ALIPHATIC ALDEHYDES AS UNDESIRABLE CONTAMINANTS IN PRECIPITATIONS

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ABSTRACT

Water pollution with low carbon aliphatic aldehydes were investigated in precipitations (rain and snow) and their effect on natural surface waters. The presence of aldehydes in environmental waters may be dangerous because of their influence on human health, some of them have been shown to be carcinogens or suspected carcinogens. Formaldehyde, acetaldehyde and propanal were the carbonyls most frequently identified in collected samples. The studies showed that the total concentration of aldehydes in rainwater may vary in a wide range and is related to meteorological conditions. The extremely high concentration of aldehydes were found in the rainwaters collected after a relatively long period of dry weather, the concentration of total aliphatic C1-C10 aldehydes exceeded 2000 $\mu g l^{-1}$. Particularly high contribution of aldehydes to total organic carbon (TOC) was observed in samples collected at the beginning of the rain event (ca 14%), whereas the average value was on the level 3.0 %. This significant change of TOC composition shows that carbonyls can be one of the faster removed organic group from the atmosphere to the rainwater. Relatively high concentrations of nonanal and decanal were found seasonally in samples. Aldehydes can be emitted to the environment by the plants during the vegetation season. Similarly to rain, snow is also responsible for aldehydes scavenging from atmosphere. On the basis of the data of average concentration of aldehydes in precipitations can be estimated their annual deposition.

Keywords: formaldehyde, precipitation, aliphatic aldehydes, wet deposition, rainwater pollution

1. Introduction

Aldehydes are commonly identified in aqueous and in the terrestrial environment. They can originate from natural and anthropogenic sources. Emission from combustion, industrial processes and vehicular exhausts are responsible for emergence of undesirable organic pollutions in the environment. However, the most important source of aldehydes is the troposphere. Aldehydes are related to photochemical processes and oxidation of volatile organic compounds (Balla *et al.*, 2014; Myriokefalitakis *et al*., 2008; Obermeyer *et al*., 2009; Posanzzini *et al*., 2007). The strong oxidants as hydroxyl radicals ($OH^{\bullet}$), ozone (O_3) and hydrogen peroxide (H_2O_2) react with primary pollutants of the atmosphere – hydrocarbons, leading to formation of secondary products. Aldehydes and ketones were demonstrated by Lou *et al*. (2009), as dominant secondary compounds. Warneck (2005) has shown the chemical mechanisms and the model reaction paths of the oxidation of ethane, ethene, acetylene, propane, propene and acetic acid. Formaldehyde, acetaldehyde, propanal, acetone, glyoxal and methylglyoxal are the main oxidation products. These carbonyl compounds can be removed from air by wet deposition (Dąbrowska *et al*., 2013; Kawamura et. al., 2001; Matsumoto *et al*., 2005; Matsunaga *et al*., 2007; Polkowska *et al*., 2006). Wet deposition is considered as significant removal route that may have significant impact on aqueous chemistry. The studies of precipitations showed the presence of more than 600 organic compounds. Ketones and aldehydes belong to the most important environmental pollutants (Polkowska *et. al*., 2000). Direct emission from the growing vegetation and the living organisms are other identified natural sources of aldehydes (Gang *et al*., 2010).

The presence of aldehydes is important because some of them have been shown to be carcinogens or suspected carcinogens (formaldehyde, acetaldehyde) (Soffritti *et al*., 1989; Takahashi *et al*., 1989). Aldehydes can be responsible for specific odour in natural surface waters, because threshold of odour detection for aldehydes is very low (Bao *et al*., 1997).
This study presents the results of determination of aliphatic aldehyde concentrations in atmospheric precipitation (rain and snow) collected over two years of sampling at various location: in large urban agglomeration (Poznań city) and in rural area (30 km from Poznań, Zielonka Forest Region) in Poland. The effect of rainy season on the concentration of aliphatic C1-C10 aldehydes in natural surface waters is discussed. The results show that rainwater is a medium which can easily transport volatile and semi-volatile aldehydes to natural aquatic system.

