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ScienceDirect
Journal of Environmental Sciences 2011, 23(10) 1600–1604
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Identification of odorous compounds in reclaimed water using FPA combined with sensory GC-MS

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Received 31 October 2010; revised 22 March 2011; accepted 23 March 2011

Abstract

Odorous compounds in the influent of a reclaimed water treatment plant (RWTP), consisting of coagulation, sedimentation, continuous micro-filtration (CMF), and chlorination in succession, in a north China city, were identified by combining flavor profile analysis (FPA) with sensory gas chromatograph-mass spectrometry (GC-MS). The sewery/swampy/septic odor with an odor intensity of 6.4 was found to be the major odor group in the RWTP influent, and the existence of well-known odorant including dimethyl disulfide, dimethyl trisulfide, indole and skatole were confirmed using GC-MS. The result of a spiking test showed that the intensity (3.6) of the sewery/swampy/septic odor caused by these four chemicals contributed to over 50% of the odor intensity of the influent. The FPA intensity for sewery/swampy/septic odor in the RWTP effluent was 3.8, showing that the treatment process was not efficient for the removal of odorants, particularly indole and skatole.

Key words: sewery/swampy/septic odor; reclaimed wastewater; flavor profile analysis; sensory-GC-MS analysis

DOI: 10.1016/S1001-0742(10)60629-8

Citation: Yan Z M, Zhang Y, Yu J W, Yuan H Y, Yang M, 2011. Identification of odorous compounds in reclaimed water using FPA combined with sensory GC-MS. Journal of Environmental Sciences, 2011(10): 1600–1604

Introduction

Reuse of secondary effluent from municipal wastewater treatment plant (MWTP) has been regarded as an important method to mitigate water shortage problems (Gardner et al., 2001; Liberti and Notarnicola, 1999). In north China, which has experienced serious water shortage problems during the last decade, more and more measures have been taken to encourage the use of reclaimed municipal wastewater for toilet flushing, lawn watering and surface water supplementation. These efforts, however, have been hindered by the water quality problems in the reclaimed water. Among them, although the odor problem is normally not as harmful to human health as pathogens, micropollutants and heavy metals, consumers react very sensitively to the changes in the organoleptic quality of water (Suffet et al., 2004).

Many efforts have been devoted to identify the odorous compounds in wastewater. Young (1984) speculated that indole and its derivatives (such as skatole) had contributed largely to the characteristic odor in sewage treatment works. Hwang et al. (1995) found that some sulfur and nitrogen containing malodorous compounds remained in the secondary treatment. An odor wheel classification scheme for wastewater have been developed by Burlingame et al. (2004), showing that important odorants might include sulfur-based and nitrogen-based compounds, organic acids, aldehydes and ketones. However, in comparison with drinking water, which has been studied extensively (Lin et al., 2002; Bruchet, 1999; Jensen et al., 1994; Mallevialle and Suffet, 1987), efforts in controlling and managing the odor problems of sewage or reclaimed water have been hindered by difficulty of identifying the odor causing compounds due to their extremely low concentrations and the complicated chemical composition of sewage. To our knowledge, few studies have been conducted on odorants identification and removal in sewage or reclaimed water in China.

In the present study, odor characteristics of influent in a typical reclaimed water treatment plant (RWTP) in a north China city, consisting of coagulation, sedimentation, continuous micro-filtration (CMF) and chlorination in succession, were assessed by using flavor profile analysis (FPA) combined with sensory gas chromatograph-mass spectrometry (sensory GC-MS). At the same time, a spiking test was conducted to determine the contribution of the odorants to the overall odor in the reclaimed water. The aim of the study was to determine the major odorous groups in the influent of the RWTP, and evaluate the removal efficiency of the odor and corresponding chemicals by the

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wastewater reclamation process.

1 Materials and methods

1.1 Water samples and chemicals

Water samples were taken from a RWTP in a north China city. The RWTP, which consists of coagulation, sedimentation, continuous micro-filtration and chlorination in succession, has a capacity of 40,000 m^3 per day. The influent of the RWTP is the effluent of a municipal wastewater treatment plant located nearby, and the reclaimed water is used for toilet flushing and plants irrigation. The characteristics of the influent are: DOC 5.0 ± 2.1 mg/L; NH_3-N concentration 1.6 ± 1.4 mg/L; turbidity 1.8 ± 0.7 NTU; color 23 ± 5; pH 7.5 ± 0.3; and conductivity 1717 ± 98 μS/cm.

