by the freshly collected sample. The increasing TRS profile during air-off period further corresponds with the disappearance of nitrate resulting in truly anaerobic conditions as shown in Fig. 3. For comparison, two profiles with (Fig. 3a and d) and without the detection of nitrate knee (NK; Kim and Hao, 2001) (Fig. 3a and c) which signifies the end of denitrification (Fig. 3f) are shown in Fig. 3. It clearly shows the inflection point on the TRS profile corresponding to the NK on the ORP profile; thereafter the ORP level kept decreasing resulting in more TRS generation (Fig. 3d). On the other hand, the TRS profiles remained relatively constant during the entire air-off cycle in which nitrate was still present in the mixed liquor (Fig. 3c and e); no NK was detected on the ORP profile.

Fig. 4 further shows characteristic TRS profiles in the AAA reactor (Fig. 4a) along with TRS emission flux calculated for one cycle (Fig. 4c). Again ORP profiles are consistent with the denitrification reactions (Fig. 4b), i.e., system ORP increases during nitrification, while it decreases during denitrification (Kim and Hao, 2001). The opposite is true for pH profiles (data not shown). Again, NK points were identified on the ORP profile (Fig. 4b). Clearly, there exists a major difference in the amount of reduced sulfur emission between air-off and air-on cycle. When the aeration is initiated, tiny air bubbles from the diffusers provide sufficient interfacial surface between the liquid and the gas phases, resulting in the significant stripping of VSCs from aeration basin as shown in the TRS emission profile. The VSC emission sources were originated from accumulated VSCs during previous air-off cycle as well as from reduced sulfide compounds present in the feed solution and RAS;

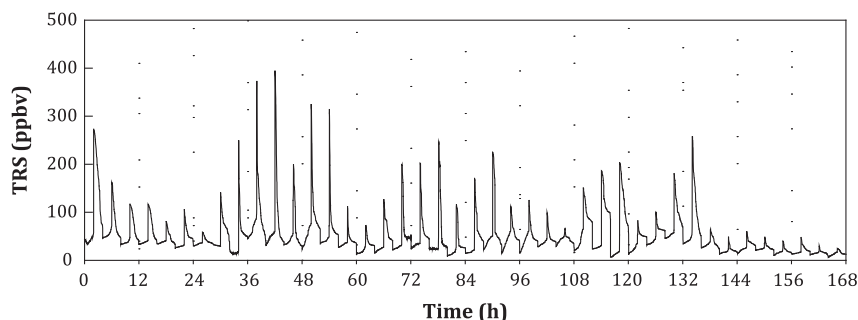


Fig. 2. TRS emission profiles from AAA reactor for a week.