Particular emphasis has been put on all aspects of the environmental sample preparation and optimisation of the analytical method, permitting to detect aldehydes at low levels of concentration in all collected samples. High polarity and reactivity of carbonyl compounds in aqueous matrices imposes the need for their derivatization, since derivatives are less polar, more volatile and can be detected using selective detectors. PFBOA (O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine) was used as derivatization agent and gas chromatography with electron capture detector as sensitive system for separation and quantification respectively.

2. Material and method description

2.1. Samples collection

Precipitation samples were collected manually during the rainy and snowy season in the years 2010-2012 from urban area of Poland in Poznan city centre and from the rural area in Zielonka Forest Region. Since aldehydes are easily biodegradable, the aqueous samples should be derivatized on the day of their collection or the samples should be protected from the biodegradation by addition of copper sulphate, which is a chemical agent does not disturb in aldehyde analysis by GC/ECD system. Sampling sites are showed in Figure 1.

Figure 1: Illustration of the sampling sites: 1– urban area, 2- rural area in Wielkopolska Region.

2.2. Analysis of aldehydes

Analytical standards of C1 – C10 aldehydes were purchase from Aldrich (Steinheim, Germany), PFBOA was prepared gravimetrically as an aqueous solution in organic free water while aldehyde solutions were prepared in methanol. Hexane (J.T.Baker, Germany) was used as a solvent for extraction. Aldehyde analysis was based on derivatization reaction with PFBOA as a derivatizing agend to obtain oximes that, after extraction with organic solvent were analysed by gas chromatography (GC 8000 series, Fisons Instruments) with ^{63}Ni electron capture detection. The Rtx-5MS (Restek) fused silica capillary column (30 mx0.25 mm i.d.x0.25 µm film) was applied for separation. Helium and nitrogen were used as a carrier gas and a detector make-up gas, respectively. The method was described previously by Dąbrowska *et al*. (2005, 2009, 2013, 2014).The detection limit was in the ppt range, and average relative standard deviation (RSD)

was about 10 % for each of the monitored aldehydes. List of studied aldehydes and their limit detections is presented in Table 1.

Table 1: List of studied aldehydes in rainwaters and their detection limit

Compound	Linear formula	Abbreviation	Limit of detection [ngl^{-1}]
Methanal, formaldehyde	HCHO	C1	2.3
Ethanal, acetaldehyde	CH_3CHO	C2	5.1
Propanal, propionalaldehyde	CH_3CH_2CHO	C3	6.3
Butanal, butyraldehyde	$CH_3(CH_2)_2CHO$	C4	3.2
Pentanal, valeraldehyde	$CH_3(CH_2)_3CHO$	C5	2.1
Hexanal, caproaldehyde	$CH_3(CH_2)_4CHO$	C6	4.3
Heptanal, enanthaldehyde	$CH_3(CH_2)_5CHO$	C7	8.3
Octanal, caprylic aldehyde	$CH_3(CH_2)_6CHO$	C8	2.1
Nonanal,pelargonaldehyde	$CH_3(CH_2)_7CHO$	C9	1.7
Decanal caprinalaldehyde	$CH_3(CH_2)_7CHO$	C10	2.6

2.3. Analysis of total organic carbon

Total organic carbon (TOC) in selected aqueous samples was measured by means of AURORA Model 1030 (I.O. Analytical) using the persulphate/100 °C wet oxidation method. The amount of carbon dioxide was measured with IR detector. The method detection limit for organic carbon was 0.01 mgl^{-1} and RSD of the method was 3 %.

3. Results

Organic compounds were presented in all samples: in precipitations collected in the urbane area as well as in rural area. The range of the total organic carbon varied from 3.6 to 23.2 mgl^{-1} and the average contribution of aldehydes to TOC (as %) varied from 1.6 to 7,3 %. Comparable results presented Kawamura *et al*. (2001): TOC determined in rainwaters collected in Los Angeles ranged from 2.0 to 18.6 mgl^{-1}. High value of correlation coefficient between concentration of TOC and aldehydes in wet deposition shows that aldehydes are contributors to rainwater organic carbon.

