HYDROCARBONS EMISSIONS FROM A MUNICIPAL WASTEWATER TREATMENT PILOT PLANT IN VIENNA

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Abstract. Hydrocarbons emissions were measured from an aeration tank of a municipal wastewater treatment pilot plant. The collected off-gas samples were characterised for C_2–C_7 hydrocarbons using GC-FID analytical technique while the total volatile organic compounds (TVOC) were measured using a continuous hydrocarbon gas analyser. Approximately, the estimated emission rates for 1 m^3 of wastewater from this aeration tank were 5 mgC of C_2–C_7 hydrocarbons, and an average of 7 gC of TVOC. With exception to toluene, all other measured hydrocarbons are emitted less than 1 mgC day^{-1}. The results support the view that a significant reduction in annual emissions of hydrocarbons from wastewater treatment plants in Vienna has taken place.

Keywords: aeration, aerobic treatment, air emissions, NMHC, VOC, wastewater treatment

1. Introduction

The emissions of non-methane hydrocarbons (NMHC) have been regulated in many countries due to their ozone formation potential. The importance of NMHC as ozone precursors and other secondary photochemical pollutants depends largely on their reactivity's and ambient concentrations (Lawrimore *et al.*, 1995). Lists of volatile organic compounds (VOC) which act as precursors of smog formation to be determined with high priority have been proposed in U.S.A. (Oliver *et al.*, 1996) and Europe (Kotzjas and Hjorth, 1991). In a urban areas, emissions from wastewater treatment plants might form a significant component of total hydrocarbon emissions. The nature and magnitude of emissions obviously depend on the nature of the influents in the urban area. As a result, emitted hydrocarbons may vary substantially from one urban area to another.

Earlier work concentrated on different aspects of VOC emissions from publicly owned treatment works (POTW) which were identified as potential sources of benzene, toluene, methane, chlorinated hydrocarbons and several other odour causing volatile organic compounds. The identity and quantity of volatile organics in wastewater and their emission varies depending on the type of wastewater, transport system, operational characteristics of the treatment plant and the weather conditions. The mechanism of aeration process in a wastewater treatment plant

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defines mass transfer characteristics between air and wastewater. During this process, several organic substances in wastewater are either adsorbed, biodegraded or volatilised.

Total annual air emissions (based on liquid phase total concentration and Joint Emission Inventory Programme emission factors) from the ALCOSAN wastewater treatment plant (0.85×10^6 m^3 day^{-1} at secondary treatment facility) by Tamilia *et al*. (1995) were 15.5 t yr^{-1} of NMHC (as carbon), 0.91 t yr^{-1} of toluene and 0.04 t yr^{-1} of benzene. Fourteen different VOC in ambient air above aeration tanks (0.5 m above) of several sewage treatment plants in Poland were measured by Suschka *et al*. (1996). VOC emissions at two POTW studied by Namkung and Rittmann (1987) exceeded 33 t yr^{-1}. Chang *et al*. (1987) estimated that 7 of 589 California WWTPs emit non-methane volatile organic compounds (NMVOC) exceeding 25 t yr^{-1}.

Anthropogenic non-methane volatile organic compound (NMVOC) emissions in Austria were estimated to be higher than 467 000 metric tons by Loibl *et al*. (1993) using statistical information on generation activities, emission factors from technical literature and regional reference data for the base year 1987 with a quite large uncertainty. The contribution of NMVOC emisssions from wastewater treatment plants in Austria was estimated to be around 5% i.e. 25 000 t yr^{-1} of total anthropgenic NMVOC emissions (Loibl *et al*., 1993). For Vienna, the contribution of municipal wastewater treatment plants (MWWTP) to total anthropogenic NMVOC emissions is estimated to be in the order of 7.5% (31 875 t yr^{-1} of total anthropogenic NMVOC emissions estimated for the year 1996, Emissionen von Ozonvorläufersubstanzen in Wien, Beiträge zum Umeltschutz, Heft 39/97). Since then, due to stringent laws concerning the use of solvents in industry and consumer products, lower emission rates were expected from Vienna MWWTP. Hence, this study was conducted to investigate the NMHC emissions from a pilot MWWTP to verify whether the emission estimates reported in the literature studies have to be reduced.

