



Dissolved total hydrolyzable enantiomeric amino acids in precipitation: Implications on bacterial contributions to atmospheric organic matter

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Abstract

We analyzed dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and dissolved enantiomeric amino acids in precipitation samples collected at two sites in Korea over a one-year period. The average concentrations of DOC, DON, and total hydrolyzable amino acids at Seoul (an inland urban area) were lower than those at Uljin (a coastal rural area). The different bulk compositions of dissolved organic matter (DOM) at these two sites (reflected by qualitative indicators) were mainly attributed to differences in contributing sources. The D-enantiomers of four individual amino acids (aspartic acid, glutamic acid, serine, and alanine) were ubiquitously present, with average enantiomeric (D/L) ratios of 0.34, 0.26, 0.21, and 0.61 for Seoul, and 0.18, 0.11, 0.09, and 0.31 for Uljin, respectively. The much higher D/L ratios observed at Seoul than at Uljin might result from more advanced diagenetic stages as well as higher contributions from bacteria inhabiting terrestrial environments. The C- and N-normalized yields of D-alanine in DOM of our samples were found to be comparable to literature values reported for aquatic systems, where a significant portion of DOM was suggested to be of bacterial origin. Our study suggests that bacteria and their remnants might constitute an important fraction of OM in the atmosphere, contributing significantly to the quality of atmospheric OM and its post-depositional bioavailability in the surface ecosystems.

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1. INTRODUCTION

Organic matter (OM) plays a significant role in the biogeochemical cycling of bio-reactive elements, especially carbon and nitrogen. While a labile fraction of OM is readily decomposed through microbially or photochemically mediated processes and remineralized to inorganic carbon and mineral nutrients, a considerable portion of OM (refractory) is relatively resistant to degradation and can persist in the natural environment for millennia, as in the case of marine dissolved OM (DOM) (Nagata, 2000;

Carlson, 2002). Although it is well known that the bioavailability of OM is closely linked to its chemical identity, OM in terrestrial, aquatic, and atmospheric environments remains largely uncharacterized at the molecular level (Hedges et al., 2000; Goldstein and Galbally, 2007), which greatly hinders our understanding of its origins and reaction potential. A consensus has recently been reached on the significance of bacterial activity in shaping OM quantity and quality through its substantial contributions to production, transformation and consumption of OM (Tremblay and Benner, 2006, 2009; Mou et al., 2008; Jiao et al., 2010).

A fraction of OM resides in the atmosphere and has increasingly been recognized to constitute a significant part of global biogeochemical cycles and nutrient budgets (Cornell et al., 1995; Willey et al., 2000; Duce et al., 2008;

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Jurado et al., 2008; Cape et al., 2011; Cornell, 2011; Kanakidou et al., 2012). The vast majority of atmospheric OM is removed through wet and dry deposition and ultimately returns to the Earth's surface (Hallquist et al., 2009), where it is subject to degradation and preservation processes. However, due to the limited knowledge on its composition, little is known about the bioavailability of this atmospheric OM (Avery et al., 2003; Duce et al., 2008; Kanakidou et al., 2012), resulting in large uncertainties in our understanding of its fate and biogeochemical role in the receiving ecosystems.

One of the most important compound classes that comprise atmospheric OM are amino acids, which are primarily derived from biological origins in terrestrial and marine ecosystems (Ge et al., 2011 and references therein). Owing to their low-volatile nature, amino acids in the atmosphere have been identified mainly in condensed phases by previous workers, such as aerosols, rainwater, fog droplets and dew water (Scheller, 2001; Zhang and Anastasio, 2001; Kieber et al., 2005; Mandalakis et al., 2011). Despite the growing number of studies being conducted on atmospheric amino acids worldwide, few of them deal with combined amino acids (e.g., peptide and protein), which is, however, the dominant form for amino acids present in most environments. It has been found that in the atmosphere, the concentrations of amino acids residing in combined form are generally 4–5 times higher than those in free form (Scheller, 2001; Zhang and Anastasio, 2003; Wedyan and Preston, 2008; Mandalakis et al., 2011; Samy et al., 2013). Moreover, to our knowledge, the enantiomeric isomers (L and D) of atmospheric amino acids have been scarcely investigated, except for two studies on marine aerosols by Kuznetsova et al. (2005) and Wedyan and Preston (2008). Since the D-isomers of amino acids occur almost exclusively in bacteria and particularly in the cell wall biopolymer peptidoglycan (Schleifer and Kandler, 1972; Benner and Kaiser, 2003; Kaiser and Benner, 2008), they can be used as biomarkers to trace and evaluate bacterial contributions to organic matter pool in natural environments (McCarthy et al., 1998; Kaiser and Benner, 2008).