Standards of dimethyl disulfide, dimethyl trisulfide, indole and skatole were purchased from Accustandard Inc. (USA). All of other chemical reagents used were of analytical grade if not noted specially.

1.2 Flavor profile analysis (FPA) and sensory-GC-MS analysis

Two sensory schemes, including FPA and sensory-GC-MS methods were employed in this study. FPA was used to identify the odour group and intensity of the water samples according to the Standard Methods for Water and Wastewater (APHA et al., 1995). Sensory-GC-MS combined with two pre-concentration techniques was used for the identification of specific odour causing compounds. Five non-smokers were trained as the panellists of FPA, and at least four panellists participated in the test. Based on the consensus of the panel, seven scales of 1–12 were used to describe the intensity of samples (Mallevialle and Suffet, 1987).

Sensory GC-MS analysis allows a simultaneous detection of off-flavors at the olfactory detector port (ODP2, Gerstel, Germany) and the MS (5975MSD, Angilent, USA). GC-separation was done on a GC 6890N (Agilent, USA) equipped with a DB-5MS column (30 m × 0.25 mm × 0.25 μm, Agilent, USA). The GC was programmed from 40°C (constant temperature for 2 min) to 60°C at 4°C/min, then to 68°C at a rate of 8°C/min (holding for 2 min) and finally to 250°C at a rate of 8°C/min and then held at 250°C for 2 min. The calibration curves for the odorous compounds were established all with good linearity and high regression coefficients (R^2 > 0.99). The detection limits were 5, 5, 10 and 10 ng/L for dimethyl disulfide, dimethyl trisulfide, indole and skatole, respectively. The analytical results of the duplicates were all within ± 10% of difference.

1.3 Extraction of organoleptic compounds

Simultaneous distillation extraction (SDE) was used to extract organoleptic compounds from water samples for the identification of odorants (Young, 1998). Solid phase micro extraction (SPME) was then used to quantify the compounds (Laura, 2007).

During the SDE procedure, 3 L of sample and 50 mL of dichloromethane were heated in two round boiling flasks and connected to a Nickerson-Lickens type of distillation-extraction head for 2 hr. At the end of the process, the dichloromethane extract was collected, dried with anhydrous sodium sulfate for subsequent concentration. The final volume of samples was concentrated to 100 μL through rotary evaporation followed by nitrogen blow, and the concentrate was used for GC-MS analysis with scan mode to find odorous compounds.

SPME was carried out using 85 μm Carboxen/PDMS fibers (Supelco, USA). The sample with 25% NaCl was first heated to 65°C followed by 30 min head-space extraction at 65°C. The SPME fiber was desorbed in a splitless-injector at 280°C during 3 min followed by the GC-MS with SIM mode.

1.4 Odor contribution test

To evaluate the contribution of the odorous compounds to the overall odor, a spiking test was designed. The influent of the RWTP in January, 2010 was analyzed for the concentration levels of the odorous compounds identified by sensory GC-MS procedure, and then treated by wood-based powdered activated carbon (PAC). The treated water was spiked with the odorous compounds according to their respective concentrations detected in the influent. The intensity of the spiked water was then compared with the original water sample.

2 Results and discussion

2.1 Seasonal changes of odor in RWTP influent by using FPA

Seasonal changes of odor in the RWTP influent were investigated using the FPA test, as shown in Fig. 1. The RWTP influent exhibited a strong sewery/swampy/septic odor accompanied with a mild earthy/musty odor. The earthy/musty odor is a prevalent odor subgroup in drinking water which has been mainly contributed by 2-methylisoborneol (2-MIB) and geosmin (Bruchet, 1999; Jensen et al., 1994; Means and McGuire, 1986; Sklenar and Horne, 1999; Suffet et al., 1999; Yagi et al., 1983). The FPA intensity of sewery/swampy/septic odor (7.6–8.0) in July and September in 2009 was stronger than that in March, 2009 and January, 2010 (5.6–6.4), showing that the FPA intensity might be related with temperature.