2. Methodology and Experiments

A small single tank pilot plant situated at University of Agriculture(Vienna) was chosen for this study. The plant receives approximately 1 m^3 day^{-1} of wastewater into the aeration tank ($2 \times 1 \times 1$ m, max. capacity 1.54 m^3) from a sewer 1.3 km long, fed by domestic sources and few small companies. The treated effluent is discharged into the main sewer of Vienna and further treated in the municipal wastewater treatment plant. The aeration tank comprises two chambers, each provided with an aerator (rod-shaped diaphragm blowers, 10 cm in diameter, *supplier Purator*), which produce air bubbles of 2 mm diameter, to pump ambient air into the water at the rate of 17 m^3 hr^{-1} (STP). In a day, the aeration phases lasted

approximately 30 min followed by 1 hr non-aeration intervals to provide nitrifying and de-nitrifying conditions.

The experimental set-up for sample collection is shown in Figure 1. The aeration tank was completely covered with a polyethylene foil (4×5 m) to form an 'enclosure' (1.5–2 m^3). Samples were collected from an outlet of the 'chamber' through a glass manifold (heated electrically to 298 K (25 °C) to prevent condensing of water vapour at the outlet) which was at a distance of 0.5 m above the water level and 0.5 m away from the aeration tank. An additional air pump was used to supply air (6 m^3 hr^{-1} at STP) through the chamber during non-aeration to prevent collapse of the polyethylene enclosure. Samples were pumped out through Teflon tubes connected to the manifold.

The total volatile organic carbon (TVOC) was measured continuously with a continuous FID analyser at an oven temperature of 448 K (175 °C) (*Model No. VE5, Supplier Messer Griesheim*). Air samples were collected during aeration phase. Ambient air used for aerating the wastewater was also collected. For the determination of NMHC, air samples of 1.5 L volume were collected into two-component adsorption tubes comprising linear glass tubes (150 mm/3 mm i.d.) filled with Carbosieve SII (60/80 Mesh size, Supelco) and Molecular Sieve 5A° (60/80 Mesh size, Chrompack) adsorbents. The tubes were cleaned prior to sampling with helium purge at the rate of 30–50 mL/min at 523.15 K (250 °C).

Analysis of collected air samples on the adsorption tubes for C_2–C_7 hydrocarbons was carried out within 24 hr after sampling by Gas Chromatography-Flame Ionisation Detector (GC-FID HP-5890 Series II) equipped with a cryogenic focussing technique. The samples were thermally desorbed for 30 min by electrical heating and collected into a cryogenic (liquid N_2) loop of the GC. The desorbed gases were carried by helium to the chromatographic column (Al_2O_3/KCl PLOT column, 30 m $\times$ 0.53 mm i.d., J&W P/N 115-3532) by flash heating of the loop with hot water. The temperature programming was 313-463 K (40–190 °C) at the rate of 283.15 K min^{-1} (10 °C). The eluted chromatographic profile was recorded using an ATS WinChrom/32 software program. The system was calibrated using propane gas standard and a multi-component hydrocarbon gas standard (C_2–C_7) (*supplier Messer Griesheim, Austria*).

3. Results and Discussion

3.1. C_2–C_7 HYDROCARBONS

Table I gives the average concentrations of measured NMHC and the estimated emission rates from the aeration tank. The total average concentrations of measured hydrocarbons in the off-gas over the measurement period were in the range of 0.19 to 177 μgC m^{-3} during aeration (values corrected for ambient air used for aeration) as the lowest and the highest value with an average of 24 μgC m^{-3}. Hydrocarbons

