

Selected carbonyl compounds in the air of Silesia region

Marianna Czaplicka, and Michał Chrobok

Institute of Environmental Engineering Polish Academy of Science, M. Skłodowskiej-Curie 34 street, 41-819 Zabrze, Poland

Abstract. This study was carried out to characterize three aldehydes of health concern (formaldehyde, acetaldehyde, and acrolein) at a three sites in Silesian region (Poland) in January and June 2015. Aldehydes in polluted atmospheres comes from both primary and secondary sources, which limits the control strategies for these reactive compounds. Average aldehyde concentration in summer period lies in range from 3.13 $\mu\text{g}/\text{m}^3$ to 10.43 $\mu\text{g}/\text{m}^3$, in winter period in range from 29.0 $\mu\text{g}/\text{m}^3$ to 32.2 $\mu\text{g}/\text{m}^3$. Acetaldehyde was dominant compound in winter period, in summer formaldehyde concentration was highest of all determined aldehydes.

1 Introduction

Aldehydes and ketones are present in almost every part of environment. These compounds can be found in: rain, dew, mist, and in the air [1]. Their presence was observed in gases emitted to atmosphere from traffic and industrial sources, including combustion of biomass and solid fuels [2]. Mentioned compounds can be created in course of photooxidation of hydrocarbons with help of radicals $\text{HO}_2\cdot$ and $\text{OH}\cdot$ and are part of photochemical smog [3]. Aldehydes play important role in tropospheric chemistry, since they are intermediate products of oxidation processes of hydrocarbons and subsequently generate photochemical products such as carbon monoxide and radical species that contribute to the production of ozone and peroxyacynitrate in the troposphere. In order to understand the chemical cycles of ozone and its related species in the troposphere as well as the impacts of air pollutants on human health, it is important to investigate the behavior of aldehydes compounds in the ambient atmosphere [4]. Formaldehyde (FA) and acetaldehyde (AD) are dominant species in the aldehyde group in the atmosphere [5]. The most important man-made source of formaldehyde are exhaust gases from cars not fitted with catalytic converters. Most common acrolein (AC) sources are exhaust gases from cars powered by petrol, diesel or other petrochemical fuels. Removal of formaldehyde from the atmosphere can occur by: chemical transformations, rain and snow scavenging of vapors and particles, dry deposition of particles, and vapor exchange across the air–water interface [6]. The objective of this study was to measure the gas-phase concentration of aldehydes in 3 sites located in Silesian region along with establishing influence of local sources upon their concentration

2 Experimental

2.1 Sample collection

Air samples were collected by passing through special sampler filed with silica gel and impregnated with solution of 2,4-DNPH (2,4-Dinitrophenylhydrazine) in hydrochloric acid. Potassium iodide was added to protect analytes from ozone influence. After collection samples were protected from sunlight and kept in temperature approximately equal to 4⁰C during transportation to laboratory. Atmospheric conditions in course of whole campaign are presented in table 1. Samples were collected around communication nodes situated in centers of cities (Zabrze, Gliwice 1) of upper Silesia urban area and in proximity of residential area (Gliwice 2) in January and June. In every sampling point 10 samples were collected both in June and January. Sampling flow rate was equal to 200 ml/min. Amount of air collected varies from 0.1 m³ to 0.2 m³.

Table 1. Summary of meteorological condition and O₃ content

	Temperature [°C]	Wind speed [m/s]	Relative humidity [%]	Ozone, O ₃ [µg/m ³]
January 2015				
Avarange	-1	1	89	27
Minimum	-8	0	65	4
Maximum	4	2	99	59
June 2015				
Avarange	15	0	70	68
Minimum	9	0	49	43
Maximum	23	1	94	113

2.2 Methods

Quantitative determination was conducted with help of Perkin Elmer Series 200 HPLC unit equipped with: UV-Vis diode array detector (DAD), Spheri - 10 RP-18 10µ (size 250 mm x 4,6 mm) column and 10 µl dispensing valve. Mobile phase composition changed from mixture of water:acetonitrile (40%:60%) to 100% of acetonitrile. Analysis was carried out at constant weavelenght equal 360 nm. Figure 1 presents chromatogram of mixture of standards.