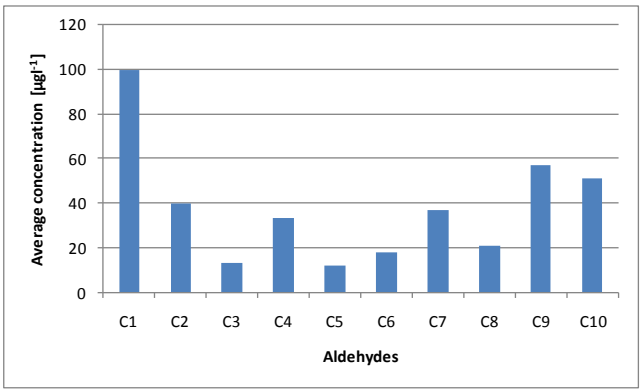


Figure 2: Average concentration of aliphatic C1-C10 aldehydes in wet deposition observed during the years 2010-2012.

The concentration of aliphatic aldehydes in rain and snow waters may vary in a wide range. Total C1 –C10 concentration was estimated in Wielkopolska Region from 300 μgl^{-1} to more than 800 μgl^{-1}, with average value about 400 μgl^{-1}. Formaldehyde (C1), acetaldehyde (C2) and propionalaldehyde (C3) are important aldehydes in wet deposition, they are identified in all of the precipitation samples, their occurrence is equal to 100%. Average concentration of C1-C10 aliphatic aldehydes in wet deposition observed in Wielkopolska Region during the years 2010-2012 is presented in Figure 2. Taking into consideration that the average annual precipitation in

Wielkopolska is 500 mm and assuming the total aliphatic aldehyde concentration of 400 $\mu g l^{-1}$, the wet deposition of C1-C10 aldehydes can be calculated to be 0.2 $g m^{-2}$ year, and the deposition value for more undesirable aldehyde i.e. formaldehyde can amount to 0.05 $g m^{-2}$ year.

Relatively high average concentration is noted for nonanal and decanal. There is a significant difference between the highest concentration of C9 and C10 aldehydes identified in spring with reference to their mean year-long values. This phenomenon is explained by some authors as caused by the vegetation processes taking place in plants as well the seasonal appearance of phytoplankton (Dąbrowska *et.al*., 2014; Bowman *et.al*., 2003).

3.1. Aldehyde concentration in rural and urban rainfall

Generally, the precipitation samples with high concentration of organic pollutions are expected rather in urban than in rural areas. However, during winter and autumn time, similar concentration level of most characteristic carbonyl compounds was observed in rain and snow waters collected in urban (Poznań city, with 600000 habitants) as well as in rural samples (Zielonka Forest Region, about 30 km from Poznań) (see Figure 3). This phenomenon can suggest that important part of carbonyl compounds identified in rainfall is derived not only directly from auto-exhausts, but are mainly produced by *in situ* photochemical reaction in the atmosphere. In consequence the rainwater is a medium which can easily transport volatile compounds over long distances to natural aquatic system.

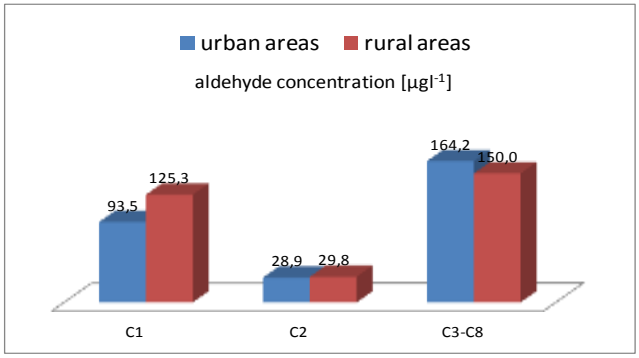


Figure 3: Comparison of aldehyde concentration measured in wet deposition collected from urban and rural areas.

3.2. Correlation between aldehyde concentration in surface waters and intensity of precipitation

A comparison of the aldehyde concentration in the surface layer of lake and river waters with the intensity of precipitation measured in the same period indicates a negative correlation between them.

