1 **An efficient method for measuring dissolved VOSCs in wastewater**

2 **using GC-SCD with static headspace technique**

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14

15 **Abstract**

16 Volatile organic sulfur compounds (VOSCs) are important sources of unpleasant odor

17 in wastewater systems. However, the study of VOSCs is usually hindered by their

18 complicated measurement method and highly reactive nature. In this work, a static

19 headspace method utilising gas chromatography (GC) with a sulfur

20 chemiluminescence detector (SCD) was developed to quantitatively analyze VOSCs

21 in wastewater matrices. The method has low detection limits and requires no pre-

22 concentration treatment. Three typical VOSCs, namely methanethiol (MT), dimethyl

23 sulfide (DMS) and dimethyl disulfide (DMDS), were chosen as examples for this

24 study. The calibration curves of all three compounds covering a wide range from 0.5

25 ppb to 500 ppb showed good linearity ($R^2 > 0.999$). The method detection limits (MDL)

26 were 0.08, 0.12 and 0.21 ppb for MT, DMS and DMDS, respectively. The

27 reproducibility (relative standard deviation) was approximately 2%. The recovery

28 ratio of MT, DMS and DMDS in spiked wastewater samples were $83 \pm 4\%$, $103 \pm 4\%$

and $102 \pm 3\%$, respectively. Sample preservation tests showed that VOSCs in wastewater samples could be preserved in vials without headspace under acidified conditions (pH ~1.1) for at least 24 h without significant changes (<1.8 ppb). The analysis of real wastewater samples from both a laboratory-scale sewer system and a full-scale sewer pipe demonstrated the suitability of this method for routine wastewater VOSC measurement.

1. Introduction

Odor problems in wastewater collection and treatment systems have become critical issues to water industry (Stuetz and Frechen 2001). In addition to hydrogen sulfide, volatile organic sulfur compounds (VOSCs), such as methanethiol (MT), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) are believed to be important sources of unpleasant odor in municipal and industrial wastewater (Devai and DeLaune 1999, Hvitved-Jacobsen 2002, Cheng et al. 2005, Sekyiamah et al. 2008, Catalan et al. 2009, Marleni et al. 2012). Because of their malodorous characteristics and low odor thresholds (0.07 - 5.9 ppbv) (van Gemert 2011), even a small amount of VOSCs can contribute to significant odor pollution. At higher concentrations (> 0.5 - 20 ppmv), they could cause health problems (Lomans et al. 2002). Some recent studies have focused on VOSC measurement in the air around wastewater treatment plants (WWTPs) (Ras et al. 2008, Sekyiamah et al. 2008, Sheng et al. 2008, Lasaridi et al. 2010). However, it is also worthwhile to monitor VOSC concentrations in the wastewater itself as it can help understand the conversion of VOSCs in wastewater and thus solve the odor problem at the root. Therefore, it is important to have a reliable and efficient method to measure VOSCs in wastewater.

58   The analyses of VOSCs in wastewater have been mainly carried out by using gas

59   chromatography (GC) with flame photometric detector (FPD) or mass spectrometry

60   (MS) (Van Langenhove et al. 1985, Hwang et al. 1995, Abalos et al. 2002, Cheng et

61   al. 2007, Sheng et al. 2008, Godayol et al. 2011). Since the detection limits of these

62   two detectors are relatively high (10^{-11} gS/s), pre-concentration of VOSCs in

63   wastewater samples is often required before the measurement. One commonly used

64   pre-concentration method is purge-and-trap (Van Langenhove et al. 1985, Hwang et

65   al. 1995, Cheng et al. 2007, Sheng et al. 2008). VOSCs are firstly stripped from the

66   aqueous phase and adsorbed on a sorbent. During the injection, the analytes on

67   sorbent are desorbed thermally and flushed to GC column with an inert gas. However,

68   major disadvantages of this method include expensive equipment, tedious procedure

69   and potential loss of VOSCs from the trap if excessive purge time or flow rates are

70   used (Wylie 1988). Solid phase microextration (SPME) was an alternative pre-

71   concentration method recently used in wastewater VOSC analysis (Abalos et al. 2002,

72   Godayol et al. 2011). This method involves the use of a thin polymer-coated silica

73   fiber to adsorb VOSCs from the headspace of the wastewater sample. The fiber is then

74   inserted directly into the GC injection port for thermal desorption and analysis.

75   Compared with the purge-and-trap process, SPME is relatively simple and

76   inexpensive. However, the extraction process is time-consuming, normally taking

77   more than half an hour for a sample. Moreover, Lestremau et al. (2004) showed that a

78   large proportion of MT was dimerized to DMDS during the SPME process, resulting

79   in errors in MT and DMDS measurements.

80

81   Sulfur chemiluminescence detector (SCD) is a relatively new gas chromatographic

82   sulfur-selective detector. It converts the sulfur compounds to sulfur chemiluminescent

83   species and detects the chemiluminescence from the reactions between ozone and

84   sulfur chemiluminescent species (Yan 2002). This detector, coupled with GC, has

85   been applied for detection of sulfur containing compounds in petroleum, atmosphere

86   and food (Di Sanzo et al. 1994, Steely Jeffrey 1994, Galán et al. 1997, López García

87 et al. 2002, Rouseff Russell 2002, Nylén et al. 2004). Compared to FPD and MS, SCD

88 is superior on the following aspects:

89 (1) Excellent sensitivity. The detection limit of SCD can reach 10^{-13} gS/s, which is

90 about 2 orders of magnitude lower than FPD and MS (Wardencki and Zygmunt 1991).

91 (2) High selectivity. The sulfur-selective characteristic of SCD makes it superior to

92 MS, as it can eliminate the signals of many other compounds that may interfere with

93 the detection. Though it is also sulfur selective, FPD has a selectivity (C/S) of about 1

94 to 4 orders of magnitude lower than SCD (Wardencki 1998).

95 (3) Easy operation. The operation of SCD is much easier than MS and also simpler

96 than FPD.

97

98 The prominent advantages and successful application of SCD in other fields suggest

99 its promising potential for measuring VOSCs in wastewater matrices. Especially for

100 its high sensitivity, the use of SCD might make it possible to eliminate the

101 complicated, time-consuming and error-prone pre-concentration processes. However,

102 to our knowledge, no studies have been reported to date on the use of SCD to detect

103 VOSCs in wastewater.

104

105 The purpose of this paper is to develop a method for the measurement of VOSC

106 compounds in wastewater using GC-SCD. The static headspace technique, rather than

107 a pre-concentration process, was used for the transfer of VOSCs from water to the gas

108 phase, which made the measurement fast and simple. Also, it would avoid errors

109 caused by sample loss or contamination during the pre-concentration. The GC was

110 operated above room temperature (28°C), so the cooling system of GC column, which

111 is usually applied to enhance separation of volatile compounds, is not required. The

112 linear ranges, detection limits, reproducibility, and recovery ratios of this method were

113 examined and compared with other VOSC detection methods. Given the highly

114 reactive nature of VOSCs, different sample preservation methods were assessed and

115 an effective method was selected. Finally, this method was applied to measure VOSC

concentrations in real wastewater samples collected from laboratory and real sewer systems.

