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REVIEW

Megacities and Large Urban Agglomerations in the Coastal Zone: Interactions Between Atmosphere, Land, and Marine Ecosystems

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Abstract Megacities are not only important drivers for socio-economic development but also sources of environmental challenges. Many megacities and large urban agglomerations are located in the coastal zone where land, atmosphere, and ocean meet, posing multiple environmental challenges which we consider here. The atmospheric flow around megacities is complicated by urban heat island effects and topographic flows and sea breezes and influences air pollution and human health. The outflow of polluted air over the ocean perturbs biogeochemical processes. Contaminant inputs can damage downstream coastal zone ecosystem function and resources including fisheries, induce harmful algal blooms and feedback to the atmosphere via marine emissions. The scale of influence of megacities in the coastal zone is hundreds to thousands of kilometers in the atmosphere and tens to hundreds of kilometers in the ocean. We list research needs to further our understanding of coastal megacities with the ultimate aim to improve their environmental management.

Keywords Air pollution · Marine pollution · Coastal zone management · Deposition · Ozone · Harmful algal blooms

INTRODUCTION

Today over half the world's population resides in urban areas, the majority of them located in a coastal zone or a zone with distinct coastal influence. A significant fraction (9.4 %) of the world's population lives in megacities, usually defined as cities or urban agglomerations (including so-called larger urban zones) with more than 10 million inhabitants, and 16 % in cities with more than 5 million inhabitants (UN 2010). In 2009, 67 % of the megacities were located at the coast and 80 % had coastal influence [calculated from data in UN (2010), see Table 1]. By 2025, four more coastal cities are expected to be classified as megacities and the population in megacities in the coastal zone (MCCZ) is expected to increase from 220.7 million in 2009 to 301.7 million people (UN 2010). Hence, the effective management of the environment within and around megacities and of the impact of megacities on the wider environment is of critical importance to a large proportion of the world's population. The coastal ecosystem provides ecosystem services of enormous value to society (Costanza et al. 1997), services which are vulnerable to human impacts. Similarly, the atmosphere has a great self-cleaning potential (Bloss et al. 2005) but atmospheric contamination can result in considerable impact on human and environmental health. Hence, the environment of MCCZ is under multiple pressures while the habitability of cities themselves is also challenged by sea-level rise and subsidence which has been covered elsewhere (Nicholls and Cazenave 2010).

In this article, we contend that the successful environmental management of large urban centers and megacities and their environment depends critically on recognising the central importance of the megacity for the coast and the coast for the megacity. The scale of megacities and the human activity associated with them and their surrounding hinterland creates an environmental impact the management of which is particular and unique. This article arises from a SOLAS/IGAC/LOICZ fast track initiative workshop sponsored by IGBP/SCOR held in Norwich in April 2010. Sekovski et al. (2012) recently published a study on the role of environmental and social management strategies in MCCZ. However, in this article, we are focussing on physical,

Table 1 Population of urban agglomerations with 10 million inhabitants or more, 2009 and 2025 in millions

2009			2025		
Rank	Urban agglomeration	Population	Rank	Urban agglomeration	Population
1	**Tokyo**, **Japan**	36.5	1	**Tokyo**, **Japan**	37.1
2	Delhi, India	21.7	2	Delhi, India	28.6
3	**São Paulo**, **Brazil**	20.0	3	**Mumbai (Bombay)**, **India**	25.8
4	**Mumbai (Bombay)**, **India**	19.7	4	**São Paulo**, **Brazil**	21.7
5	Ciudad de México (Mexico City), Mexico	19.3	5	*Dhaka*, *Bangladesh*	20.9
6	**New York-Newark**, **United States**	19.3	6	Ciudad de México (Mexico City), Mexico	20.7
7	**Shanghai**, **China**	16.3	7	**New York-Newark**, **United States**	20.6
8	**Kolkata (Calcutta)**, **India**	15.3	8	**Kolkata (Calcutta)**, **India**	20.1
9	*Dhaka*, *Bangladesh*	14.3	9	**Shanghai**, **China**	20.0
10	**Buenos Aires**, **Argentina**	13.0	10	**Karachi**, **Pakistan**	18.7
11	**Karachi**, **Pakistan**	12.8	11	**Lagos**, **Nigeria**	15.8
12	**Los Angeles-Long Beach-Santa Ana**, **United States**	12.7	12	Kinshasa, Democratic Republic of the Congo	15.0
13	*Beijing*, *China*	12.2	13	*Beijing*, *China*	15.0
14	**Rio de Janeiro**, **Brazil**	11.8	14	**Manila**, **Philippines**	14.9
15	**Manila**, **Philippines**	11.4	15	**Buenos Aires**, **Argentina**	13.7
16	**Osaka-Kobe**, **Japan**	11.3	16	**Los Angeles-Long Beach-Santa Ana**, **United States**	13.7
17	*Al-Qahirah (Cairo)*, *Egypt*	10.9	17	*Al-Qahirah (Cairo)*, *Egypt*	13.5
18	Moskva (Moscow), Russian Federation	10.5	18	**Rio de Janeiro**, **Brazil**	12.7
19	Paris, France	10.4	19	**Istanbul**, **Turkey**	12.1
20	**Istanbul**, **Turkey**	10.4	20	**Osaka-Kobe**, **Japan**	11.4
21	**Lagos**, **Nigeria**	10.2	21	**Shenzhen**, **China**	11.1
			22	Chongqing, China	11.1
			23	**Guangzhou**, **Guangdong**, **China**	11.0
			24	Paris, France	10.9
			25	**Jakarta**, **Indonesia**	10.8
			26	Moskva (Moscow), Russian Federation	10.7
			27	Bogotá, Colombia	10.5
			28	**Lima**, **Peru**	10.5
			29	Lahore, Pakistan	10.3