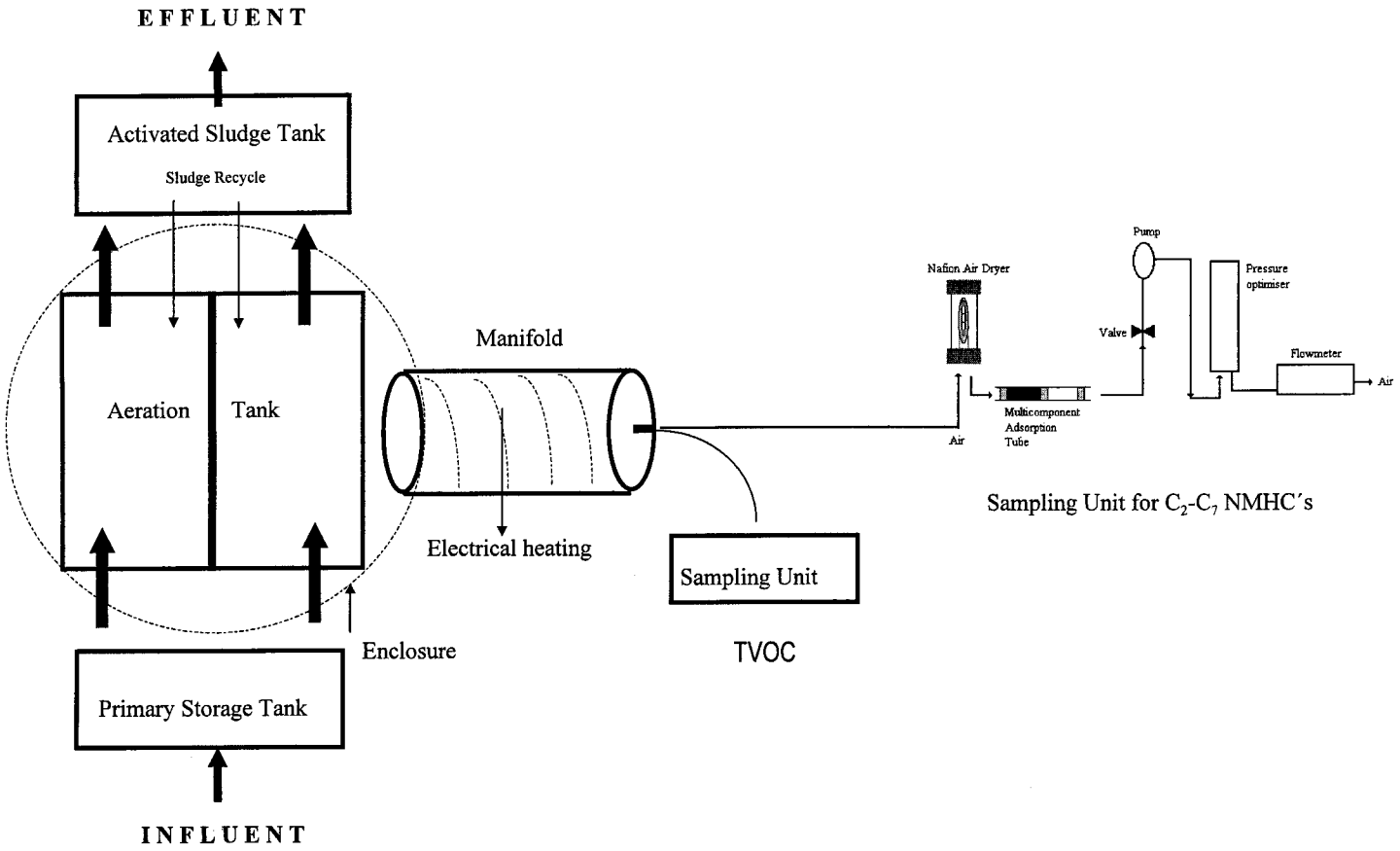

Figure 1. Sample collection unit with the layout of the treatment plant.