2. Material and Methods

2.1 The GC-SCD method with static headspace technique

The whole procedure of the VOSC analysis using GC-SCD includes 6 steps as illustrated in Figure 1. The details of all these steps are described in following sections.

Figure 1- A schematic diagram of the steps involved in VOSC measurement with the static headspace technique using GC-SCD.

2.2 Standard solution

Methanethiol (MT), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) were chosen as examples of VOSCs in this work, which are VOSCs typically found in wastewater (Wu et al. 2006, Sheng et al. 2008, Lasaridi et al. 2010). Analytical reagent grade of CH_3SNa, DMS and DMDS (Sigma-Aldrich, Australia) were used to prepare the standard solutions using MilliQ water (Merck Millipore, Germany). As these compounds can be easily oxidized, the MilliQ water was deoxygenated before making the solution by purging it with nitrogen gas (99.99%, BOC, Australia) for at least 1 h. A concentrated stock solution (50 ppm) was firstly prepared, which was further diluted to 5 different levels (0.5-500 ppb) for calibration purpose. All the standard solutions were prepared without headspace to avoid loss of compounds through volatilization.

2.3 Sample preparation

A 12 ml glass headspace vial (Labco Limited, United Kingdom) was used to prepare samples for GC-SCD analysis. The vial was firstly purged with nitrogen gas for 10 min to remove oxygen. Subsequently, 3ml of standard solution or filtered wastewater

sample (0.22 μm membrane) was injected into the vial. The possible adsorption of VOSCs on the membrane filter was investigated by comparing response areas with and without sample filtration, and the results showed insignificant difference (Figure S1, Supplementary Information). To further reduce the risk of adsportion, the filter was used to filter an initial 3 ml of the same wastewater without collecting the filtrate. If there was any adsorption, the VOSCs on membrane surface would be saturated.

Wastewater usually contains a high concentration of H_2S. Its peak could create a large tail on the chromatogram, which could affect the detection of MT as the MT peak would appear on the tail of the H_2S peak. In order to solve this problem, two different buffers, namely a boric buffer (pH=8.1 ± 0.1) and a phosphate buffer (pH=7.6 ± 0.1), each with two different strengths at 0.05 M and 0.15 M, were tested. Three milliliters of buffer was added to the headspace vial and their effect on reducing the spread of the H_2S peak were investigated.

As the vial was sealed and gas inside would not be released when injecting sample or buffer, it resulted in overpressure in the vial. The overpressure would not change the patial pressure of the VOSCs in the headspace, which is determined by the amount of VOSCs in the liquid sample at equilibrium conditions (according to Henry's Law). However, the relative concentration of VOSCs (ppmv) in the headspace would vary with the overall pressure in the vial headspace, which could affect the detection limits of the method. The addition of 6 ml liquid into the vial would result in relatively high concentrations of VOSCs (Figure S2) so that relitavely low detection limits could be achieved.

The vial was then mixed using a vortex mixer for 2 min to ensure that the gas-liquid equilibrium was reached (There were no increase of GC response areas of all three compounds for mixing time longer than 2 min). At last, 300 μL of headspace gas was drawn with a gas-tight syringe (SGE Analytical Science, Australia) and injected into

173 the GC for analysis.

174

2.4 Instrumentation

176 The analysis was performed on an Agilent 7890A GC (Agilent Technologies, Santa

177 Clara, California) coupled with an Agilent 355 SCD. The GC uses a capillary column

178 (30 m × 320 μm × 5 μm, Zebron™, Phenomenex) for VOSC separation and helium as

179 a carrier gas. The injection was operated in pulsed splitless mode. In order to optimize

180 GC separation of targeted compounds in both standard solutions and wastewater

181 samples, the injection temperatures ranging from $80^{o}C$ to $120^{o}C$ were tested. Also

182 different GC oven temperature programs were performed (temperature starting at

183 $28^{o}C$, $40^{o}C$ and $50^{o}C$ respectively; total retention time varying from 8.5 min to 11.6

184 min). The SCD was operated according to the manufacturer's guidelines. The burner

185 was operated at $800^{o}C$. The hydrogen and air flow rates were maintained at 42 ml/min

186 and 62 ml/min, respectively, and the pressure in the reaction cell was at ~8 Torr.

187

2.5 Sample preservation method

189 As GC-SCD is normally unavailable in field and VOSCs are highly reactive, it is

190 critical to preserve wastewater samples prior to their analysis for VOSCs. In this study,

191 two different preservation methods were evaluated. One method was to store the

192 headspace of the wastewater sample in a separate glass vial (hereinafter referred to as

193 "separated headspace method"). 4ml gas was drawn from the aforementioned 12ml

194 headspace vial containing wastewater sample and injected into a separate 4ml glass

195 vial containing $CaCl_2$ (0.5 g) and ascorbic acid (0.3 g). These two compounds were

196 used to remove moisture and oxygen in the VOSCs-containing air and prevent the

197 oxidation of VOSCs (Tangerman 1986, Inomata et al. 1999). The vial with gas only

198 was covered with aluminum foil to avoid light and then stored at $\sim 4^{o}C$.

199

200 The second method was to acidify the wastewater samples (hereinafter referred to as

201 "acidification method") since VOSCs were found more stable in acidified wastewater

202 (Cheng et al. 2007). This method was carried out in the following steps. A 40 ml glass

203 vial, capped with butyl rubber septa, was firstly flush by nitrogen gas for 10 min to

204 remove oxygen. The vial was then filled to the top with 37.5 ml wastewater sample

205 filtered through a 0.22 μm membrane, and 2.5 ml HCl (3 M) so that the pH was

206 adjusted to ~1.1. The vial was covered with aluminum foil to avoid exposure to light

207 and stored at ~4°C. Before doing the analysis, the sample was heated in a water bath

208 (20°C) for 10 min and the pH of sample was raised to ~7.0 by adding 2.4 ml NaOH

209 (3M) into the bottle, with an equivalent volume of the HCl and wastewater mixture

210 withdrawn. The dilution effects of HCl and NaOH addition were considered while

211 calculating the VOSC concentrations in wastewater. Then, 3 ml of sample was taken

212 from the bottle and the normal static headspace technique and GC-SCD analysis was

213 performed as previously described (Section 2.1).

214

215 The capabilities of sample preservation by these two methods were evaluated by

216 monitoring the change of MT, DMS and DMDS concentrations in wastewater after

217 different time intervals. The wastewater used for the test was obtained from an

218 anaerobic sewer reactor mimicking a rising main sewer as will be further described in

219 Section 2.6. In each test, several samples were taken at the same time and one of them

220 was measured immediately. Then, samples stored directly in headspace vials and

221 preserved by separated headspace method were measured after 8 h, while samples

222 preserved by acidification method were analyzed after 24 h and 48 h. Spiked

223 wastewater samples were also tested for the effect of acidification method at a high

224 concentration range using the same method as described before.