Coastal agglomerations are in bold, those with coastal influence in italics. Data from UN (2010)

chemical, and biological processes in the atmosphere and oceans and their interactions which lead to MCCZ having some unique characteristics which require unique strategies. We cover atmospheric processes in somewhat greater detail due to the importance of air quality for human health and the scarcity of investigations of the role of the atmosphere as recipient and transfer vector for anthropogenic pollutants into coastal ecosystems.

In our discussion, we include large coastal agglomerations as the problems and challenges are the same as for megacities. The abbreviation of MCCZ will refer to both.

KEY INFLUENCE FACTORS FOR MCCZ

We begin our discussion of key influence factors for MCCZ by considering physical atmospheric processes followed by a discussion of relevant changes to atmospheric composition and their implications and processes in the coastal water column including biological effects in the marine ecosystem and feedbacks within the system especially to the atmosphere. This leads to a discussion of the current challenges for MCCZ. A schematic of the main processes is provided in Fig. 1.

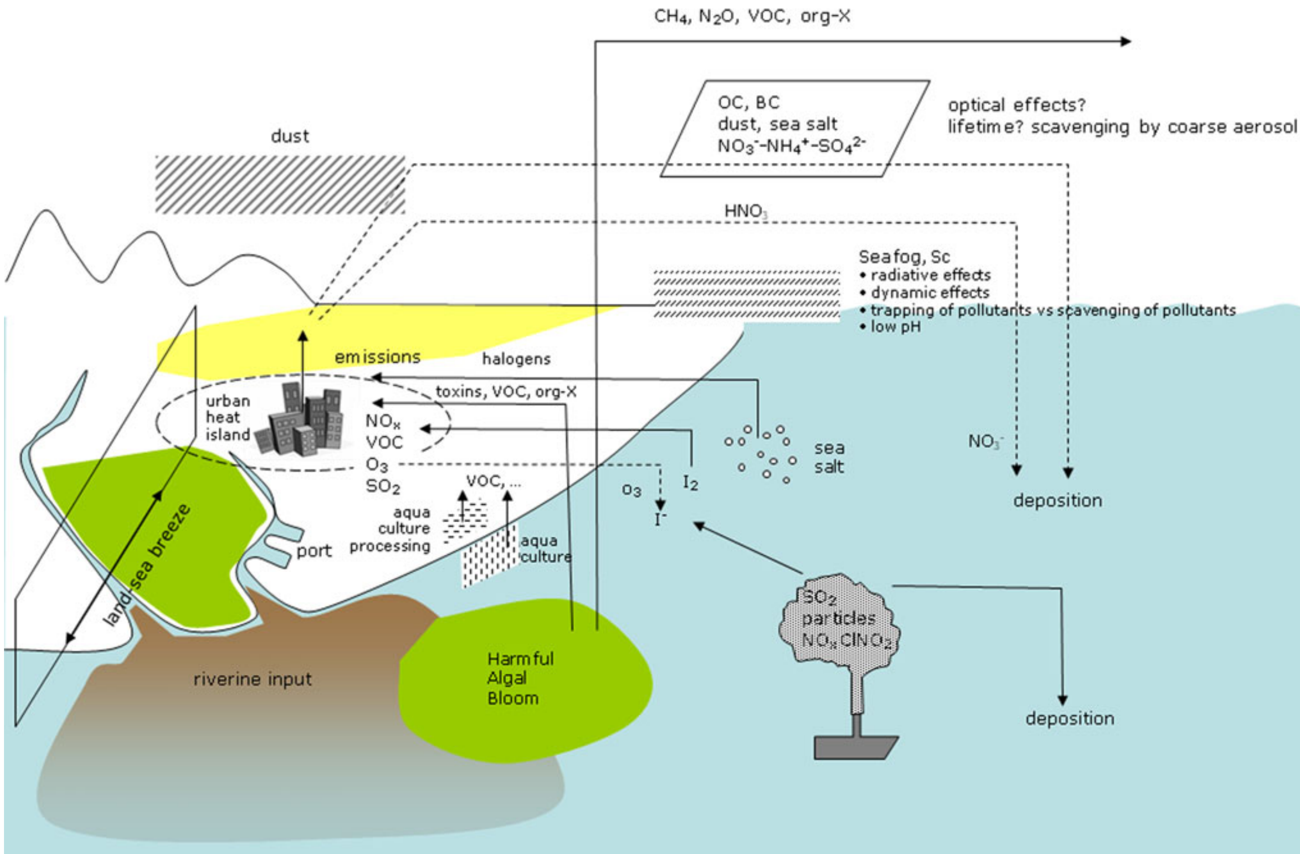

Fig. 1 Schematic depiction of the main processes and feedbacks in MCCZ. Details see text. *OC* organic carbon, *BC* black carbon, *VOC* volatile organic compounds, *org-X* organic halogens compounds

Atmospheric Physics and Climatic Links

The existence of megacities modifies the local and regional climate with effects that can become global. In this section, we highlight particularly the impacts of megacities on boundary layer circulation in and around megacities that profoundly affect local air quality, the local hydrological cycle and impact the local and regional radiation balance. These are treated as separate issues but in reality are closely coupled because of the relevance of circulation and precipitation for aerosol concentrations and radiation balances.

Atmospheric Circulation and Mixing

The microclimate as well as mesoscale (up to a few hundred km) atmospheric circulations and boundary layer dynamics in and around MCCZ are complex due to a variety of different processes and two-way interactions. The most important factors that are specific for MCCZ are urban heat island (UHI) effects, the land–sea breeze and its modification in the MCCZ, as well as effects caused by complex local geography and the buildings themselves within the megacity.