TABLE I

Average concentrations and estimated emission rates of measured C_2–C_7 hydrocarbons in off-gas (μg C m^{-3})

Hydrocarbons	Off-gas (Std. Dev.) (no. of samples = 10)	Ambient air (Std. Dev.) (no. of samples = 6)	Net concentration (off-gas – ambient air)	Average emission rate during aeration (mg C day^{-1})
Ethane	4.37 (4.58)	2.79 (2.56)	1.58	0.27
Ethylene	4.62 (4.35)	8.92 (14.12)	–4.30	–0.73
Propane	3.11 (3.65)	3.03 (4.27)	0.08	0.02
n-Butane	6.69 (9.64)	2.65 (3.09)	4.04	0.69
C-4 components	12.64 (17.16)	14.50 (17.51)	–1.86	–0.32
n-Pentane	0.45 (0.45)	0.09 (0.24)	0.36	0.06
C-5 components	6.96 (8.46)	3.15 (3.94)	3.81	0.65
n-Hexane	1.14 (3.27)	ND	1.14	0.19
C-6 components	2.05 (6.46)	0.15 (0.38)	1.90	0.32
n-Heptane	ND	ND	ND	ND
C-7 components	2.40 (1.11)	ND	2.40	0.41
Benzene	4.44 (13.22)	0.20 (0.37)	4.24	0.72
Toluene	10.45 (13.04)	0.23 (0.43)	10.22	1.74
Total	59.32	35.71	23.61	4.02

are generally considered to be present in the wastewater and the concentration variations are considered to depend on the nature of the influent. Another possibility could be the adsorption or biodegradation within the system. Hydrocarbons were identified from the eluted chromatograms (Figure 2). The peak shape and the retention of the compounds on the eluting column was disturbed by the presence of traces of moisture content. Not all hydrocarbons mentioned were detected in all samples. Concentrations reported as not detected were assumed to be zero for average concentrations. Standard deviations of the hyrocarbons concentrations for both the off-gas and air samples was between 0 and 10.

The measured concentrations of some compounds in off-gas are lower than the ambient air concentration. The measured concentrations are negative for ethylene and C_4 components while heptane was not detected in any of the samples. The concentrations of benzene and toluene were higher in the first few collected samples but were not detected later. Low concentrations of benzene and toluene are as expected due to the strict enforcement of environmental laws in Austria (*BGBl. 492/1991, BGBl. 872/1995, BGBl. 873/1995*) regarding the use and discharge of all

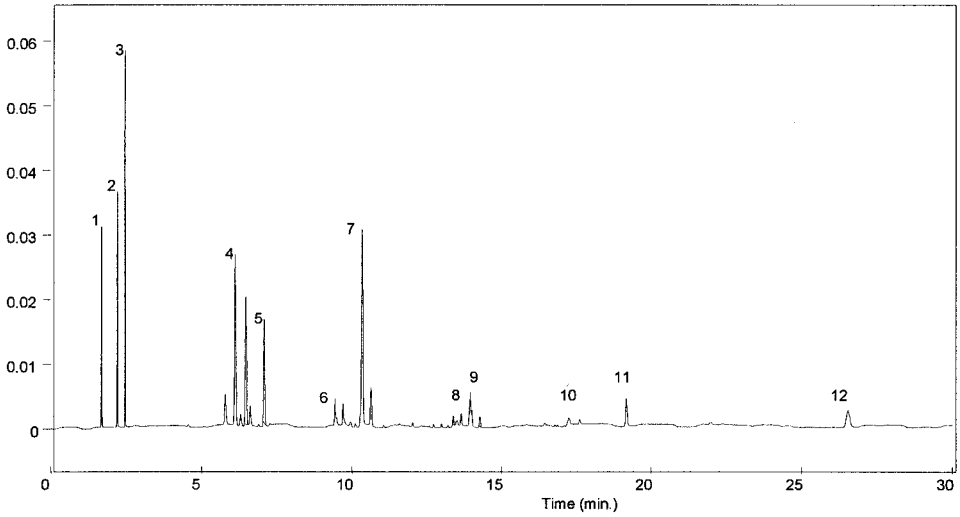

Figure 2. Eluted chromatogram collected (off-gas during aeration process on 12 February, 1998 from 12:24 to 12:54. 1. Ethane, 2. Ethylene, 3. Propane, 4. n-Butane, 5. C-4 components, 6. n-Pentane, 7. C-5 components, 8. n-Hexane, 9. C-6 components, 10. C-7 components, 11. Benzene, 12. Toluene.

solvents (including benzene and toluene) which contribute to the TVOC. However, toluene is still the major contributor of all the components in the air emissions.