225

226 *2.6 Real wastewater sample analysis*

227 Real wastewater samples from both a laboratory-scale sewer system and a real sewer

228 pipe were tested to evaluate the application potential of the method developed in this

229 study. The laboratory sewer reactor used was a cylindrical gas-tight reactor, which

230 mimicked a section of a rising main sewer pipe under anaerobic conditions (Guisasola

8

231 et al. 2008). The reactor was fed intermittently (6 pumping events per day) with

232 municipal wastewater collected weekly from a local sewage pump station in Brisbane

233 (Queensland, Australia). The wastewater was stored in a cold room (4^oC) to minimize

234 the biotransformation and was heated up to 20^oC before being pumped to the reactor.

235 Further details of the reactor and its operation can be found in Zhang et al. (2009).

236 The reactor was under the steady state at the time of conducting the tests described

237 below. Batch tests were applied to investigate the change of VOSC concentrations in

238 the reactor. At the beginning of each test, the reactor was filled with fresh wastewater.

239 Then samples were collected every 30 min for VOSC measurement during 6-hour

240 experiments.

241

242 Field samples were obtained from a rising main sewer pipe (C016) in the Gold Coast

243 area (Queensland, Australia). The C016 rising main had an internal pipe diameter of

244 300 mm (surface area to volume ratio, A/V = 13.3 m^{-1}), a total daily flow of ~700 m^3,

245 with 33 pump events (typically 4–6 min in duration) per day. Samples were collected

246 at two locations: (1) wet well of the C016 pump station; (2) a sampling point at

247 1100m downstream of the pump station. Hourly samples were taken from 10:00 am

248 until 2:00 pm and preserved using the acidification method described in Section 2.5.

249 All samples were measured immediately after being delivered to the laboratory.

250 Inorganic sulfide and soluble methane concentrations were also measured using ion

251 chromatography (IC) with UV and conductivity detector (Dionex ICS-2000) (Jiang et

252 al. 2009) and GC with a flame ionization detector (FID) (PerkinElmer, Inc.)

253 (Guisasola et al. 2008), respectively.

254

3 Results and Discussion

3.1 Optimizing analytical conditions

The boric buffer (pH=8.1 ± 0.1) with the strength of 0.15 M was proven to achieve the best effect of reducing H_2S peak on the chromatogram (Figure 2). Since the acid disassociation constant (pk_a) of H_2S is around 7.0 (20^oC), pH 8.1 would ensure over 90% of the total dissolved sulfide being in the form of HS^-. This would greatly decrease the H_2S concentration in the headspace of the vial and thus improves separation of the H_2S and MT peaks. While the addition of 3 ml boric buffer of 0.15 M to a 3 ml sample is effective in separating the H_2S and MT peaks for the municipal wastewater we tested, specific tests may be needed to determine a suitable buffer concentration for wastewater samples with different sulfide and MT concentrations or pH levels, to achieve satisfactory separation of H2S and MT peaks.

Figure 2- The effect of boric different buffers on the separation of H_2S and MT peaks on the chromatogram.

For GC parameters, the GC injector temperature was finalized to 120^oC. The oven temperature was programmed at 28^oC for 5 min then increased at a rate of 20^oC/min to 160^oC with the total retention time of 11.6 min. Under the analytical conditions described above, optimized GC-SCD performance could be achieved, judged based on the separation and magnitudes of the peaks. Figure 3 shows examples of chromatograms of both standard solutions and wastewater samples. The peaks of all three targeted compounds (MT, DMS and DMDS) were in good sharp shapes. They were well separated in the wastewater samples and were not interfered by other compounds. As shown in Figure 3(B), the small peak next to the DMS peak is an ethanthiol peak. Though these two peaks are very close, there was no overlapping between the two peaks in all wastewater samples tested. The DMS concentration measured would thus not be affected by the presence of ethanthiol in municipal wastewater.

Figure 3- (A) Chromatogram of MT, DMS and DMDS in standard solution at 100 ppb of each compound; (B) Chromatogram of MT, DMS and DMDS in a wastewater sample.

3.2 Calibration curve

The calibration curves for MT, DMS and DMDS were constructed in the concentration range of 0.5 - 500 ppb (Figure 4). This range covered the possible concentration range of these substances in wastewater (see Section 3.5). All the three calibration curves presented good linearity with correlation coefficients over 0.999. The calibration results indicate that this method covers a broad linear dynamic range (4 orders of magnitude).

Figure 4- Calibration curves of MT, DMS and DMDS (0.5 - 500ppb)

3.3 Method detection limits

Method detection limit (MDL) is defined as the lowest concentration of a substance that can be determined by a given method with 99% confidence that the concentration is higher than zero (US EPA 2010). In this study, the MDL is determined based on analyzing 8 samples at the concentration of 0.5 ppb. The MDL was calculated as follows (US EPA 2003):

MDL=S × t

where S is the standard deviation of the 8 samples at the concentration of 0.5 ppb; t is the one-sided student's t value (2.998) for a 99% confidence interval with 7 degrees of freedom. The method detection limits of MT, DMS and DMDS of this method were determined as 0.08, 0.12 and 0.21 ppb, respectively. The detection limits of this method may be further decreased by optimizing the liquid volume injected into the

11

313 vial or reducing the buffer solution volume by for example increasing the buffer

314 solution concentration.

315

316 *3.4 Reproducibility*

317 The reproducibility was determined by repetitive measurement of 5 separately

318 prepared spiked wastewater samples at the concentration of 50 ppb. The relative

319 standard deviations (RSD) of MT, DMS and DMDS calculated based on the 5

320 measurements were 2.3%, 2.2% and 2.1%, respectively.

321

322 *3.5 Recovery ratios*

323 The recovery ratios of MT, DMS and DMDS in wastewater were tested by spiking a

324 pre-known amount of these compounds into a VOSC-free wastewater matrix and

325 calculating the relative difference between measured concentrations and real

326 concentrations. The VOSC-free wastewater was obtained by purging with nitrogen for

327 20 min to remove any preexisting VOSCs. The result was obtained based on 5 tests

328 for each compound with concentration ranging from 5 ppb to 500 ppb. The recovery

329 ratios of MT, DMS and DMDS were $83 \pm 4\%$, $103 \pm 4\%$ and $102 \pm 3\%$, respectively.

330 The recovery ratio for MT is relatively low, but still reasonable. The underlying

331 reason for this recovery is not clear, which may be due to wastewater matrix effect.

332 Further research is needed to idenfity the reason and to improve the recovery.

333

334 *3.6 Sample preservation*

335 The effect of two sample preservation methods, i.e. the separated headspace method

336 and the acidification method, are shown in Figure 5. The initial concentrations of

337 VOSCs in different tests varied to a certain extent since these experiments were

338 carried out using different batches of real wastewater. The MT concentration in

339 wastewater samples stored directly in headspace vials or preserved by the separated

340 headspace method decreased 11.9 - 13.5 ppb after 8h. DMS and DMDS

12

concentrations decreased by 0.2 - 0.5 ppb during the same period. With the acidification method, wastewater samples could be preserved for 24 h without significant changes in composition (MT concentration decreased by 1.8 ppb, DMS by 0.4 ppb and DMDS by 0.2 ppb). After 48h, MT concentration decreased by 7.2 ppb. In addition, there were no significant variations of DMS and DMDS concentrations after 48 h. In the high concentration range (spiked wastewater tests), with the acidification method, the concentration of three compounds decreased slightly (<1%) after 48h preservation. These results suggest that MT in the wastewater could be preserved using the acidification method for at least 24h while DMS and DMDS could be preserved for at least 48 h.

