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Anthropogenic loads and biogeochemical role of urea in the Gulf of Trieste

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HIGHLIGHTS

- The Gulf of Trieste is subjected to a large load of urea by sewage systems.
- The levels of urea in the coastal waters are not reduced compared to the past.
- Urea is a specific marker to trace the sewage loads in the coastal waters.
- Urea is not negligible compared to the other N-nutrients at the gulf scale.
- Urea largely accumulates during summer periods characterised by weak circulation.

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ABSTRACT

In order to assess the role of urea in the Gulf of Trieste, oceanographic data collected from 2002 to 2011 were analyzed together with ancillary ambient information and compared to past studies. The recent levels of urea found in these coastal waters (median = 1.1 μM N, maximum value = 19.7 μM N) are often high and similar to those reported in the early 1980s. A preliminary estimate of the external inputs indicated that this enrichment in urea is mainly due to emissions from urban sewage systems, whereas the contributions of rivers and atmospheric deposition are scarce. As a consequence, urea appears to be a reliable tracer of the diffusion of wastewaters in the coastal marine environment, more specific and sensitive than other nutrients, with a behavior that also reflects the technology of the treatment plants. The stability of urea levels over the last three decades suggests that the upgrade of wastewater treatment technologies was probably balanced by the concomitant increase of the anthropogenic pressure in the area (477,000 to 1,300,000 inhabitant equivalent).
Budget estimates on the gulf-wide scale indicate that urea (177–530 t N) is not negligible compared to dissolved inorganic nitrogen (409–919 t N) and that it can constitute up to 56% of the nitrogen available for plankton growth. A large accumulation of urea can occur during summer periods characterized by stable weather conditions and weak circulation, whereas a biologically mediated degradation to ammonium is observed in autumn in concomitance to a strong shift of the marine ecosystem toward heterotrophic conditions. These processes, together with a potential competition between phytoplankton and bacteria for the utilization of this nitrogen form, suggest that the biogeochemical role of urea should be better investigated in mid-latitude coastal zones subjected to highly variable ambient conditions and to overloads of this compound.
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1. Introduction

During the last decades, studies on urea have found their way into a wide range of clinical, industrial and environmental applications. Given that urea is the predominant final metabolite that permits the excretion of nitrogen from mammals (7.7 g l^{-1} in human urine; Udert et al., 2006), great attention has been focused on the molecular biology and the clinical diagnostics of this compound, as well as on the pharmacokinetics of its derivatives (Taylor and Vadgama, 1992; Goyal et al., 2010; Li et al., 2009; Pan et al., 2013). At the same time, many industrial processes utilize urea, while its determination in foods and beverages is important to evaluate the quality of these products and the efficiency of livestock feeding practices (Francis et al., 2002).

In the terrestrial ecosystems, urea is a widespread compound. The utilization of urea-based fertilizers has increased more than 100-fold in the past four decades and now they constitute ~50% of world nitrogen consumption (Glibert et al., 2006; Lambert at al., 2004). The inclusion of urea in several herbicides (phenylureas and sulfonylureas) and insecticides (benzoylureas) causes diffusion and transformations of their by-products in the environment (Berrada et al., 2003), resulting in concentrations of urea as high as 50 μM N in riverine systems adjacent to heavily fertilized areas (Solomon et al., 2010). Long thought to be retained in soils, consumed by crops or oxidized to nitrate, urea is also transferred from the land to the atmosphere because of wind-blown particulates, the evaporation of soil moisture and sublimation. These processes cause significant atmospheric depositions of urea over several continental regions, including the Mediterranean basin (Bo et al., 2009; Violaki and Mihalopoulos, 2011).

In the marine environment, urea is an important component of the biogeochemical cycle of nitrogen (Antia et al., 1991; Bronk, 2002; Solomon et al., 2010). Rather low levels of urea are found in the open sea (<0.3 μM N), whereas higher values (0–13 μM N) are often observed in the coastal and estuarine zones. This abundance is mainly ascribed to terrestrial and atmospheric inputs of anthropogenic origin, being the production *in situ* (0.6–20.6 nM N h^{-1}) too low to sustain high concentrations. Nevertheless, these external sources of urea have been seldom quantified as most of the coastal monitoring programs include only the determination of nutrients and total nitrogen (Glibert et al., 2005, 2006). In particular, urban and farming sewage systems are a significant source of urea. The extent to which urea reaches the marine environment depends on the efficiency of the steps of mineralization, nitrification and removal of nitrogen in the wastewater treatment plants (WWTP; Maurer et al., 2003; Udert et al., 2006).

