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Aldehyde concentrations in wet deposition and river waters

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HIGHLIGHTS

- ► Atmosphere pollutants are responsible for the appearance of aldehydes in surface waters.
- ► Volatile aldehydes are commonly present in precipitations as well as in surface waters.
- ► Semi-volatile and poorly soluble aldehydes as nonanal and decanal were observed seasonally.
- ► High concentration of carbonyls were noted after periods of drought and at the beginning of rain.
- ► Carbonyl concentration in river is correlated to meteorological conditions.

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ABSTRACT

The process of pollutants removal from the atmosphere can be responsible for the appearance of aldehydes in surface waters. We observed that formaldehyde, acetaldehyde, propanal, glyoxal, methylglyoxal and acetone were commonly present in precipitations as well as in surface water samples, while semi-volatile and poorly soluble aldehydes as nonanal and decanal were observed seasonally. Particularly high level of carbonyls concentration was noted after periods of drought and at the beginning of rainy periods. We estimated that ca. 40% of aldehydes from wet precipitations were delivered into river waters. The level of carbonyl concentration in river was positively correlated with specific local meteorological conditions such as solar radiation and ozone concentration, in contrast, there was negative correlation between aldehyde concentration in the river samples and the precipitation intensity.

1. Introduction

The presence of aldehydes in air and environmental waters may be important because of their influence on human health. Some of them are toxic (formaldehyde, acetaldehyde, glyoxal, methylglyoxal) and have been shown to be carcinogens or suspected carcinogens (Richardson et al., 2007; Homann et al., 1997; Standard Methods, 1995; Soffritti et al., 1989; Takahashi et al., 1989). Additionally, aldehydes are undesirable in water because they can be sometimes blamed for odour problems. Human olfactory sense is responsive to presence of carbonyl compounds. Thresholds of odour detection for aldehydes is very low, e.g. 4.0 μg/l for acetaldehyde or even lower 0.15 μg/l for pentanal (Nijssen et al., 1996). Thus, the low level of aldehydes concentration can be responsible for the specific odour of natural waters. Bao et al. (1997) identified hexanal, heptanal, octanal, nonanal, decanal, benzaldehyde, 2,4-decadienal, β-cyclocitral, citral, among other undesired odorous compounds in Arno river (located in central Italy and used as a raw water source for the supply of drinking water to Florence). Authors suggested that carbonyls in conjunction with geosmin were the main odour-causing organic compounds.

Aldehydes are widely present in aqueous and in the terrestrial environment as well as in the troposphere. Carbonyl compounds can originate from natural and anthropogenic sources. Natural sources of aldehydes are related to photochemical and microbial oxidation of volatile organics (Myriokefalitakis et al., 2008; Obermeyer et al., 2009; Possanzini et al., 2007). Ozone (O_3), hydrogen peroxide (H_2O_2) and hydroxyl radicals ($OH^{\bullet}$) are the most important oxidants in the troposphere. They react with primary pollutants of the atmosphere — hydrocarbons, leading to formation of secondary products. Lou et al. (2009) demonstrated, that aldehydes and ketones dominate as secondary compounds, and the maximum of their concentration in air depends on daytime. Matsunaga et al. (2007) have indicated isoprene oxidation as the main source of glycolaldehyde, hydroxyacetone and methylglyoxal. 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, acetone, glyoxal and methylglyoxal are the main oxidation products. These water-soluble compounds are scavenged from air by precipitation (Kawamura et al., 2001; Matsumoto et al., 2005; Matsunaga et al., 2007). Direct emission from the growing vegetation, the biomass burning, and the living organisms are other identified natural sources of aldehydes (Gang et al., 2010). C_6–C_{10} aldehydes can be emitted from several plant species. Emission occur from plant exposed to stress. Elicitors of aldehyde

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emission are ozone uptake, and insect and pathogen attack on plants, and growing rival vegetation (Wildt et al., 2003).

The presence of aldehydes in the environment can result also from anthropogenic pollution coming from fuel combustion and manufacturing (industrial contaminants). The sunlight and high temperature contribute to the formation of carbonyls as products of thermooxidative or chemical degradation of plastics. To the best of our knowledge, no attempt has been made so far to estimate which sources of aldehydes are more significant. One of the most important sources of aldehydes to the aquatic system seems to be atmospheric deposition.