Figure 5-Variation of MT (A), DMS (B) and DMDS (C) in the wastewater samples with difference preservation methods. "Headspace vial", "Separated headspace" and "Acidification I" refer to real wastewater samples preserved in a headspace vial directly, by the separated headspace method and by the acidification method, respectively. "Acidification II" refers to the spiked wastewater sample preserved by the acidification method.

3.7 Comparison with other methods

A comparison of this method and other reported methods for wastewater VOSC measurement is listed in Table 1. As this method does not require the pre-concentration processes, the analytical time is reduced by at least 40 min for the measurement of each sample. In addition, the complication of sample handling is avoided. The calibration range of this method covers 4 orders of magnitude, which is comparable to results of other methods. The higher correlation coefficients (R^2) and relatively lower RDS values obtained indicate a better precision of measurement. The detection limits of this method are lower than or comparable to those obtained using purge-and-trap pre-concentration, although they are about 10 times higher than those achieved by the SPME pre-concentration method. The recovery ratios are also

370   comparable to results obtained using GC system with pre-concentration processes.

371

372   Table 1. A comparison of different methods for wastewater VOSC measurement.

373

374   *3.8 Application of the method to real wastewater samples*

375   *3.8.1 Laboratory reactor study*

376   Time series of MT, DMS and DMDS concentrations in the lab-scale anaerobic sewer

377   reactor obtained in two separate batch tests are presented in Figure 6. The MT

378   concentration increased from about 45 ppb to a peak value of 77 - 103 ppb in the first

379   hour and then decreased gradually to around 10 ppb after five hours. In contrast, DMS

380   and DMDS concentrations were at relatively low levels (0.5 - 2 ppb) during the entire

381   test period in both cases. The results indicate that MT could be produced and

382   subsequently degraded under anaerobic sewer conditions. This trend of MT

383   transformation was also observed in other anaerobic systems such as anaerobic

384   digestion and fresh water sediments (Lomans et al. 1999, Du and Parker 2012). The

385   production might be due to the cleavage of sulfur containing amino acids or

386   methylation of sulfide, while the degradation likely resulted from the activity of

387   methanogens and/or sulfide reducing bacteria (Lomans et al. 2001, Higgins et al.

388   2006).

389   Figure 6- Time series of MT, DMS and DMDS concentrations in the lab-scale

390   anaerobic sewer reactor obtained in two separated tests (A) and (B).

391   *3.8.2 Field study*

392   The concentration profiles of VOSCs, dissolved sulfide and methane concentrations

393   measured in the field study are shown in Figure 7. In the pump station, concentrations

394   of all the three VOSCs remained at low levels. Most values were lower than 2 ppb,

395   with MT concentrations being the exception, which increased from below 2 ppb

396   slightly to 5-6 ppb after 12:00 pm. The MT concentration at the pump station in this

397   study is similar to what reported by Lasaridi et al. (2010). They measured the MT

398   concentration in the air above the sewage in a pump station in the range of 160 – 487

399 μg/m^3, which indicated that the concentration in the sewage at that pump station could

400 be around 0.8 – 2.4 ppb (calculated by Henry's Law assuming gas-liquid equilibrium).

401 To our knowledge, the DMS and DMDS concentrations at wastewater pump stations

402 have not been reported yet. In agreement with previous studies (Guisasola et al. 2008,

403 Foley et al. 2009), the dissolved sulfide and methane concentrations were low,

404 constant below 1 ppm.

405

406 Figure 7- Presence of VOSCs, H$_2$S and CH$_4$ in the CO16 rising main sewer: in the

407 pump station (A, B) and at 1100 m downstream (C, D).

408

409 At the sampling point in the rising main sewer (1100 m downstream of the pump

410 station), the MT concentration varied between 18.6 to 72.8 ppb, which was much

411 higher than DMS and DMDS concentrations between 0.7 - 3 ppb. The MT

412 concentration is in the range of 11 - 322 ppb reported by Hwang (1995), who

413 measured the concentration in the influent of a WWTP. DMS and DMDS

414 concentrations in this study are lower than Hwang's results with 3 - 27 ppb for DMS

415 and 30 - 79 ppb for DMDS, respectively. However, our result of DMDS concentration

416 is close to what reported by Godayol et al. (2011), who measured the DMDS

417 concentration in the influent of a WWTP with concentrations in the range of 0 - 5 ppb.

418 The VOSC concentrations are indeed expected to be dependent of wastewater

419 composition and the sewage retention time in sewers.

420

421 The concentrations of MT and DMS in the wastewater samples obtained in the main

422 at 1100 m downstream of the pump station were constantly higher than those obtained

423 from the pump station. This suggests MT and DMS were produced in this anaerobic

424 sewer line. We hypothesize that the increase is dependent of the hydraulic retention

425 time (HRT) of the sewage in the pipe. From the pump operation data, we calculated

426 that the HRT at 10:00 am to 11:00 am was about 1.5 h while the HRT at 12:00 pm to

427 2:00 pm was around 3 h. The longer HRT around the midday was likely responsible

428 for the higher increase in MT and DMS concentrations in this period. Figure 8A-D

429 plotted the correlation between MT and DMS concentration and sulfide or methane

430 concentration based on linear regression. Both MT and DMS concentrations showed

431 high correlation with sulfide and methane concentrations (R^2 = 0.84-0.94). This could

432 also support that HRT plays important role for MT and DMS concentrations in rising

433 main sewers, since sulfide and methane concentrations in rising main sewer are

434 known to be highly correlated with HRT (Sharma et al. 2008, Guisasola et al. 2009).

435

436 In contrast to the cases of MT and DMS, the DMDS concentration did not vary

437 significantly between the two locations. The correlation between DMDS and sulfide

438 or methane concentration was low (R^2 = 0.04-0.21, Figure 8 E, F). So the production

439 of DMDS in rising main sewers might follow a mechanism different from that of MT

440 and DMS. More research needs to be conducted before clearly understanding the

441 transformation of VOSCs in sewer systems.

442

443 Figure 8. Correlation analysis between MT and sulfide concentrations (A), MT and

444 methane concentrations (B), DMS and sulfide concentrations (C), DMS and Methane

445 concentrations (D), DMDS and sulfide concentrations (E) and DMDS and Methane

446 concentrations (F).

447

448 The VOSCs concentrations measured in real wastewater samples from both our

449 laboratory sewer reactor and field sites were in the detection range (0.5-500 ppb) of

450 this GC-SCD method. This range also covered the VOSC concentrations in sewage

451 sampled from WWTPs, pump stations and drainage systems reported by other

452 researchers (Hwang et al. 1995, Cheng et al. 2005, Sheng et al. 2008, Godayol et al.

453 2011). Therefore, we suggest this GC-SCD method with static headspace technique is

454 suitable for routine wastewater VOSCs measurement.