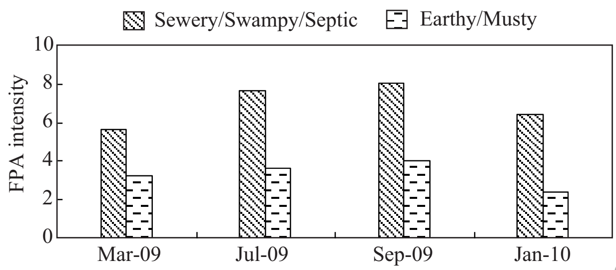

Fig. 1 Flavor profile analysis (FPA) intensity variation in a year.

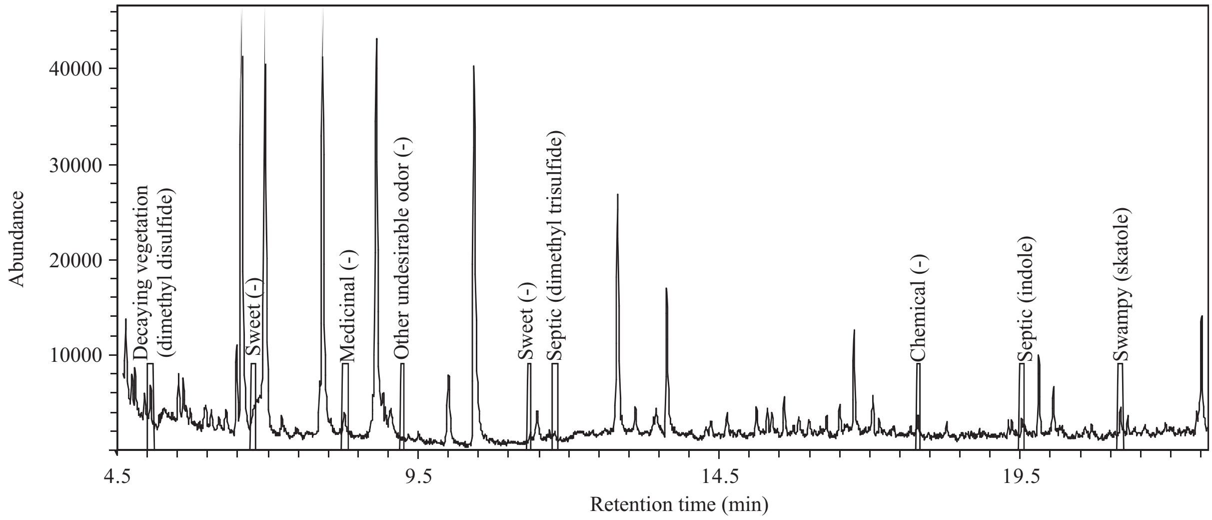

Fig. 2 Sensory GC-MS identification of odors and corresponding chemicals.

2.2 Identification of main odor causing compounds using sensory GC-MS

Figure 2 shows the sensory GC-MS chromatogram of the RWTP influent extracted by the SDE technique. A decaying vegetation odor perceived at a retention time of 5.1 min was detected as dimethyl disulfide. And a septic odor at a retention time of 11.8 min was identified as dimethyl trisulfide by GC-MS. The odor threshold concentration (OTC) of dimethyl disulfide was reported as 0.2–5 μg/L in water (Young, 1998), and Young (1998) categorized dimethyl disulfide as a kind of compound which can cause marshy/swampy/septic/sulfurous odor. The reported OTC of dimethyl trisulfide in water is 10 ng/L (Buttery et al., 1976), which is significantly lower than that of dimethyl disulfide. Wajon et al. (1988) observed a correlation between the presence of dimethyl trisulfide and a swampy odor. Swampy and septic odors are sometimes difficult for panelists to differentiate (Khiari et al., 1997). Therefore, dimethyl trisulfide was assigned to the main chemical causing the septic odor described by FPA in the study.

Two other odors at 19.6 and 20.8 min were assigned to indole and skatole, respectively, by sensory GC-MS. The OTCs of indole and skatole have been reported as 0.3 mg/L and 1.2 ug/L in water (Islam et al., 1998; Young, 1998). Indole was described as having a fecal and stench odor at high concentrations (Vainstein et al., 2001). Dravnieks (1985) indicated that skatole exhibits sewer odor. On the other hand, two sweet odors (6.7 and 10.9 min), a medicinal odor (7.8 min), an other undesirable odor (8.8 min), and a chemical odor (17.7 min) were detected by sensory GC without identifiable compounds.