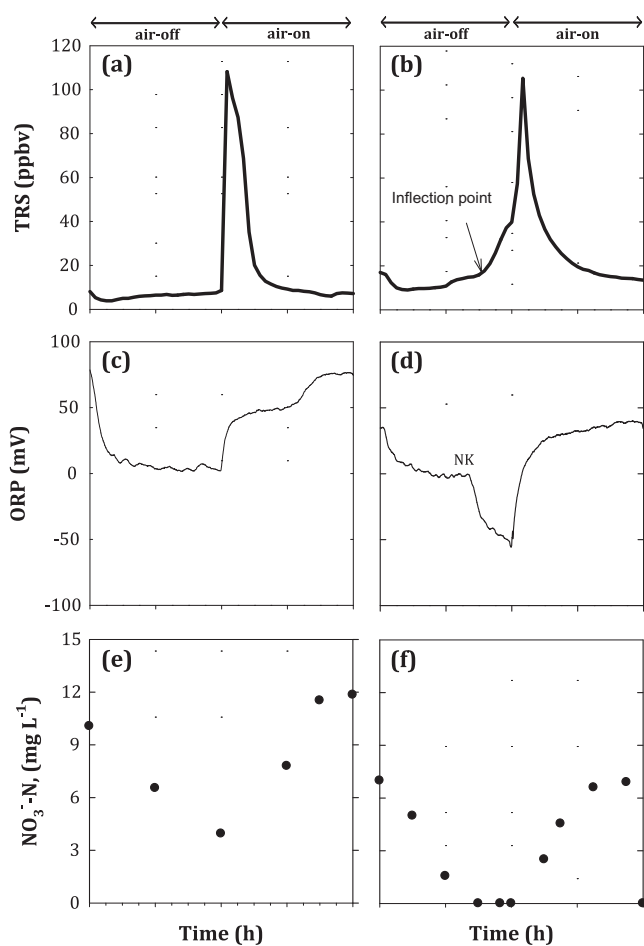


Fig. 3. Profiles of (a) TRS, (b) ORP, and (c) NO_3^- -N.

S^{2-} level was about 2–3 times higher than that in the feed. After a sharp peak in the beginning of aeration, the TRS concentration rapidly drops to the baseline as the aeration continues. On the other hand, during the air-off cycle, there is a continuously increasing trend of TRS emission apparently due to sulfide compounds present in the influent as well as those accumulated in the bioreactor even under gentle mixing.

The TRS emission flux as H_2S was calculated based on air-flow rate of 620 mL min^{-1} and surface area of 0.025 m^2 . Fig. 4c shows TRS emission flux from the AAA system for one full air on/off cycle (middle cycle from Fig. 4a at 12 h). About 2.7 times more reduced sulfur emission flux was observed during air-on cycle than during air-off. The average TRS emission rate for this 2-h aeration cycle was $1.35 \mu\text{g m}^{-2} \text{ min}^{-1}$, as compared to $0.56 \mu\text{g m}^{-2} \text{ min}^{-1}$ during

2-h air-off period. But more importantly, 42% of the total sulfur compounds released from the system for one full cycle of 4 h were released during the first 30 min of the air-on. It must be noted that these numbers are from one cycle and the result may not be applicable to the overall TRS emission from the AAA system. For example, TRS emission flux increased noticeably after denitrification was completed (signified by an NK occurrence on the ORP profile) during air-off cycle. In fact, the next to last air-off cycle shown in Fig. 4a indicates that the TRS emission flux during air-off period is even higher than that from air-on cycle. Nonetheless, since the highest odor emission occurs after the initiation of aeration, the future control of exhausted air from an AAA system should deal with air collected during the initial aeration period (e.g., 30 min), a similar concept for the treatment of first flush in combined sewer overflow. In addition, application of a control scheme to initiate aeration right after denitrification is completed during air-off cycle should be beneficial in preventing the increased TRS emission.

3.1.3. Anaerobic reactions in secondary sedimentation tank

The depth of sludge blanket at a secondary settling basin exerts a significant influence on odor emission due to the presence of anaerobic conditions in the sludge blanket (Sekyiamah et al., 2008). The effect of anaerobic conditions in the bottom of the secondary settling basin on some biological reactions was observed in the present study. Liquid samples were collected from three different depths of the settling basin and was analyzed for sulfate, nitrate, and phosphate. As shown in Fig. 5, the water sample collected from the top of the settling basin showed the highest level of sulfate and nitrate, while those collected from the bottom showed higher phosphorus levels, clearly indicating nitrate denitrification, sulfate reduction and P release within the sludge blanket. Thus, it is expected that RAS with 100% recycle provides some reduced sulfur compounds to the aeration tank. The analysis of S^{2-} in RAS and feed samples confirmed that supply of sulfur from settling tank; S^{2-} present in the RAS was 9 ppm while that in the feed was 3 ppm. In fact, sulfur compounds (e.g., DMS) in mixed liquor is known strongly correlated with sludge blanket depth (Sekyiamah et al., 2008).

3.1.4. Impact of DMSO addition on TRS emission

In order to investigate influent sulfur contents on the TRS emission from the AAA system, DMSO, a well-known precursor of VSCs (especially, DMS) formation in wastewater was added into the feed tank and the TRS emission was evaluated as shown in Fig. 6. Both the stored feed and RAS contain reduced sulfur compounds as reflected by the VSC emissions in the absence of DMSO feed.