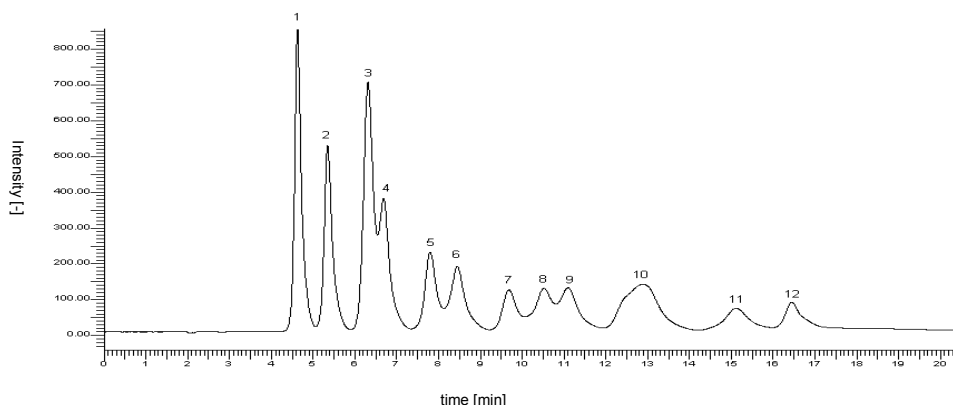


Fig.1. Chromatogram of standard solution 1; formaldehyde 2; acetaldehyde. 3; acetone 4; acrolein. 5; propionaldehyde. 6; Crotonic aldehyde. 7; butyl aldehyde 8; benzaldehyde. 9; *isovaleric* and valeric aldehyde . 10; methylbenzaldehydes 11; caproic aldehyde. 12; 2,5-dimethylbenzaldehyde

Quantitative determination was done by means of external standard method. DAD detector response was linear in concentration range from 0.15 µg/ml to 0.75 µg/ml. As limit of detection (LOD) three times value of signal to noise ratio was applied. Limit of quantification (LOQ) equals three times value of LOD. Tabel 2 presents statistical parameters of method.

Table 2. Values of LOD, LOQ and relative standard deviation for selected carbonyl compounds

Compound	Limit of detection [µg/m ³]	Limit of quantification [µg/m ³]	Relative standard deviation [%]
Formaldehyde	0.3	1.0	8.0
Acetone	0.2	0.5	6.0
Acrolein	0.2	0.6	9.5
Acetaldehyde	0.5	1.5	8.5
Benzaldehyde	0.5	1.5	14.6
Metyl- <i>isobutyl</i> ketone	0.3	1.0	14.0

3 Results and discussion

Conducted studies prove important influence of year period and sampling points characteristics upon aldehyde content in the air.

Table 3. The average total concentration of aldehydes (µg/m³) during June and January at the sites Zabrze and Gliwice

Parameter	Mean (SD)	Max	Min
Zabrze			
June	10.43 (4.9)	16.36	4.19
January	29.07 (12.6)	51.00	12.33
Gliwice 1			
June	7.67(1.8)	9.58	4.69
January	32.20(12.7)	60.14	16.73
Gliwice 2			
June	3.17(1.5)	4.04	0.02
January	30.24(13.4)	53.99	14.92

In June, independently of location average total concentration of aldehyde was lower in comparison with data obtained from January sampling campaign. Lowest average aldehyde concentration – 3.17 µg/m³ was recorded in June at point Gliwice 2 located at residential area, highest – 10.4 µg/m³ in Zabrze at communication nod. In course of January sampling campaign minor differences occurs in concentration of aldehydes regardless of sampling points. Obtained results were similar to result of air quality monitoring of Milan surroundings obtained by Andreini et al. [7]. Andreini et al. indicated that during winter total concentration of aldehydes varies from 16.7 to 30.7 µg/m³ at the urban locations and 11.7 µg/m³ at the rural-industrial location.

3.1 Aldehyde profile

Formaldehyde, acetaldehyde and acrolein were present in all samples collected in January. Average concentration of formaldehyde in winter varies from $4.53 \mu\text{g}/\text{m}^3$ to $6.39 \mu\text{g}/\text{m}^3$ depending upon sampling point location and equals 14% to 21% of total aldehydes concentration (table 4). These concentrations were within the ranges previously measured at different sites around the world. By comparison, the rural site formaldehyde concentrations measured equals $4.17 \pm 1.7 \mu\text{g}/\text{m}^3$ [8] in New Mexico USA and $0.05 - 9.1 \mu\text{g}/\text{m}^3$ at different sites in Canada [9].