3.2. TVOC

The measured TVOC showed a symmetric pattern of rapid increase in the emission at the start of aeration phase gradually steeping down and eventually a slow rise during the non-aeration phase (Figure 3). The observed TVOC concentrations of the off-gas measured during aeration and non-aeration phase of the sampling days are given in Figure 4. The aeration process runs continuously for 30 min followed by an hour of non-aeration phase. It is clearly seen that the hydrocarbons are emitted also during the non-aeration phase. This is explained by the possible mechanism of volatilisation or the non-complete oxidation of organic by the microorganisms. Ambient air, used for aeration, was also measured which can be seen as the steep fall in the emission curve in Figure 3.

3.3. EMISSION RATES

The emission rates were estimated by multiplying appropriate air flow rates with average concentrations. The total emission rate of C_2–C_7 hydrocarbons during the aeration phase is approximately 4 mgC day^{-1}. With the exception of toluene, all components are emitted less than 1 mgC day^{-1} (Table I).

The estimated average emission rates of TVOC per m^3 of wastewater processed on the three sampling days are given in Figure 5. The emission rate during a day is estimated to be in the range of 5–9 gC with an average of 7 gC.

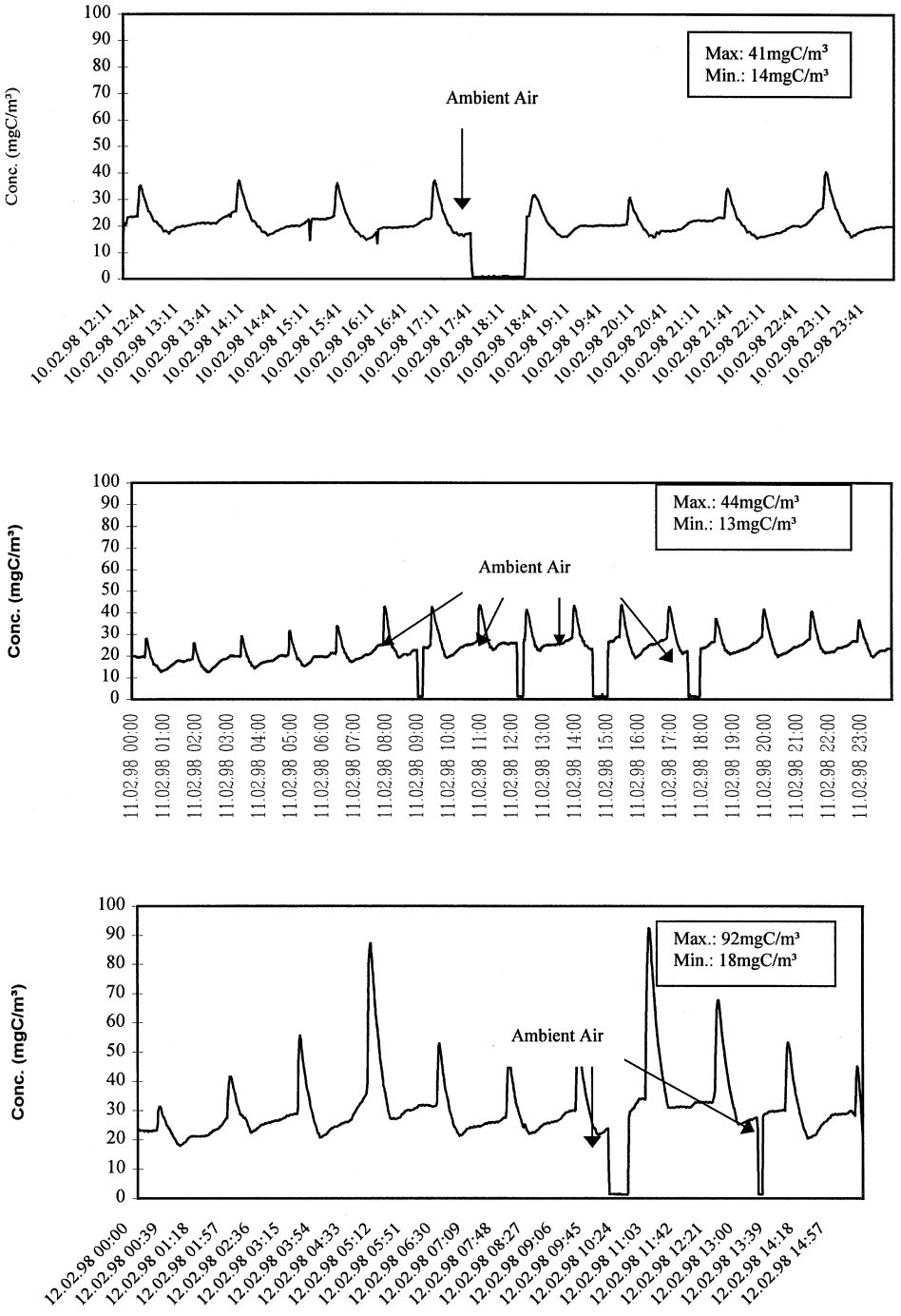

Figure 3. An overview of continuously measured TVOC on three sampling days.

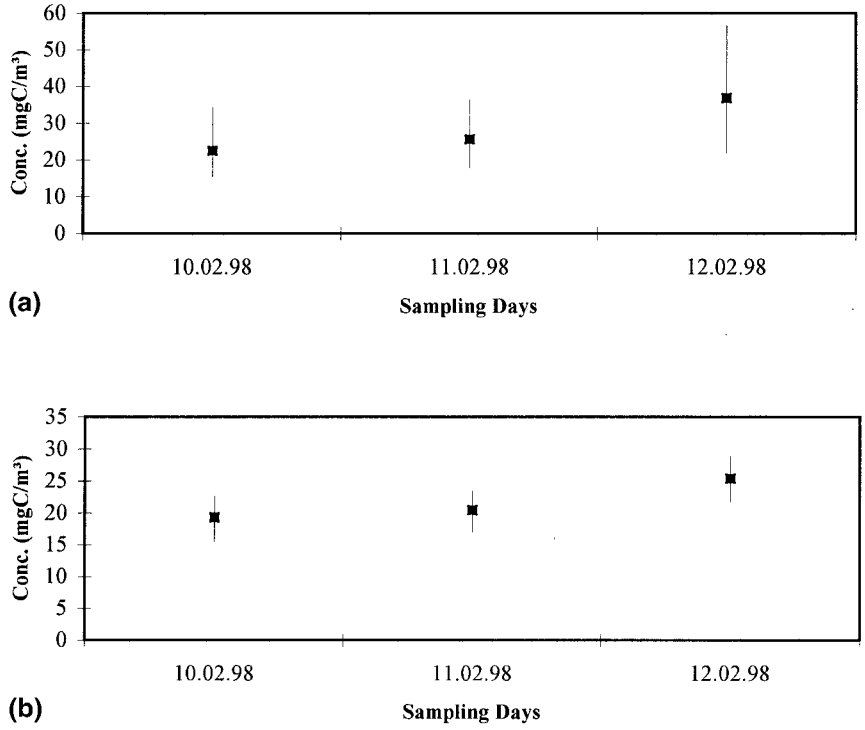

Figure 4. Observed maximum, minimum and average concentrations of TVOC during aeration phase.