Figure 3 shows the evolution of the above four compounds over a year. It is clear that all of the four compounds were detected in different seasons. Variations of the four chemicals were consistent with the FPA intensity during the whole year (Fig. 1). The concentration of dimethyl disulfide varied between 80 ng/L in Jan, 2010 and 202 ng/L in Mar, 2009. Dimethyl trisulfide varied between 70 ng/L (Jan, 2010) and 212 ng/L (Sep, 2009), all of which were

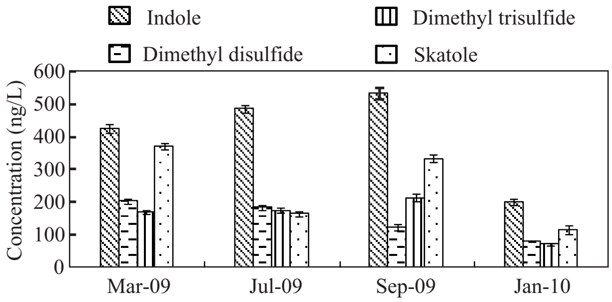

Fig. 3 Variation of the four odorous chemicals in a year.

higher than the OTC. Indole varied between 199 ng/L (Jan, 2010) and 423 ng/L (Sep, 2009). Skatole varied between 113 ng/L (Jan, 2010) and 370 ng/L (Mar, 2009). It seemed that the temperature might affect the production of the odorants.

The levels of the odour compounds in wastewater have been reported by some researchers. Hwang et al. (1995) investigated the levels of odour compounds in secondary effluent of a sewage wastewater treatment plant, in which the concentration of dimethyl disulfide is 6.3 ug/L, indole and skatole were not detected. Although the level of dimethyl disulfide, indole and skatole were generally lower than their OTCs in the study, the compounds may be linked to the overall odor detected by FPA panel while other odorous compounds co-exist. Similar conclusion has been reported by Khiari et al. (1997), who found that the combination of dimethyl disulfide, dimethyl trisulfide and 2-isobutyl-3methoxypyrazine contributed to decaying vegetation odor in drinking water supplies, while no single compound appeared to produce the characteristic decaying vegetation odor.

2.3 Contribution of typical odorous compounds to overall odor

The above four odorants were spiked into the PAC-treated RWTP influent at different doses shown in Table 1. The odor intensity of the resulting spiked systems was evaluated using the FPA technique. The different concentrations of dimethyl trisulfide, which OTC is the lowest in

Table 1 Doses of the four odorous chemicals in the powered activated carbon (PAC)-treated reclaimed water treatment plant (RWTP) influent

Compound	Dose 1	Dose 2	Dose 3	Dose 4
Dimethyl disulfide (ng/L)	–	–	–	80
Dimethyl trisulfide (ng/L)	20	40	80	70
Indole (ng/L)	–	–	–	200
Skatole (ng/L)	–	–	–	113

the four odorants, were added to RWTP influent samples after treated with 60 mg/L PAC. Before the experiment, it was confirmed that no perceptible odor existed in the RWTP influent samples after treated with 60 mg/L PAC.

Contributions of odorants to complex aromas have been studied by some researchers in food field. Grosch (2001) evaluated the key odorants of foods and their contribution to the overall odor by FPA and an aroma models. To our knowledge, however, little is known about the contribution of mixtures of odour compounds to the overall odor in the field of reclaimed water. Therefore this work provides valuable information of identification of key odorants in reclaimed water for the odor management.

As shown in Fig. 4, FPA intensity of sewery/swampy/septic odor in both dose 1 and dose 2 was 2, which increased to 2.8 when the dose of dimethyl trisulfide was increase to 80 ng/L. The FPA panelists perceived decaying vegetation odor at low dimethyl trisulfide concentrations and septic odor at higher concentrations. The intensity of sewery/swampy/septic odor increased to 3.6 when all of the four odorants were spiked into the PAC-treated influent, showing that the four chemicals possibly contributed more than 50% of the odor in influent (the odor intensity of the RWTP influent was 6.4). The result indicates that there were other unknown odorants causing the sewery/swampy/septic odor in the influent.