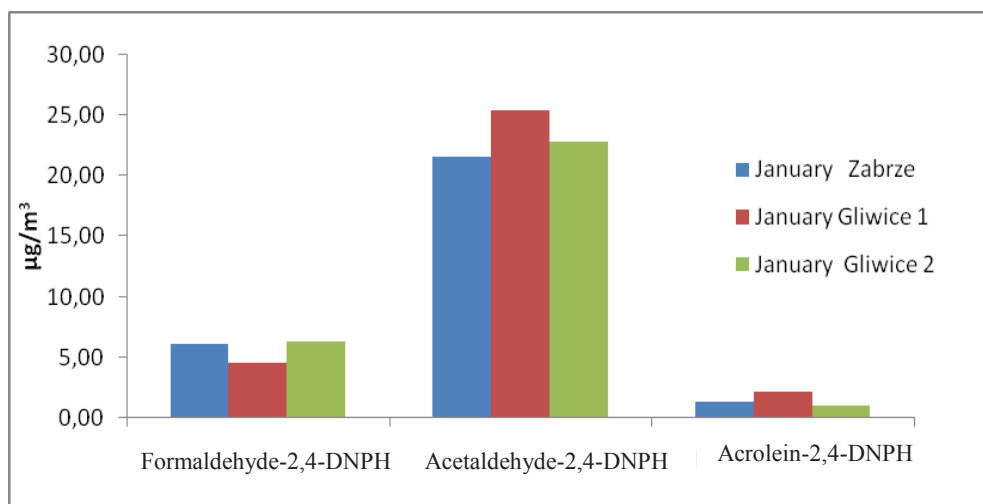


Fig. 2. Average concentration of aldehydes in January 2015

Table 4. Mass participation of FA, AD and AC in total concentration of aldehydes in January 2015

Compound	Zabrze [%]	Gliwice 1 [%]	Gliwice 2 [%]
Formaldehyde	21.0	14.1	21.1
Acetaldehyde	74.2	79.0	75.6
Acrolein	4.8	6.9	3.3

Acetaldehyde concentration exceeds $22 \mu\text{g}/\text{m}^3$ at every sampling point giving an maximal average value $25.5 \mu\text{g}/\text{m}^3$. Presented results indicate that dominant determined aldehyde was acetaldehyde, it's concentration equals 74% to 79% of total aldehyde concentration. Such high mass participation in total concentration may be result of influence of local combustion sources upon air quality.

Acetaldehyde is formed and released by the combustion of organic materials, a variety of natural processes and human activities. In addition, secondary formation of acetaldehyde occurs in the atmosphere through oxidation of natural and anthropogenic volatile organic compounds. Important matter is to consider half-life of determined compounds. It is widely known that under atmospheric conditions, formaldehyde is readily photo-oxidized in to carbon dioxide. Reaction with trace substances and pollutants in the air is relatively fast so that its half-life in urban air, under the influence of sunlight, is short. In the absence of nitrogen dioxide, the half-life of formaldehyde is approximately 50 minutes during the daytime. In the presence of nitrogen dioxide, this drops to 35 minutes. On the other hand

the atmospheric half-life of acetaldehyde, calculated based on hydroxyl radical reaction rate, is less than six hours. The night time decomposition of acetaldehyde is expected to occur by the gas-phase reaction with nitrate radicals, this tends to be more significant in urban areas, where the concentration of the nitrate radical is higher than in rural areas. A half-life of 35 days was calculated based on an average atmospheric concentration of nitrate radicals in typical mildly polluted urban center.

The major sources of acrolein emissions were mobile and unspecified stationary combustion sources. Acrolein is relatively unstable in the atmosphere, therefore transport within the air is expected to be limited. On the other hand the relatively high vapor pressure of acrolein (274 mm Hg at 25 °C) suggests that this compound will not partition from the vapor phase to particles in the atmosphere. Acrolein concentration in January varies from 1 µg/m³ to 2.2 µg/m³ and its mass participation in total aldehyde content ranges from 3.3% to 6.9%.

Profile of determined aldehydes in summer period undergo significant qualitative and quantitative changes in same sampling points. In June samples, collected at point Gliwice 2, acrolein presence was not detected. Lack of this compound is most likely a result of sampling point location situated in low traffic residential area. In sampling points located near communication routes (Gliwice 1 and Zabrze) acrolein concentration equals to approximately 2.3 µg/m³. Formaldehyde concentration ranges from 0.83 µg/m³ to 4.81 µg/m³ depending upon sampling point (Fig. 3). Highest concentration was recorded in Zabrze.