455

456 **4. Conclusions**

The following conclusions are drawn regarding the suitability of the GC-SCD method for VOSC measurement in wastewater:

(1) VOSCs in the wastewater can be measured by GC-SCD with the static headspace technique.

(2) This method is simple and rapid as pre-concentration of samples is not required.

(3) The calibration curves obtained by this method present good linearity (>0.999). The detection limit is lower than 1.0 ppb.

(4) The recovery ratio tests and real wastewater sample analysis demonstrate that this method is suitable for routine VOSCs measurement in wastewater.

(5) VOSCs in wastewater samples can be preserved for at least 24 hours by acidification of wastewater samples (pH ~1.1).

Acknowledgements

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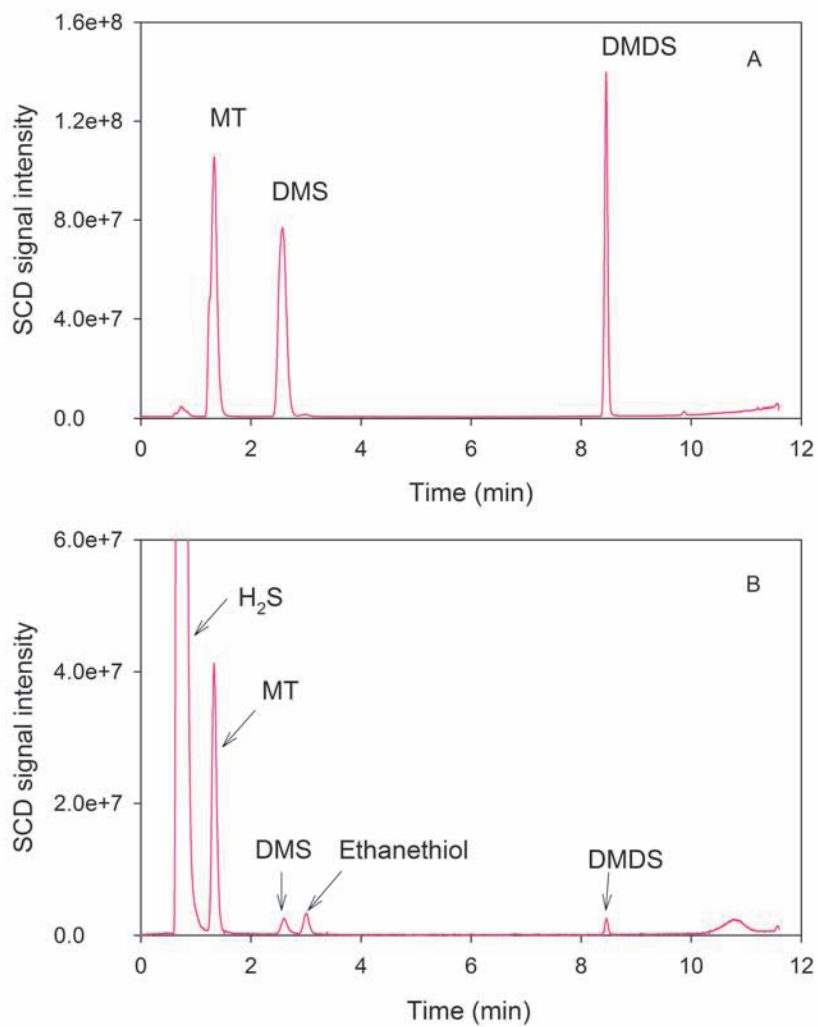603   Research 43(17), 4123-4132.

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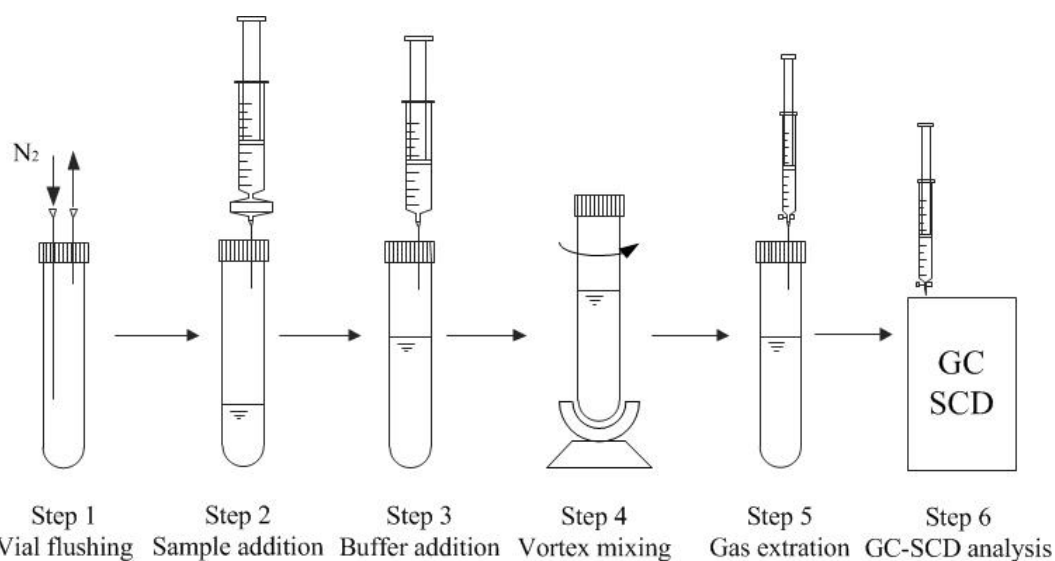
607 Figure 1- A schematic diagram of the steps involved in VOSC measurement with the