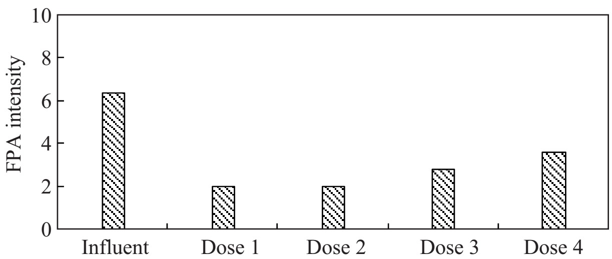

Fig. 4 Variation of FPA intensity at different chemical doses.

2.4 Removal of odor during the wastewater reclamation process

Changes of the sewery/swampy/septic odor intensity as well as the four odorants along the wastewater reclamation process are shown in Fig. 5. It is clear that coagulation/sedimentation (CS) and CMF only resulted in a slight reduction of the odor and the corresponding chemicals. Disinfection using chlorine removed the dimethyl disulfide and dimethyl trisulfide significantly, resulting in the decrease of the sewery/swampy/septic odor. However,

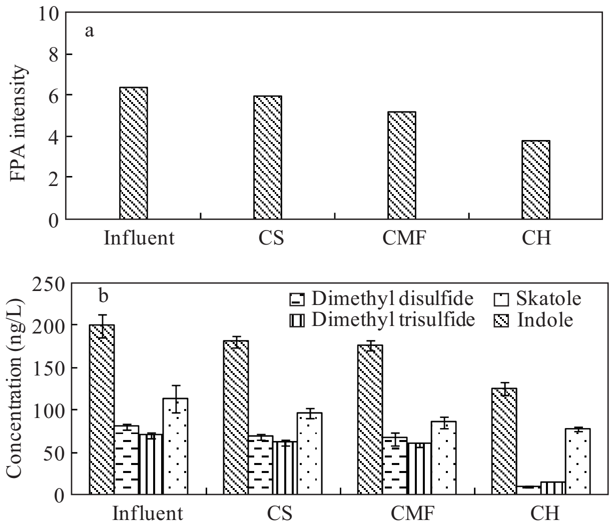

Fig. 5 Variations of FPA intensity (a) and odorous chemicals (b) at different treatment process stages in the RWTP. CS: coagulation and sedimentation; CMF: continuous micro-filtration; CH: chlorination.

chlorine was not very effective for the removal of the other two chemicals, particularly skatole. The removal efficiencies of indole and skatole by the whole treatment process were only 37.2% and 31.3%, respectively. Therefore, indole and skatole as well as some unknown ordorants might contribute a lot to the sewery/swampy/septic odor in the RWTP effluent. The relatively high FPA intensity of the sewery/swampy/septic odor (3.8) in the effluent demonstrated that the current treatment process was not sufficient for the removal of the odor. Peter and Von Gunten (2007) reported that ozonation is a powerful tool capable of oxidizing most of odor compounds to more than 50%. It has been reported that ozone is very effective for the removal of the swampy odor in water (Tobiason et al., 1992). Therefore, to get further removal of the odor in the reclaimed water, some other supplementary treatment procedures such as ozonation might be useful.

3 Conclusions

Combining FPA with sensory GC-MS analysis, it was found that the sewery/swampy/septic odor was the major odor group in the RWTP influent, and dimethyl disulfide, dimethyl trisulfide, indole and skatole were important odorants. The conventional wastewater treatment process including mainly coagulation, sedimentation, continuous micro-filtration and chlorination was not effective enough in the removal of the odor, particularly for the removal of indole and skatole. The above information was useful for solving the odor problems in reclaimed water.

Acknowledgments

This work was supported by the National Water Project of China (No. 2008ZX07314-003), the National Natural Science Foundation of China (No. 50808171), the Chinese Academy of Sciences (No. KZCX1-YW-06) and the Research Fund of Tianjin Key Laboratory of Aquatic Science and Technology.

References

APHA (American Public Health Association), AWWA (American Water Works Association), WPCF (Water Pollution Control Facility), 1995. Standard Methods for the Examination of Water and Wastewater (19th ed.). Washington, DC, USA.

Bruchet A, 1999. Solved and unsolved cases of taste and odor episodes in the files of Inspector Cluzeau. *Water Science and Technology,* 40(6): 15–21.

Burlingame G A, Suffet I H, Khiari D, Bruchet A L, 2004. Development of an odor wheel classification scheme for wastewater. *Water Science and Technology,* 49(9): 201–209.

