New directions: Need for better understanding of source and formation process of phthalic acid in aerosols as inferred from…

Article · June 2016

DOI: 10.1016/j.atmosenv.2016.05.058

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Atmospheric Environment 140 (2016) 147–149

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

New directions: Need for better understanding of source and formation process of phthalic acid in aerosols as inferred from aircraft observations over China

HIGHLIGHTS

- Phthalic acid was measured during three aircraft measurements over China.
- Phthalic acid was 15–2000 times greater than those from ground measurements.
- Phthalic acid was sometimes even higher than oxalic acid in warm seasons.
- Evaporation of plasticizers may contribute substantially to phthalic acid.
- It is urgently needed to explore the source and formation process of phthalic acid.

Phthalic acid, which is an aromatic dicarboxylic acid, has been broadly detected in ambient aerosols. Several studies have already proposed that phthalic acid could serve as an organic marker for secondary organic aerosol (SOA) or a surrogate for the estimation of SOA mass (Schauer et al., 2002; Zheng et al., 2002; Fine et al., 2004). Recent smog chamber experiments and field campaigns have demonstrated that a possible source of particle-phase phthalic acid is the oxidation of polycyclic aromatic hydrocarbons (PAHs) such as naphthalene (Fraser et al., 2003; Kleindienst et al., 2012; Kawamura and Ikushima, 1993) or benz[*a*]anthracene (Jang and McDow, 1997) which can be produced in diesel exhaust, coal combustion and biomass burning (Schauer et al., 1999). In addition, phthalic acid can be also emitted from primary sources such as off-gassing of plasticizers from plastics (Fraser et al., 2003) and vehicle emissions (Kawamura and Kaplan, 1987). The occurrence of phthalic acid has been reported with a large concentration range in the marine, remote, background and urban aerosols from the ground observations (Table 1). However, phthalic acid has rarely been reported in ambient aerosols from aircraft measurement at high attitudes (Table 1).

Here, we collected $PM_{2.5}$ (i.e., particulate matter with a diameter smaller than 2.5 μm) samples at different heights from 0.5 km to 4 km over the coastal China in winter (12/25/2002–01/06/2003, n = 18) and inland China during summer (08/08/2003–09/13/2003, n = 14) and spring (05/19/2004–06/10/2004, n = 16) using Yun-12 and Yun-5 airplanes (Wang et al., 2007; Zhang et al., 2016). The mass concentrations of dicarboxylic acids were measured using the method as described elsewhere (Zhang et al., 2016). Briefly filter samples were extracted with pure water and the extracts were analyzed for dicarboxylic acids using a gas chromatography with a flame ionization detector. Identification of the organic compounds was performed by retention times in GC with authentic standards and GC/mass spectrometry analyses. Small peaks of phthalic acid and oxalic acid were detected on the field blank filters, however, blank values were less than 10% of those in the real samples. The recoveries were >85% for phthalic acid. We reported the concentrations after blank corrections.

We found that phthalic acid concentrations ranged from 10.4 to 167.4 ng m^{-3} (average 70.7 ± 41.7 ng m^{-3}) in winter, 768–2570 ng m^{-3} (average 1590 ± 510 ng m^{-3}) in summer, and 158–676 ng m^{-3} (359 ± 174 ng m^{-3}) in spring, which are 15–2000 times greater than those reported for urban aerosols from North America, Europe and Asia as well as marine aerosols from the Pacific Ocean (Table 1). Their concentrations were often dominant over oxalic acid in warm seasons (i.e., 286 ± 216 ng m^{-3} and 183 ± 111 ng m^{-3} for spring and summer), being contrasting to the molecular distributions previously reported globally including the tropospheric and surface aerosols (i.e., predominance of oxalic acid over the other organic acids identified). Phthalic acid accounted for 1.3–10.5% (4.9 ± 2.5%) and 0.5–3.4% (1.6 ± 0.7%) of organic carbon (OC) in summer and spring, respectively.

The seasonality of phthalic acid concentrations (i.e., summer > spring > winter) was also contrasting to organic aerosols from primary emissions with the highest abundance in winter from the same campaigns due to enhanced anthropogenic emissions from coal combustion and biomass burning (Wang et al., 2007). We proposed two explanations for the maximum phthalic acid concentration during summer. First, secondary production from naphthalene is significant enhanced due to favorable photochemical conditions in summer. Second, primary emissions from evaporation processes of plasticizers widely used in China is also increased due to higher temperatures (Deshmukh et al., 2016). Note that gas-phase naphthalene concentrations have been reported as high as to 5970 ng m^{-3} in urban areas of China (Tao et al., 2007). Taken together with the mechanism of reactions of OH + aromatic hydrocarbons (Kleindienst et al., 2012), we could postulate that secondary production of phthalic acid in the polluted atmospheric over China is enhanced in summer associated with higher solar

http://dx.doi.org/10.1016/j.atmosenv.2016.05.058

Table 1
Mass concentrations (ng m^{-3}) of atmospheric phthalic acid in different locations over the world.