608 static headspace technique using GC-SCD.
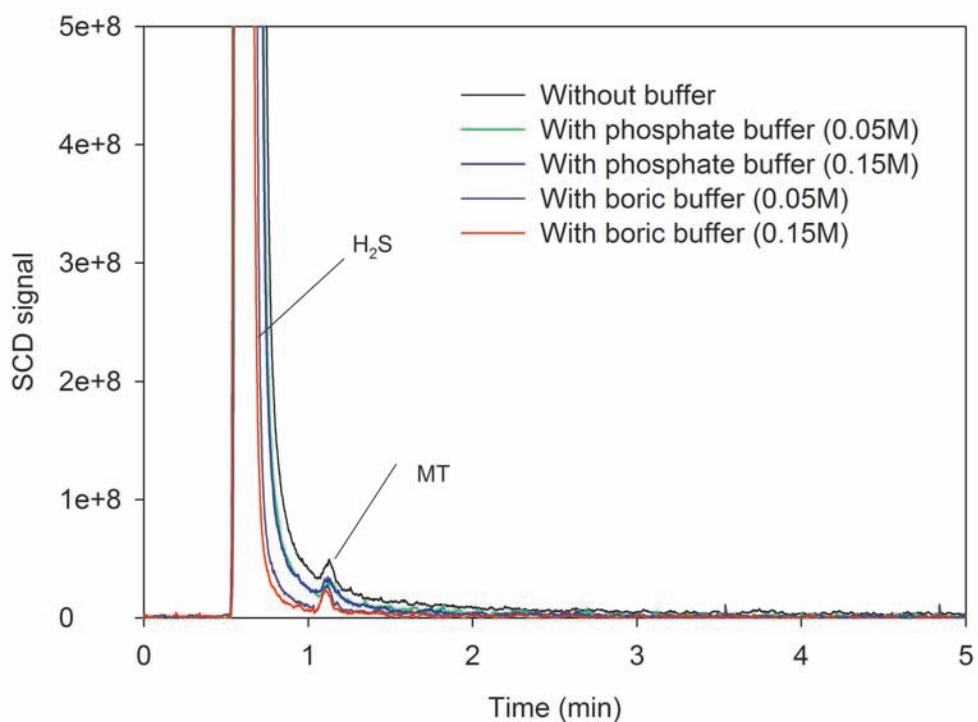
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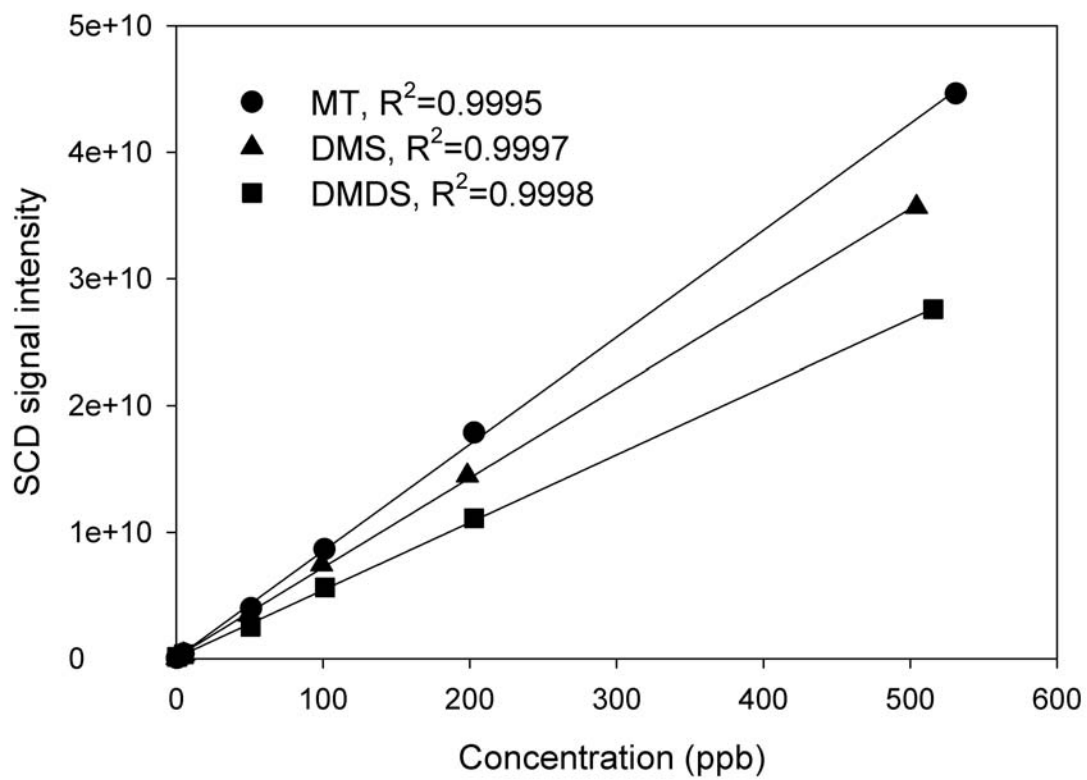610 Figure 2- The effect of different buffers on the separation of H_2S and MT peaks on the

611 chromatogram.

612

Figure 3- (A) Chromatogram of MT, DMS and DMDS in standard solution at 100 ppb

of each compound; (B) Chromatogram of MT, DMS and DMDS in a wastewater

sample.

616

617   Figure 4- Calibration curves of MT, DMS and DMDS (0.5 - 500ppb)
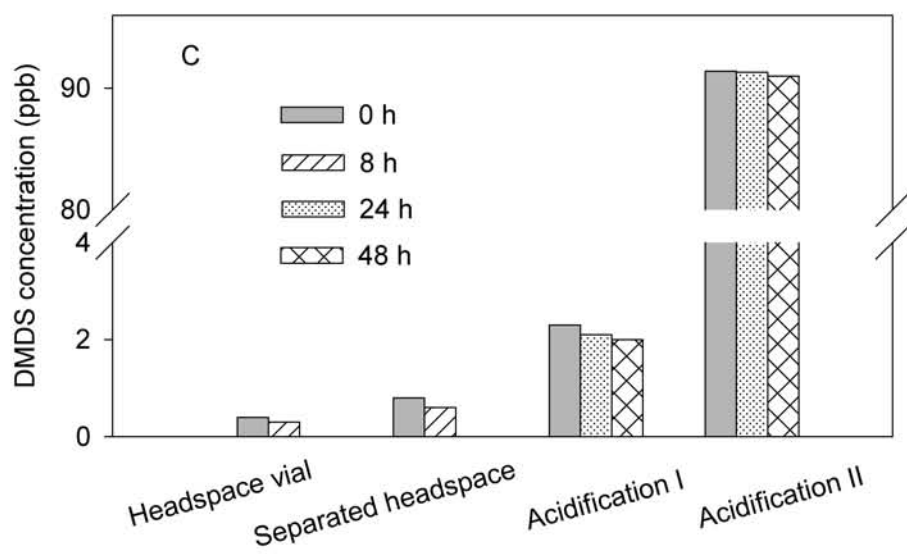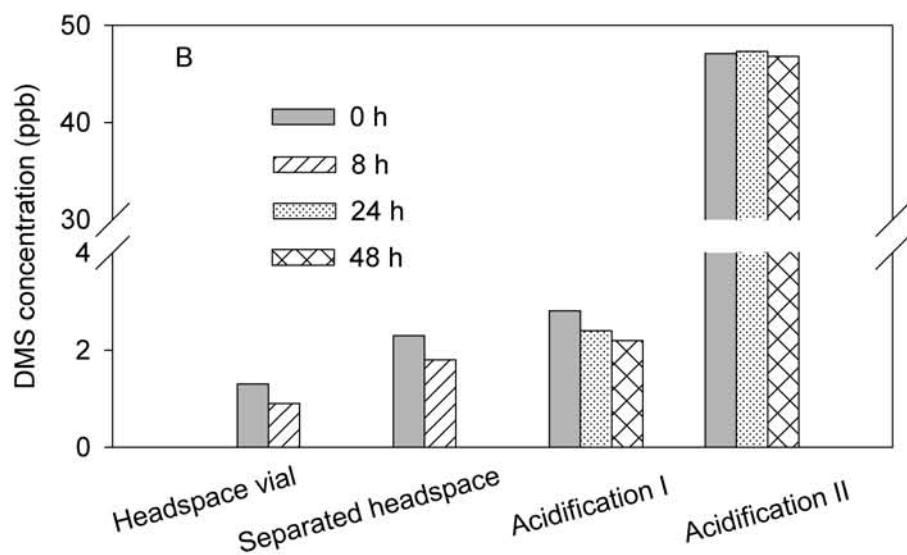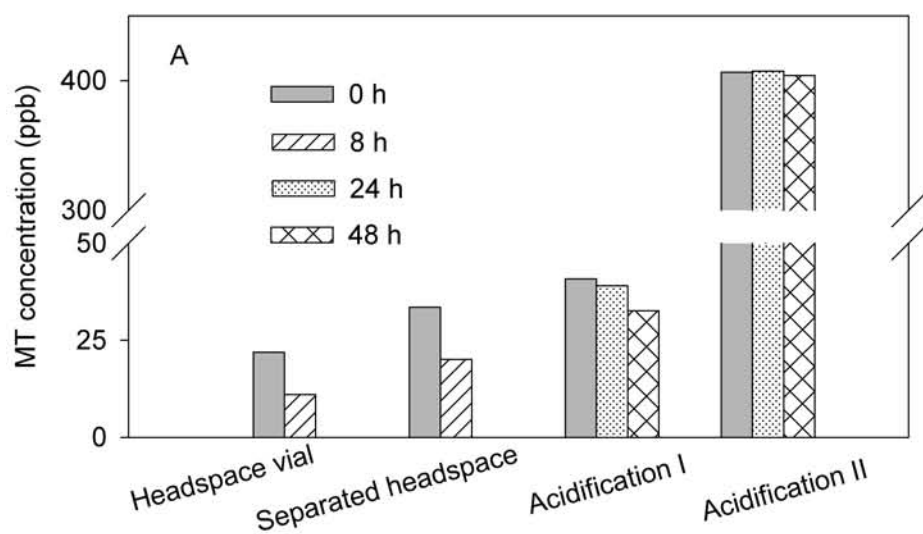
619 Figure 5-Variation of MT (A), DMS (B) and DMDS (C) in the wastewater samples