Before DMSO was added into the feed, TRS concentration of the headspace gas from the reactor in the beginning of aeration was 90–120 ppbv (Fig. 6a). DMS of the gas samples taken at the same time varied from 30 to 50 ppbv (Fig. 6b), which is two orders of magnitude higher than the published DMS odor threshold of

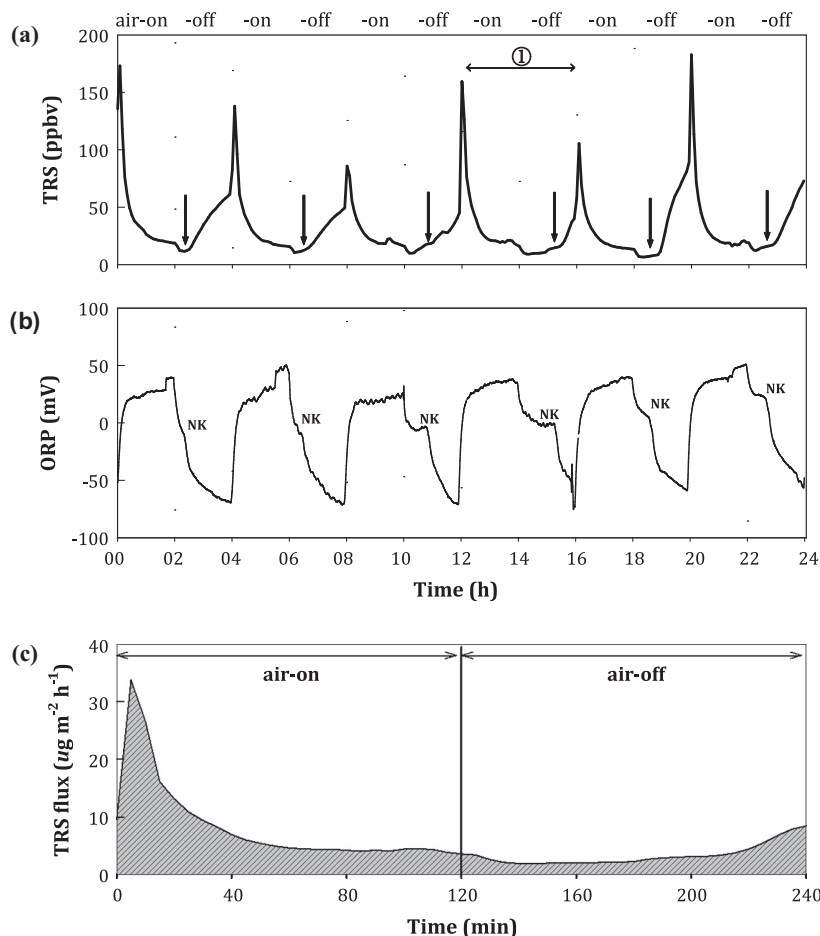


Fig. 4. TRS emission profiles from AAA reactor (a) TRS emission concentration for 6 cycles (down arrows indicating inflection point for NK); (b) ORP (c) TRS emission flux for cycle ①.

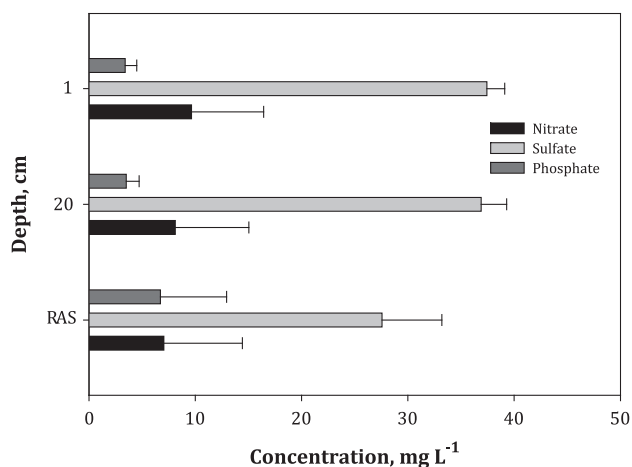


Fig. 5. Variation of sulfate, phosphate and nitrate at the sludge blanket level of secondary sedimentation tank ($n = 3$).