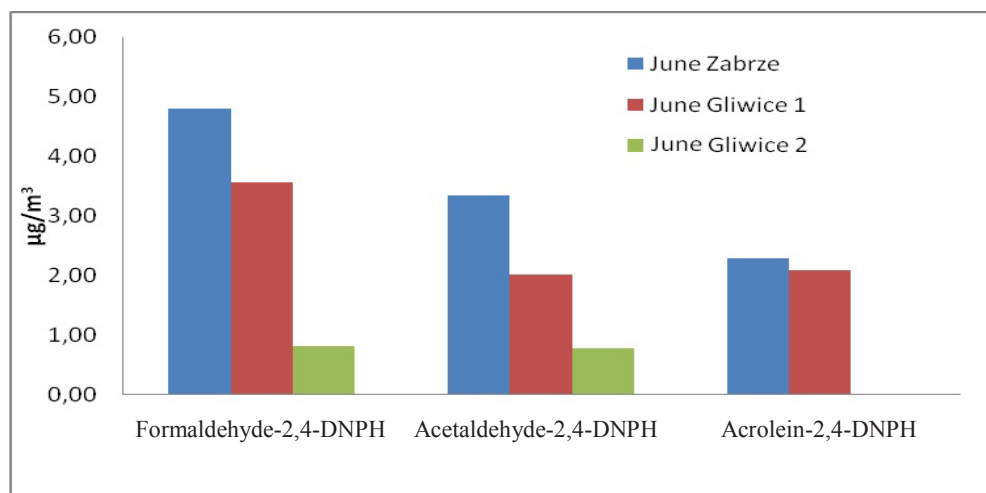


Fig. 3. Average concentration of aldehydes in June 2015

Table 3. Mass participation of FA, AD and AC in total concentration of aldehydes in June 2015

Compound	Zabrze [%]	Gliwice 1 [%]	Gliwice 2 [%]
Formaldehyde	46.1	46.5	51.5
Acetaldehyde	32.0	26.2	48.5
Acrolein	21.9	27.3	no

Formaldehyde content in total aldehyde concentration equals on average: 46% for Zabrze and Gliwice 1, 51% for Gliwice 2 (Table 3.). Acetaldehyde concentration in June was significantly lower in comparison to January and ranges from 0.8 µg/m³ to 3.3 µg/m³. Furthermore, its average share in determined compounds ranges from 26% to 48%.

Diversified aldehyde profile in summer and winter indicate important influence of local aldehyde emission sources upon air quality. Atmospheric conditions like: precipitation, solar radiation and ozone content can influence concentration of determined aldehydes.

4. Conclusion

Conducted studies indicate significant differences in aldehyde gas phase concentration in respect to year period. In summer aldehyde concentration was from three to ten times lower in respect to winter period, depending upon localization of sampling point. This tendency is most likely result of influence of local emission sources on air quality.

Differences were observed in profile of aldehydes gas phase concentration. In winter period dominant species present in the air was acetaldehyde in summer however highest concentration of formaldehyde was observed. In summer period acrolein was present only in places being communication nodes.

References

1. M. Czaplicka, K. Jaworek, and A. Wochnik, Archives of environmental protection. **41** 21-31 (2014)
2. W. Chongming, W Lixia, C Zhanjun, X. Hongming, D. Ritchie, and S. Shijin Combustion Science and Technology. **188**, 329-345 (2016)
3. R. Sommariva¹, J. A. de Gouw, M. Trainer, E. Atlas, P. D. Goldan, W. C. Kuster C. Warneke, and F. C. Fehsenfeld, Chem. Phys., **11**, 7081–7096 (2011)
4. R. M. LoPachin, and T. Gavin, Chem Res Toxicol, **27** 1081–1091 (2014)
5. C. Marchand, S. Bulliot, L. Calvé, and P. Mirabel, Atmospheric Environment, **40**, 1336-1345 (2006)
6. M. Odabasi, R. Seyfioğlu Atmospheric Environment **39**, 5149–5156 (2005)
7. B. P. Andreini, R. Baroni, E. Galimberti, U. G. Sesana, Microchemical Journal **67**, 11-19 (2000).
8. I.V. Fierro, C.J. Popp, R.S. Martin, Atmospheric Environment **38**, 249–260 (2004).
9. R. Che´nier, Human and Ecological Risk Assessment **9**, 483–509 (2003)