Sample information	Range	Average ± SD	Reference
Coastal China in winter, 2002/2003	10.4–167	70.7 ± 41.7	This study[a]
Inland China in summer, 2003	768–2570	1590 ± 510	This study[a]
Inland China in spring, 2004	158–676	359 ± 174	This study[a]
Hong Kong, 2003	40.1–105	83.9 ± 21.3	(Ho et al., 2006)
Mainz, Germany, 2006/2007	0.69–3.38	3.76 ± 2.87	(Zhang et al., 2010)
Beijing, China, summer 2006	49.5–102	77.5 ± 17.6	(Ho et al., 2010)
Yufa, China, summer 2006	41.0–86.1	68.3 ± 4.1	(Ho et al., 2010)
2010 CalNex Study	<0.1–19		(Kleindienst et al., 2012)
14 cities of China, summer 2003	30.8–231	102 ± 53	(Ho et al., 2007)
14 cities of China, winter 2003	29.9–235	78.2 ± 38.8	(Ho et al., 2007)
Raipur, India, 2009/2010	6.7–79.5	26.8 ± 13.4	(Deshmukh et al., 2012)
Four Urban Sites in Southern California, USA, late summer 1993	4.1–242	80.2	(Fraser et al., 2003)
Los Angeles, USA	229–324		(Kawamura and Kaplan, 1987)
Tokyo, Japan, April 1988 to February 1989	4.9–30	15 ± 7	(Kawamura and Ikushima, 1993)
Alert, Arctic, July 1987 to June 1988	<0.005–5.8	1.5 ± 1.5	(Kawamura et al., 1996)
Pacific Ocean, 1990	<0.01–7.6	0.66 ± 0.35	(Kawamura and Sakaguchi, 1999)

[a] Except for this study using aircraft sampling, all the other studies reported concentrations from surface measurements.

radiations, temperatures and OH radical concentrations.

Furthermore, we roughly estimated an average secondary organic carbon (SOC) for naphthalene as 40 μg m^{-3} in summer by taking the mass fraction (i.e., $f = 0.04$ in the presence of nitrogen oxides) of phthalic acid in SOC concentrations previously determined in smog chamber studies (Kleindienst et al., 2012) and also assuming phthalic acid is exclusively produced from atmospheric oxidation of naphthalene in this study. Interestingly, we found the SOC estimate even exceeds OC concentration (24 μg m^{-3}), and this indicates SOC from naphthalene is significantly overestimated likely due to underestimation of mass fraction (i.e., f) associated with different atmospheric conditions between chamber studies and ambient atmosphere at attitudes (0.5–4 km) in China. Another possible explanation could be primary emissions that are also very important contributors of phthalic acid in China considering large amounts of vehicle exhausts and plasticizers evaporation.

Our results suggest that phthalic acid is a major constituent of water soluble organic species in the polluted troposphere (0.5–4 km) over China, suggesting that phthalic acid have significant impacts on the chemical and physical properties of organic aerosols and also have important implications for regional climate effects. Therefore, it is urgently needed to further explore the sources (e.g. primary versus secondary) and formation processes (e.g. mechanism of secondary formation) of phthalic acid in the polluted troposphere over China.

Acknowledgements

The authors acknowledge the Ministry of Education, Culture, Sports, Science, and Technology for financial support to perform the aircraft campaigns through Scientific Research on Priority Areas on Atmospheric Environmental Impacts of Aerosols in East Asia (no. 416, 2002–2005). The authors also acknowledge Dr. Hong Li from Chinese Research Academy of Environmental Sciences for her support and help during the aircraft measurements. This study was also supported by a grant-in-aid no. 14204055 and 24221001 from the Japan Society for the Promotion of Science (JSPS) as well as the Natural Science Foundation for Young Scientists of Jiangsu Province, China (BK20150895), and the Startup Foundation for Introducing Talent of NUIST (No. 2015r023 and 2015r019).

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1 February 2016
Available online 1 June 2016

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