0.3 ppbv (Guadagni et al., 1963). After the addition of 30 ppm DMSO, both DMS and TRS increased significantly (note the different scales in Fig. 6). There are several points that need to be mentioned. Firstly, when DMSO was added into the feed, TRS and DMS concentrations at the beginning of aeration cycle were increased to about 1800 and 750 ppbv, respectively. This high DMS concentration is attributed to the increased DMSO content of the feed

solution which was reduced to DMS (Alef and Kleiner, 1989); the amount of DMS produced is related to the quantity of microorganisms and incubation time (Sklorz and Binert, 1994). The reduction rate from DMSO to DMS is about $2 \mu\text{mol h}^{-1} \text{g}^{-1}$ dry activated sludge during 6-h batch test as reported by Sklorz and Binert (1994). Coupling with high gas/water partition coefficient, DMS can be easily transferred to the headspace even under mild turbulence created by gentle mixing during air-off cycle. Next cycle yielded the highest TRS level of about 8400 ppb and the peak then began to decrease with successive cycles possibly due to the replacement of feed solution and finally it was reduced significantly after the termination of DMSO dosage and reached the baseline level. Note that there are clear inflection points in the TRS profile which correspond the point of complete denitrification; TRS increases rapidly after the inflection points as mentioned before. In particular, RAS stream also contains high level of sulfides including DMS, meaning that the RAS can be a major potential odor source; headspace DMS concentration of RAS samples collected before and after DMSO addition was 20–40 and 200–3200 ppbv, respectively.

The profile of DMS is similar to that of TRS; it increases to a peak value and then peak value is gradually decreased. The highest DMS concentration measured is about 2600 ppbv; for comparison, 37 ppm DMS was detected in the headspace of a bottle containing 2 mg L^{-1} DMSO exposed to anaerobic sludge for 6 h (Glindemann et al., 2007). In the presence of O_2 , DMS can be oxidized to methyl mercaptan (Lei et al., 2010), which can be reduced to H_2S and formaldehyde under anaerobic condition (Suylen et al., 1987). In fact,