620 with difference preservation methods. "Headspace vial", "Separated headspace" and

621 "Acidification I" refer to real wastewater samples preserved in a headspace vial

622 directly, by the separated headspace method and by the acidification method,

623 respectively. "Acidification II" refers to the spiked wastewater sample preserved by
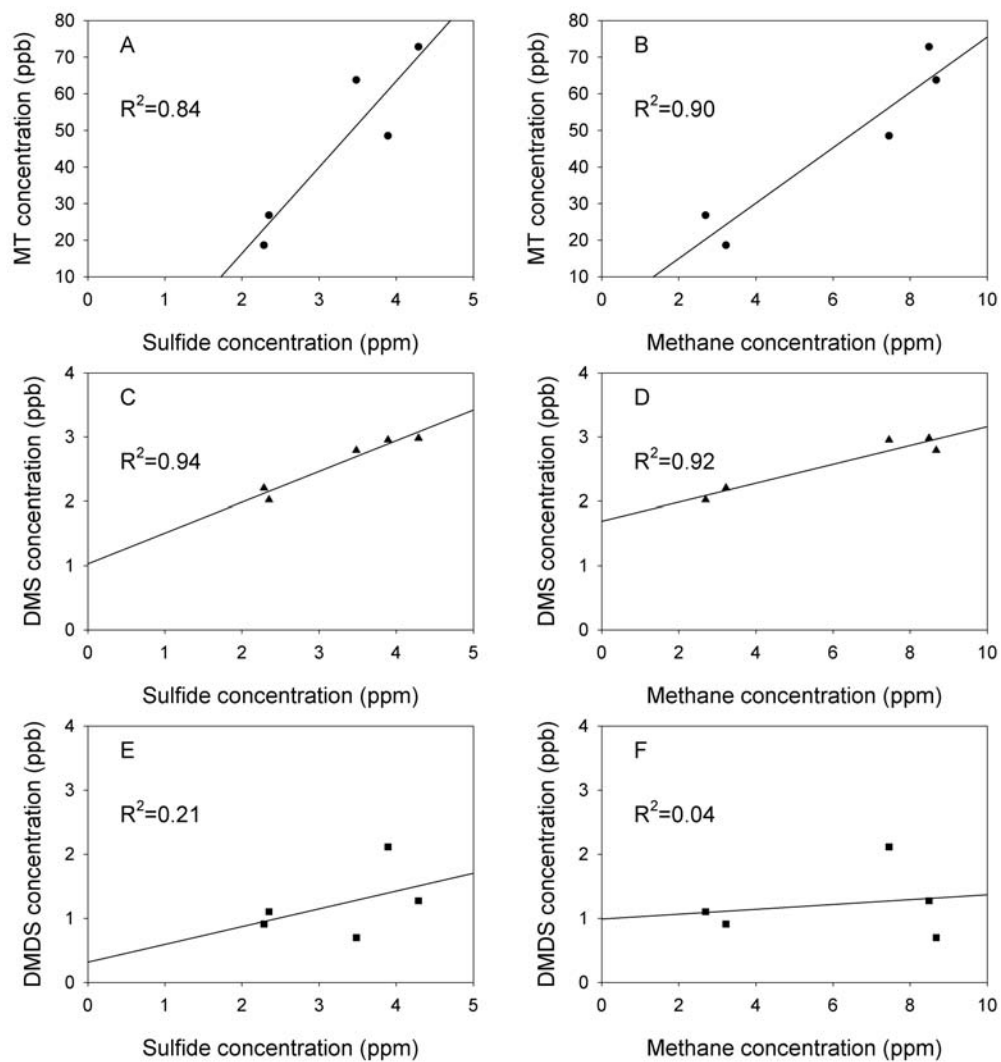
624 the acidification method.
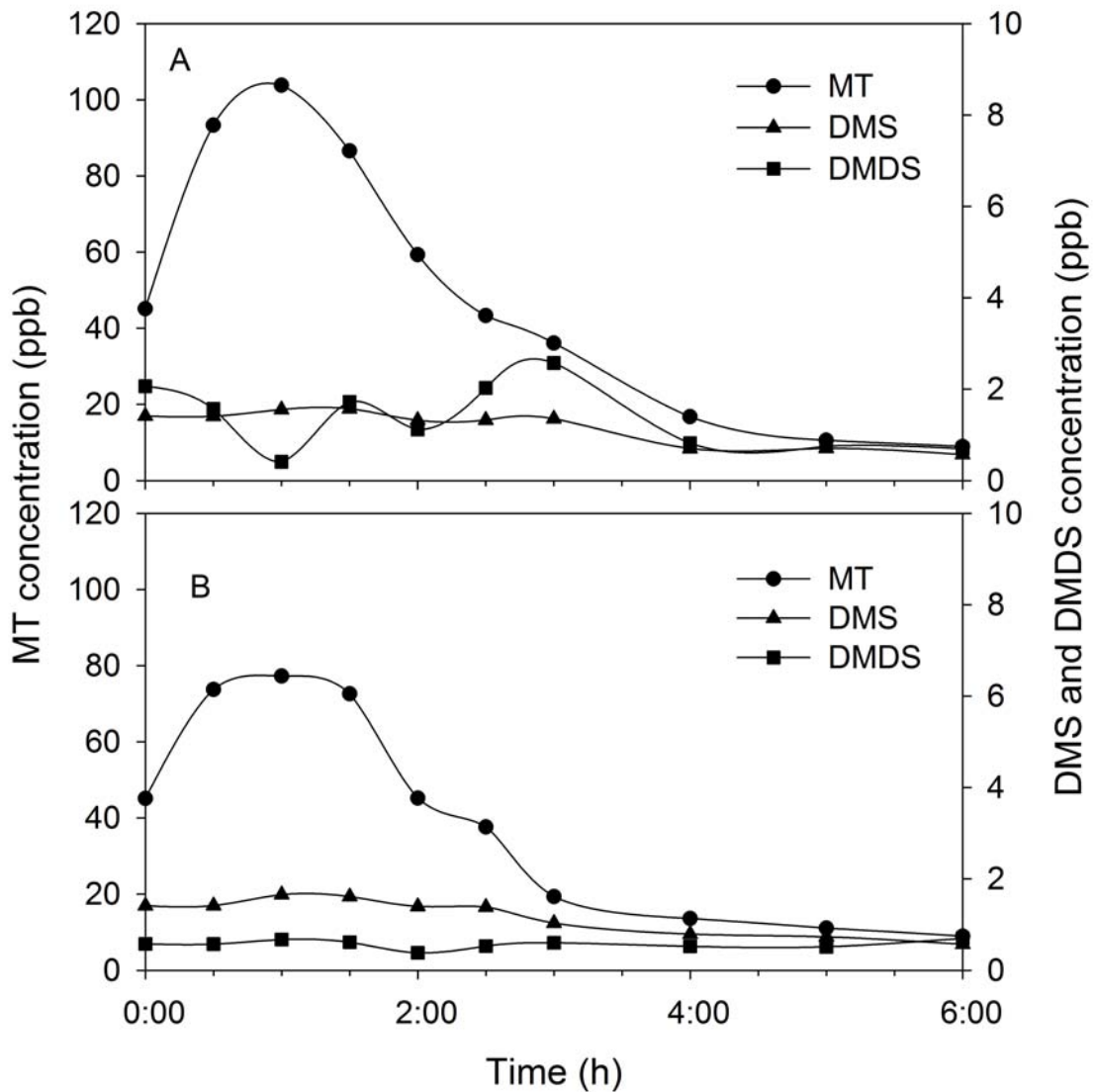
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626 Figure 6- Time series of MT, DMS and DMDS concentrations in the lab-scale