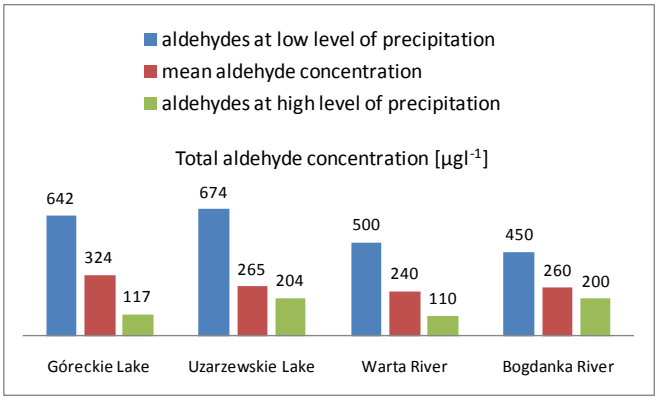
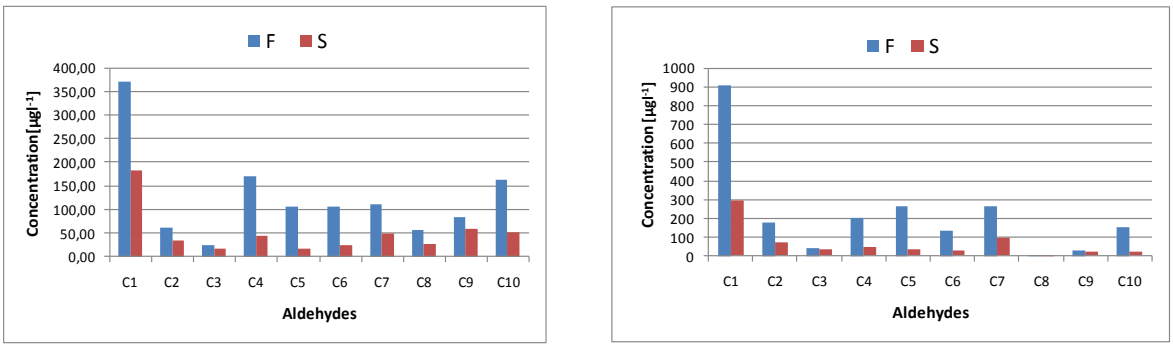


Figure 4: Comparison o ftotal aldehyde concentration in surface layer of natural waters with precipitation intensity

Less intensive precipitation delivers much higher concentration of aldehydes from the atmosphere via rainwater to the surface aquatic systems, more intensive precipitation means the higher dilution effect. The pollution level is very high at small amount of rainfall. A similar trend was demonstrated by Kawamura *et al*. (2001) for carboxylic acids. Particularly small amount of rainfall - about 5 mm was noted during April 2011, and in the same time total C1-C10 aldehyde concentration was evidently higher in monitored surface waters than at high level precipitation (Figure 4).

3.3. Elevated aldehyde concentration at the beginning of precipitation

Rapid removal of aldehydes from atmosphere starts already at the beginning of precipitation. This tendency suggests that organic species in the atmosphere are scavenged by rain droplets during early stage of precipitation events and aldehydes are the compounds easily transferred from the air. Significantly high concentration of aldehydes was detected in the sample collected at the beginning of the first rainfall appeared after drought period (compare Figure 5A,B), concentration of formaldehyde amounted almost 1000 $\mu g l^{-1}$.



(A) (B)

Figure 5: Aldehyde concentration in precipitation samples: A - water collected during the rainy season (14 May 2010) and B – water collected after the drought period (17 March 2011); F - samples collected at the beginning of the rain and S - sample collected a few hours later.

4. Conclusions

Aliphatic aldehydes are the undesirable pollutions in the environment. A significant part of them is formed as results of photochemical transformations in troposphere. Aldehydes are the group of organic compounds that are easily washed out of the atmosphere and with wet depositions can penetrate natural surface waters. The total C1 – C10 aldehyde concentration identified in the precipitations is high and generally varies from 300 $\mu g l^{-1}$ to more than 800 $\mu g l^{-1}$, or even higher when wet deposition starts after period of drought. On the basis of the data of average concentration of aldehydes in precipitations it was estimated their annual deposition.

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