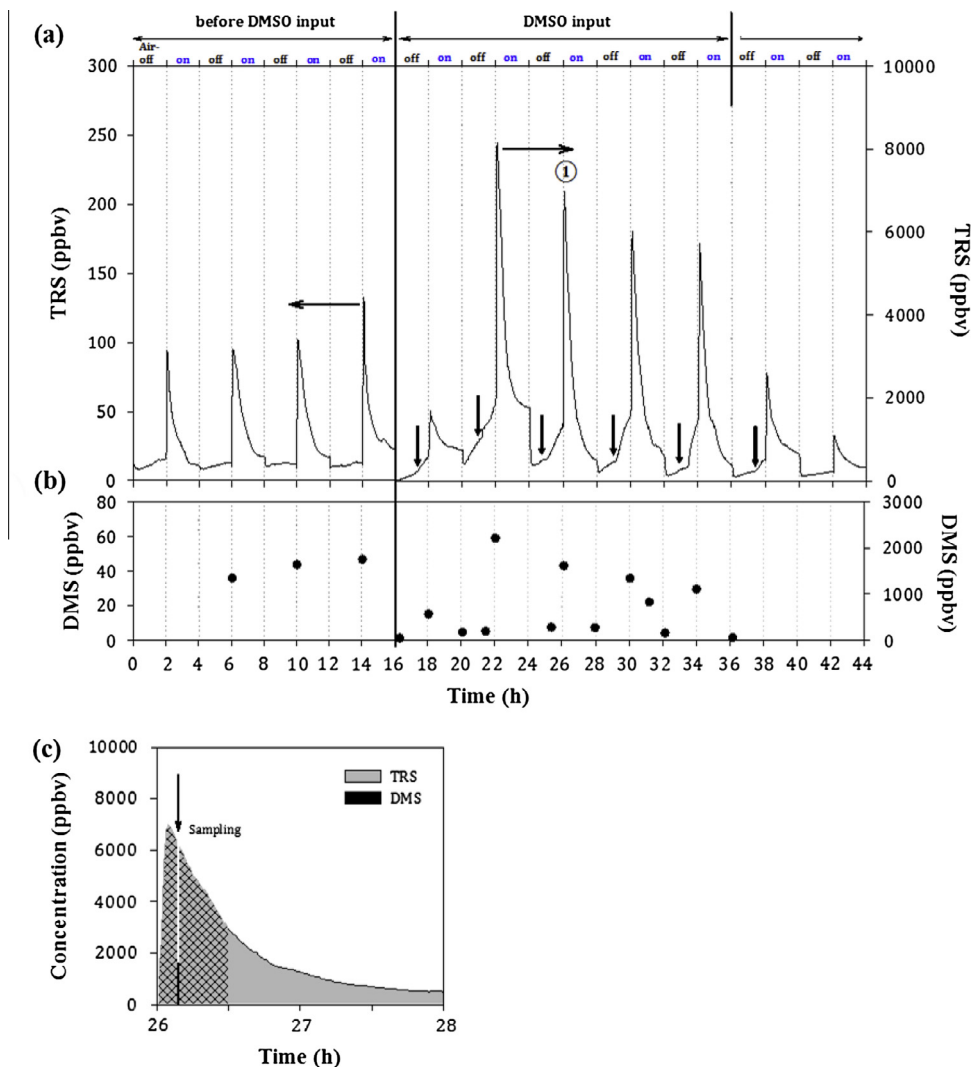


Fig. 6. Reduced sulfur concentration in the absence of and presence of DMSO. (a) TRS emission concentration (down arrows indicating inflection point for NK); (b) DMS concentration; (c) comparison of DMS and TRS concentration for cycle ①.

Table 2
TRS and DMS concentration over headspace of AAA system before and after DMSO addition.

Status of the reactor		TRS, ppb ^a	DMS, ppbv
Before DMSO added	Anoxic	12 ± 2	BDL [*]
	Oxic	40 ± 25	40 ± 4 ^b (n = 3)
After DMSO added	Anoxic	500 ± 420 ^c	200 ± 100 ^d (n = 6)
	Oxic	1700 ± 1500	500 ± 380 ^d (n = 6)

^{*} BDL = below detection limit.

^a Average and standard deviation of TRS concentration measured by analyzer.

^b Average and standard deviation of 3 DMS concentrations measured in the beginning of air-on.

^c Average and standard deviation of TRS concentration measured only for 4.5 cycles where DMSO was added to the feed tank.

^d Average and standard deviation of DMS obtained using regression curve from Fig. 7.

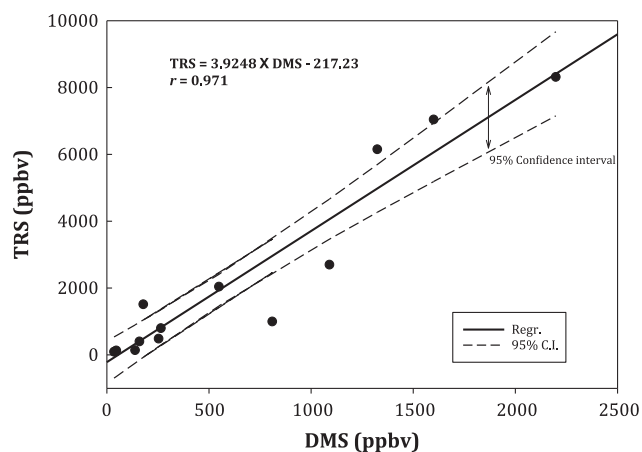


Fig. 7. Regression curve between TRS and DMS concentration.

methyl mercaptan oxidase responsible for the degradation of methyl mercaptan to H₂S also has been isolated (Suylen et al., 1987; Gould and Kanagawa, 1992).