627 anaerobic sewer reactor obtained in two separated tests (A) and (B).
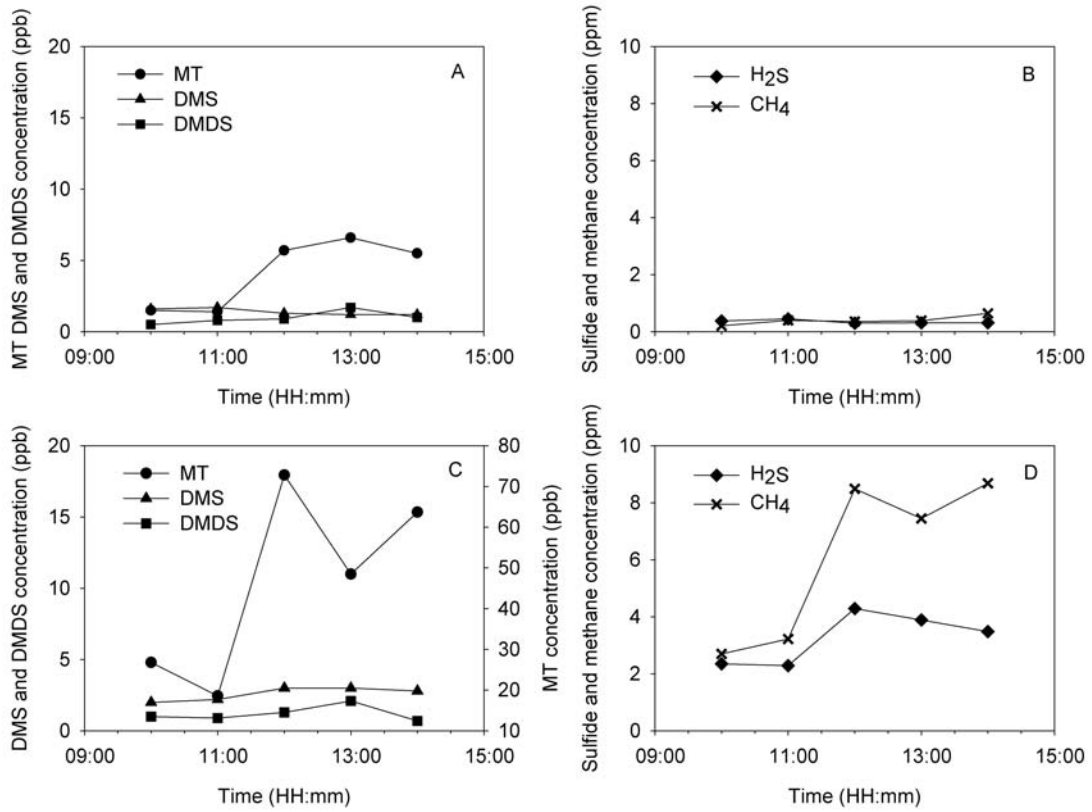
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629 Figure 7- Presence of VOSCs, H_2S and CH_4 in the CO16 rising main sewer: in the

630 pump station (A, B) and at 1100 m downstream (C, D).

Figure 8. Correlation analysis between MT and sulfide concentrations (A), MT and methane concentrations (B), DMS and sulfide concentrations (C), DMS and Methane concentrations (D), DMDS and sulfide concentrations (E) and DMDS and Methane concentrations (F).

637　　　Table 1. A comparison of different methods for wastewater VOSC measurement.

638

No.	Compounds measured	Apparatus	Pre-concentration	Analytical time per sample	Calibration range	R^2	RSD (%)	Detection limits	Recovery (%)	Reference
1	MT; DMS; DMDS	GC-SCD	No	17 min	0.5 - 500 ppb	0.9995 - 0.9998	2.1% - 2.3%	0.08 - 0.21 ppb	83%-103%	This study
2	MT; DMS; DMDS	GC-MS	Purge-and-trap	58 min	5 - 500 ppb	0.993 - 0.998	0 - 8%	1.2 - 4.8 ppb	81% - 100%	(Cheng et al. 2007)
3	DMS; EMS[a]; THIO[b]; DES[c]; DMDS	GC-MS	HS-SPME	70 min	0.0044 - 10.6 ppb	0.995 - 0.997	4.08% - 6.12%	0.006-0.035ppb	N.A.[d]	(Abalos et al. 2002)
4	DMDS	GC-MS	HS-SPME	72 min	0.1 - 100 ppb	0.9719	14%	0.03 ppb	86%	(Godayol et al. 2011)
5	H_2S; CS_2; MT; DMS; DMDS	GC-FPD	Purge-and-trap	>72 min	N.A.[d]	N.A.[d]	15%	ppt level	N.A.[d]	(Hwang et al. 1995)

639　　　　　[a] EMS: ethylmethyl sulfide; [b] THIO: thiophene; [c] DES: diethyl sulphide; [d] N.A: Data not available ;