Indeed, there is an increasing number of studies demonstrating the substantial contributions from bacteria to the OM pool in various aquatic environments, including marine waters and sediments (McCarthy et al., 1998; Dittmar et al., 2001; Ogawa et al., 2001; Perez et al., 2003; Kaiser and Benner, 2008, 2012; Kawasaki et al., 2011), freshwaters (Tremblay and Benner, 2009; Carstens et al., 2012; Kawasaki et al., 2013), and estuaries (Bourgoin and Tremblay, 2010; Fernandes, 2011). In view of the significance of bacterially derived OM in these aquatic systems, and the well-known presence of bacterial activity in the atmosphere (Sattler et al., 2001; Brodie et al., 2007; Burrows et al., 2009; Vaithilingom et al., 2012), we may expect noteworthy bacterial contributions to atmospheric OM, which have, however, not been evaluated yet. In addition to the bacterial imprint, OM is usually characterized by using various qualitative indicators, such as carbon to nitrogen atomic ratios and amino acids yields (Davis et al., 2009; Tsukasaki and Tanoue, 2010). Nevertheless, the sources, compositions, and transformation pathways

of OM in the atmosphere are highly complex and significantly different from those in other environments. OM emitted as aerosols (primary organic aerosol) into the atmosphere is mostly derived from incomplete combustion processes (i.e., fossil-fuel and biomass burning), whereas OM from biogenic sources (i.e., produced by modern plants and animals in terrestrial and aquatic systems) enters the atmosphere primarily in the gaseous phase, a fraction of which is subsequently converted to aerosols (secondary organic aerosol) (Hallquist et al., 2009). As a result, the bacterial degradation processes can take place in the surface ecosystems before the OM is emitted, as well as on the aerosols in the air and in the cloud water (Amato et al., 2007; Husárová et al., 2011) after the emission. The latter process probably occurs on a relatively short time scale, considering residence time of aerosols in the troposphere (Balkanski et al., 1993; Papastefanou, 2006). Therefore, it is generally believed that OM in the atmosphere is mainly subject to abiotic photochemical aging processes and the biological degradation is less important, although the in-situ biodegradation of OM in the atmosphere has rarely been evaluated.

In the present work, we sought to improve our understanding of OM in the atmosphere from the biogeochemical perspective by investigating precipitation samples. Total hydrolyzable enantiomeric amino acids along with the bulk parameters (i.e., carbon and nitrogen) were analyzed to examine the distributions and characteristics of OM in the dissolved fraction. In addition, the contributions from bacteria to DOM in precipitation were explored using D-amino acids as bacterial biomarkers.

2. MATERIALS AND METHODS

2.1. Study sites and sample collection

Taking into account the geographical features of Korea (i.e., a peninsula), two sites with contrasting environmental settings and anthropogenic influence levels were selected as representatives: Seoul (an inland urban area with large terrestrial input) and Uljin (a coastal rural area with large marine input). Seoul (37.5°N, 127°E) is a typical Asian metropolis situated in the midwestern part of the Korean peninsula, of which a detailed description has been given in our previous study (Yan and Kim, 2012). The other sampling site, Uljin (37°N, 129.4°E), is located on the eastern coastline of Korea and has a small population of around 52,000 inhabiting an area of 989.06 km². Its proximity to the East/Japan Sea and weak human impacts render it an area characterized by a relatively pristine atmospheric environment, which we have employed as a reference for the Seoul study in terms of marine contribution and anthropogenic impact.

The sampling campaigns were carried out on a four-storey building rooftop at the Gwanak campus of Seoul National University in Seoul from March 2012 to February 2013, and on the roof of a research facility at Korean Institute of Ocean Science and Technology in Uljin from February 2011 to January 2012, respectively. Rainwater was collected on an event basis using a home-made sampler,

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