Buttery R G, Guadagni D G, Ling L C, Seifert R M, Lipton W, 1976. Additional volatile components of cabbage, broccoli, and cauliflower. *Journal of Agricultural and Food Chemistry,* 24(4): 829–832.

Dravnieks A, 1985. Atlas of odor character profiles, ASTM DS61. American Society of Testing and Materials Philadelphia, Pennsylvania, USA.

Gardner E A, Morton D, Sands J, Matthews P, Cook F J, Jayawardane N S, 2001. The filter system for tertiary treatment of sewage effluent by land application – its performance in a subtropical environment. *Water Science and Technology,* 43(10): 335–342.

Grosch W, 2001. Evaluation of the key odorants of foods by dilution experiments, aroma models and omission. *Chemical Senses*, 26(5): 533–545.

Hwang Y, Matsuo T, Hanaki K, Suzuki N, 1995. Identification and quantification of sulfur and nitrogen containing odorous compounds in wastewater. *Water Research*, 29(2): 711–718.

Jensen S E, Anders C L, Goatcher L J, Perley T, Kenefick S, Hrudey S, 1994. Actinomycetes as a factor in odour problems affecting drinking water from the North Saskatchewan River. *Water Research,* 28(6): 1393–1401.

Khiari D, Barrett S E, Suffet I H, 1997. Sensory GC analysis of decaying vegetation and septic odors. *Journal American Water Works Association*, 89(4): 150–161.

Laura V P, 2007. Comparison of sensory characteristics, and instrumental flavor compounds analysis of milk produced by three production methods. Master Thesis. University of Missouri-Columbia. 20–22.

Liberti L, Notarnicola M, 1999. Advanced treatment and disinfection for municipal wastewater reuse in agriculture. *Water Science and Technology*, 40(4-5): 235–245.

Lin T, Wong J, Kao H, 2002. Correlation of musty odor and 2-MIB in two drinking water treatment plants in South Taiwan. *Science Total of Environment*, 289(1-3): 225–235.

Mallevialle J, Suffet I H, 1987. Identification and treatment of taste and odors in drinking water. AWWA Research Foundation and Lyonnaise Des Eaux Cooperative Research Report. American Water Works Association, Denver, CO, USA.

Means E G III, McGuire M J, 1986. An early warning system for taste and odor control. *Journal American Water Works Association,* 78(3): 77–83.

Nurul Islam A K M, Hanaki K, Matsuo T, 1998. Fate of dissolved odorous compounds in sewage treatment plants. *Water Science and Technology*, 38(3): 337–344.

Peter A, Von Gunten U, 2007. Oxidation kinetics of selected taste and odor compounds during ozonation of drinking water. *Environmental Science and Technology,* 41(2): 626–631.

Sklenar K S, Horne A J, 1999. Horizontal distribution of geosmin in a reservoir before and after copper treatment. *Water Science and Technology,* 40(6): 229–237.

Suffet I H, Khiari D, Bruchet A, 1999. The drinking water taste and odor wheel for the millennium: beyond geosmin and 2-methylisoborneol. *Water Science and Technology*, 40: 1–13.

Suffet I H, Schweitze L, Khiari D, 2004. Olfactory and chemical analysis of taste and odor episodes in drinking water supplies. *Reviews in Environmental Science and Biotechnology,* 3(1): 3–13.

Tobiason J E, Edzwald J K, Schneider O D, Fox M B, Dunn H J, 1992. Pilot study of the effects of ozone and peroxone on in-line direct filtration. *Journal American Water Works Association,* 84(12): 72–84.

Vainstein A, Lewinsohn E, Pichersky E, Weiss D, 2001. Floral fragrance. New inroads into an old commodity. *Plant Physiology*, 127(4): 1383–1389.

Wajon J E, Kavanagh B V, Kagi R I, Rosich R S, Alexander R, 1988. Controlling swampy odors in drinking water. *Journal American Water Works Association,* 80(6): 77–83.

Yagi M, Kajino M, Matsuo U, Ashitani K, Kita T, Nakamura T, 1983. Odor problems in lake Biwa. *Water Science and Technology*, 15(6-7): 311–321.

Young C C, 1998. Analysis of taste- and odor-causing compounds in drinking water. Ph.D Thesis. University of California, Los Angeles. 30–33.

Young P, 1984. Odours from effluent and waste treatment. *Effluent and Water Treatment Journal,* 24(5): 189–195.