Urea is also formed in the marine environments because of cellular metabolic processes. Heterotrophic bacteria produce urea during the regeneration of particulate/dissolved organic nitrogen. Urea is released by phytoplankton and excreted by marine organisms like micro- and macro-zooplankton, bivalve molluscs, some copepods, teleost fishes, spot prawns and blue sharks. In the benthic compartment, it can be generated by bacteria and macrofauna and released from the sediments to the water column (Antia et al., 1991; Solomon et al., 2010). Urea is also an important source of nitrogen for plankton communities. Bacteria contribute to urea uptake, but the largest uptake is often due to phytoplankton species as urea can cover 20%–50% of their total nitrogen demand (Bronk, 2002; Solomon et al., 2010). Changes in the structure of plankton communities impacted by large inputs of urea were also hypothesized: concomitant increases of urea load and of the frequency of harmful algal blooms (HABs), mostly constituted by dinoflagellates and cyanobacteria, have been reported in several coastal zones. This correlation implies that negative effects for marine organism and human health might arise due to the current global shift toward the utilization of urea fertilizers (Glibert et al., 2006).

The aim of the present study is to analyze the impact of urea in the Gulf of Trieste (GoT), a semi-enclosed coastal zone subjected to a pronounced variability of ambient conditions and to a strong anthropogenic pressure. The available historical information on urea in this area was completed with more recent oceanographic and monitoring data in order to obtain an overall picture of its potential biogeochemical role in this complex marine system. Three different aspects were considered: i) a preliminary assessment of the allochthonous inputs of urea in the GoT was inferred from experimental data and ancillary ambient information; ii) the dynamics of urea at the outfalls of the sewage systems was analyzed with respect to the physico-chemical conditions of the water column and the efficiency of treatment methods; and

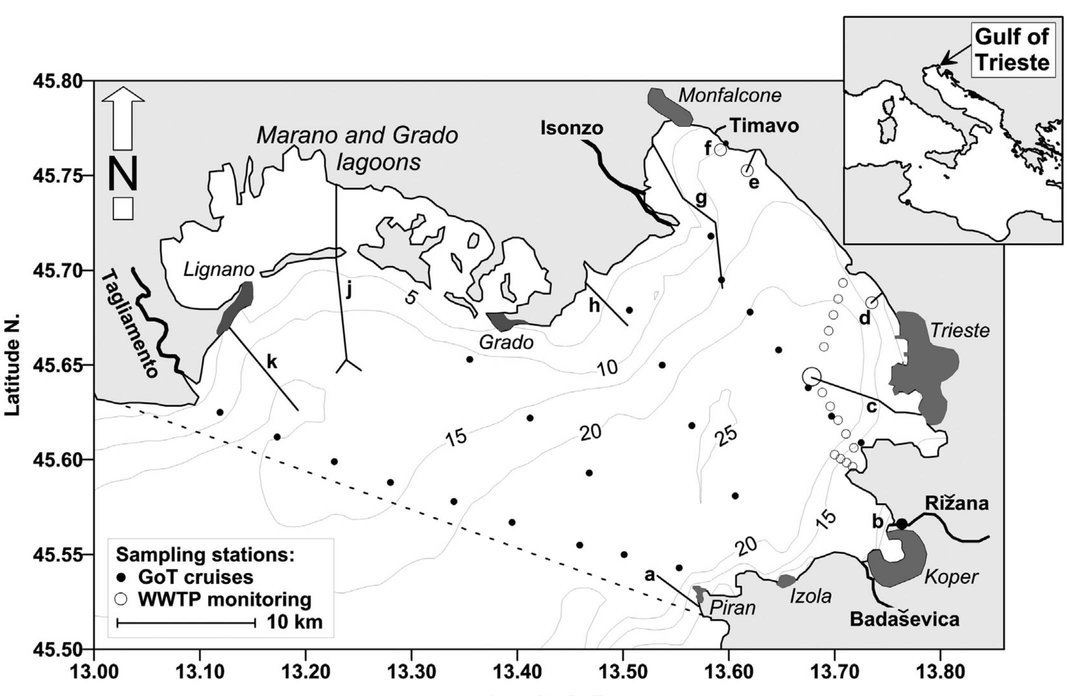

Fig. 1. Rivers and WWTP pipelines (a–k) in the considered area of the GoT (dashed line), the sampling stations of the three cruises in 2011 and of the monitoring programs in 2002–2010 are also shown.

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