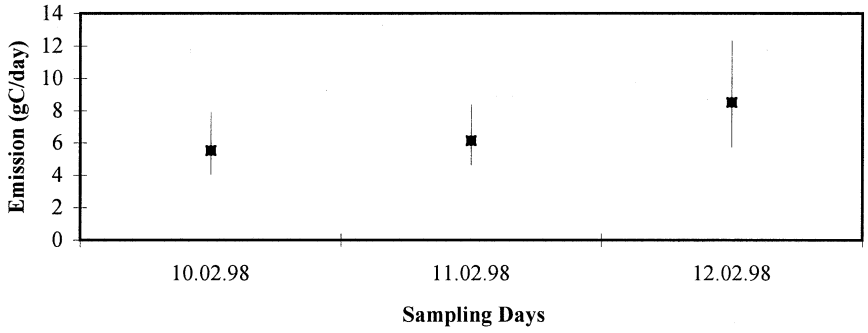

Figure 5. Maximum, minimum and average estimated TVOC emissions.

The non-aeration phases are contributing an average of approximately 40% of aeration phase emission loads. In this estimation, it is assumed that 40% of aeration phase emission loads of C_2–C_7 hydrocarbons are also emitted during non-aeration phase i.e. 9.44 μgC m^{-3} or 0.83 mgC day^{-1}. Therefore, the total C_2–C_7 hydrocarbon emissions in a day per m^3 of wastewater are 4.85 mgC. In such a case, C_2–C_7 hydrocarbons contribute on an average of around 0.07% of TVOC.

If an assumption is made that the main wastewater treatment plant in Vienna (Population = 1.6 million, Equivalent Inhabitants = 3.2 million, Gewasserschutzbe-

richt, 1996) is operated under similar conditions, then it would emit approximately an average range of 437–875 t yr^{-1} of TVOC and less than 0.5–1 t yr^{-1} of C_2–C_7 hydrocarbons. Thus, the results of this study suggest that either there has been either a significant reduction in the annual emission of non-methane hydrocarbon emissions from MWWTP in Vienna in the past years or the NMVOC emissions of the central sewage plant in Vienna have been overestimated to a considerable extent. We would like to mention here that TVOC includes methane. From preliminary experiments, we found that the major component of TVOC (>90% v/v) is methane.

4. Conclusions

1. The average concentrations of measured C_2–C_7 hydrocarbons in off-gas are less than measured ambient air concentration.
2. There are low emissions of benzene and toluene.
3. There is a contribution of hydrocarbon emissions also during the non-aeration phase.
4. The emission rates per m^3 of wastewater processed are approximately an average of 5 mgC of C_2–C_7 hydrocarbons and 7 gC of TVOC.
5. C_2–C_7 hydrocarbons contribute only 0.07% of the TVOC emissions.
6. The study reported here should be extended by including real time large treatment plants and data for different seasons in order to reduce uncertainties in the annual estimates.

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References

BGBl: 492/1991, *Lösungsmittelverordnung*, Austria.
BGBl: 872/1995, *Lösungsmittel-VO*, Austria.
BGBl: 873/1995, *Lackieranlagen-Verordnung*, Austria.
Chang, D. P. Y. *et al*.: 1987, *Final Report Submitted to California Air Resources Board*, Contract No. A5-127-32.
Gewasserschutzbericht: 1996, *Bundesministerium für Land- und Forstwirschaft*, Section IV.
Kotzjas, D. and Hjorth, J.: 1991, *Pollution Atmospherique Numero Special de Juillet*, pp. 209–216.
Lawrimore, H. J., Das, M. and Aneja, P. V.: 1995, *J. Geophys. Res.* **100**, 22.785.

Loibl, W., Orthofer, R. and Winiwarter, W.: 1993, *Atmos. Environ.* **27**, 2575.
Namkung, E. and Rittmann, E. B.: 1987, *J. of Water Poll. Control Fed.* **59**, 670.
Oliver, K. D., Adams, J. R., Daughtrey Jr., E. H., MacClenny, Yoong, M. J. and W.A. (???), Pardee, M. A.: 1996, *Atmos. Environ.* **30**, 2751.
Suschka, J., Mrowiec, B. and Kuszmider, G.: 1996, *Water Sci. Tech.* **33**, 273.
Tamilia, A., Marchese, N., Easter, C., Fredericks, D., Mayer, G. and Gaudes, R.: 1995, *Proc. Water Environ. Fed.*, Annu. Conf. Expo 68th, **5**, pp. 329–340.