Secondly, there is a linear correlation between TRS and DMS (Fig. 7), but DMS only contributed a small fraction of TRS (25% from Fig. 7). The other major contribution to TRS is from H₂S as was also

reported by Glindemann et al. (2007) who found the presence of both H₂S and DMS when the DMSO was exposed to anaerobic sludge. For comparison, the ratio of DMS/H₂S present in the reduced sulfur compounds in environmental samples ranged from

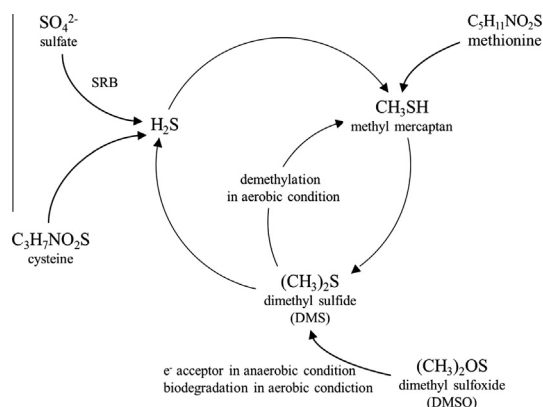


Fig. 8. Reduced sulfur compounds present in wastewater with DMSO.

0.3% (industrial sources; Kim and Park, 2008) to 19% (swine effluent, Zahn et al., 2001) to 25% (industrial complex, Kim et al., 2006) to 168% (activated sludge in bottle, Glindemann et al., 2007).

Thirdly, the average DMS concentrations were much higher under aerobic conditions as compared to those of anoxic conditions (Table 2). The data for DMS in air-off and air-on cycles were obtained from TRS results based on the correlation from Fig. 7. The liquid–vapor partition coefficient of DMS is about 15 (Glindemann et al., 2005), or $0.27 \mu\text{g L}^{-1}$ aqueous DMS concentration would yield saturated 7 ppbv in the headspace. Thus, it is not surprising that the Philadelphia's WWTP has encountered terrible odor problems with the average $250 \mu\text{g L}^{-1}$ aqueous DMS concentration present in the aeration tanks.

Fourthly, there is a clear inflection NK points in the TRS profile. Since redox potential of NO_3^-/N_2 is much higher than that of DMSO/DMS (0.75 vs. 0.16 V; Lei et al., 2010), the DMSO as an electron acceptor being reduced to DMS only occurs in the absence of nitrate. Consequently, after these inflection points, significant amounts of DMS is produced over the remaining air-off cycle duration and emitted via aeration stripping at the beginning of subsequent air-on cycle.

The potential TRS sources and DMS occurrence from the addition of DMSO are illustrated in Fig. 8. Some of the pathways are reported by Higgins et al. (2006), except for the DMS conversion to methyl mercaptan and the role of DMSO. Under aerobic conditions, DMSO is enzymatically reduced to DMS to methyl mercaptan and eventually to CO_2 (Suylen and Kuenen, 1986; Suylen et al., 1986). Under anaerobic conditions, DMSO serves as electron acceptor and is reduced to DMS (Zinder and Brock, 1978) as also demonstrated in the present study. Under both aerobic and anaerobic conditions, increased TRS and DMS could be observed.

4. Conclusions

In this study, we showed how odor-causing VSCs develop and release out of the MLSS in an AAA system. From the study, the following results were obtained.

As a result of the stripping phenomenon of VSCs, which were built up during the previous anoxic cycle, sharp peaks were obvious in the TRS profile in the beginning of each air-on cycle. VSCs were also supplied with influent wastewater and RAS from the secondary settling tank. This VSCs formation and release over cyclic operation of the AAA system was more clearly demonstrated with the addition of DMSO, a precursor of sulfur odorants in the feed. VSCs released from the AAA system during the initial stage of aeration cycle (i.e., first 30 min) accounted for more than 40% of total VSCs released during one full cycle. Therefore, if headspace gas from an AAA system is collected only for first 30 min or more of

each air-one cycle and treated, significant reduction of odor emission can be achieved.

In fact, the amount of VSC emissions during anoxic cycle can be increased if complete nitrate removal is achieved within the cycle. Right after nitrate is completely removed from MLSS, a clear inflection point could be identified in the TRS profile as the case of NK in the ORP. This finding implies that odor production during anoxic cycle time of an AAA system can be minimized if the system aeration is initiated immediately after denitrification is completed.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.08.008>.

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