Various aldehydes have been identified in rain, snow, dew and fog samples (Basheer et al., 2010; Kawamura et al., 2001; Li et al., 2008; Matsumoto et al., 2005; Matsunaga and Kawamura, 2000; Matsunaga et al., 2007). Kawamura et al. (2001) and Sakugawa et al. (1993) collected rainwater samples in Los Angeles from 1981 to 1991. The most prevalent formaldehyde and acetaldehyde were determined by them in the amounts from 25 to 1920 μg/l and from 3 to 211 μg/l respectively, glyoxal from 5.8 to 359.6 μg/l and methylglyoxal from 7.2 to 504.0 μg/l. Gang et al. (2010) observed the concentration of formaldehyde in the rainwater measured in the Guiyang city (China) from 2006 to 2007 and HCHO concentration ranged from lower than method detection limit to 1206 μg/l. In contrast, Giokas et al. (2009) did not detect carbonyl compounds in rainwater from Ioannina in Greece. Li et al. (2008) detected high concentration of aldehydes in cloud water: that of formaldehyde ranged from 138 to 696 μg/l and that of acetaldehyde — from 35 to 708 μg/l. Matsumoto et al. (2005) investigated the concentration of aldehydes in rain, fog and dew waters collected in 2003 in Yokohama in Japan. Formaldehyde, acetaldehyde, glyoxal and methylglyoxal were identified in all of the samples studied. These results confirm the hypothesis of Blando and Turpin (2000), that organic pollutants are absorbed by suspended droplets and can readily penetrate into atmospheric cloud and fog water.

It seems reasonable to assume that this process of pollutants removal from the atmosphere can be responsible for the appearance of aldehydes in surface waters. However, no systematic studies on aldehydes presence in surface waters have been performed. The average level of aldehydes in natural waters and their significance in the environment have not yet been discussed in the literature. The major part of available works have been focused mainly on the volatile and well water-soluble carbonyls such as formaldehyde and acetaldehyde, sometimes glyoxal and methylglyoxal were presented in precipitations (Table 1).

The aim of the presented study was to check the seasonal oscillations in the carbonyl compounds content in precipitations and the assessment of their impact on surface water. In contrast to other studies, also less water soluble aldehydes were observed in environmental samples. Our attention was focused on all aliphatic aldehydes including nonanal and decanal, whose concentrations in water samples were unexpectedly high. Nonanal and decanal were seasonally identified by us in rainwaters, snow waters as well as in river waters. Particular emphasis has been put on all aspects of the environmental sample preparation and optimisation of the analytical method.

2. Materials and methods

2.1. Collection of natural water samples

Samples from two rivers in Poznan (Poland) area — Warta and Bogdanka were collected more or less systematically in the years 2009 and 2011, always from the selected points in the same place in the city centre (Fig. 1), three to five times month by month and average values of aldehyde concentration were calculated.

Samples of precipitations: rain and snow were collected manually during the rainy and snowy season from urban area (Poznan city) as well as from the rural area (30 km from Poznań, Zielonka Forest Region). Ozone concentration, UV_B radiation, level of precipitation

Table 1
Concentration of aldehydes in aqueous environmental samples detected by different authors.

Aldehyde	Rain	Concentration [μg/l]										
		Snow									River	
Formaldehyde	40.0–1920.0	25.5–1350			36.6	30–180	9–630	50.9–127.56		5.02		nd–5.25
Acetaldehyde	4.4–101.2	3.5–211.2			4.4			nd–29.76		3.08		0.09–0.53
Propanal		0.6–52.2			nd			nd–38.76		nd		nd
Butanal		0.7–36								nd		
Pentanal								nd–15.54				
Hexanal											nd–0.11	
Heptanal											nd–0.06	
Octanal											nd–0.09	
Nonanal											0.10–0.47	
Decanal											0.19–1.16	
Benzaldehyde											nd–0.04	
Glyoxal	5.8–359.6	0.6–696	5.1–76	13.9–16.2	26.7				12.6			0.64–2.09
Methylglyoxal	7.2–504.0	0.7–792	8.9–66	3.7–6.8	8.64				17.1			
Glycolaldehyde			3.4–75		9.6				34.8			
Acetone			1.8–26	2.6–8.0	nd					7.36		
References	Sakugawa et al., 1993	Kawamura et al., 2001	Matsunaga et al., 2007	Matsunaga and Kawamura, 2000	Matsumoto et al., 2005	Kieber et al., 1999	Khare et al., 1997	Basheer et al., 2010	Matsunaga and Kawamura, 2000	Liu et al., 2010	Bao et al., 1997	Takeda et al., 2006

nd—no detected