Megacities have strong UHIs, due to differences in surface properties and waste heat from anthropogenic activity. The effects of UHI can be substantial. Anthropogenic heat fluxes for megacities can be very high: up to 50–500 W m^{-2}, similar to solar heating, but locally reaching 1600 W m^{-2} (e.g., Tokyo in winter time, Ichinose et al. 1999). Importantly, the UHI effect is not limited to daytime, unlike solar heating. Hence, megacities can be warmer than surrounding rural environments by up to 10°C (Hidalgo et al. 2008). This heating not only impacts the local environment directly but also profoundly affects the regional air circulation, which is also modified by the density and height of buildings. For MCCZ this includes changes to the land–sea breeze which is a diurnal change in on-shore to off-shore circulation caused by differential heating of the land and the ocean. The land–sea breeze leads to mixing of air of urban and marine origin which can influence air quality. MCCZ in general have two opposing effects on a sea breeze: the enhanced surface drag, caused by buildings etc, can lead to a slowing of the inland propagation of the sea breeze front (e.g., Thompson et al. 2007); and the UHI effect increases the temperature in the city and therefore increases the temperature difference between land and sea which can lead to a deeper penetration of the sea breeze into the MCCZ (e.g., Freitas et al. 2007). Sea breezes can also modify the UHI pattern by reducing, delaying, or displacing it inland (e.g., Gedzelman et al. 2003). Therefore, the UHI and sea-breeze circulations should be regarded as interactive processes with a delicate balance between them (e.g., Mestayer et al. 2005). MCCZ, such as New York and Tokyo, often possess multiple dense urban cores dictated by geography, resulting in highly irregular distributions of building heights and heating footprints (Pullen et al. 2008). Colle et al. (2003) showed that the complex coastal geometry of the New York metropolitan area supports the development of multiple sea-breeze boundaries. Sea-breeze fronts can travel substantial distances inland (up to 200 km) and when combined with the strong UHI effect of an inland megacity, the resulting extended circulation that connects coast and the megacity can turn inland megacities into effectively a MCCZ (e.g., Dhaka, São Paulo).

Sea breezes are important because of their impact on air quality. If a sea-breeze pattern is present for several days a "see-saw" pattern can lead to drastically decreased air quality as the same air mass is "trapped" in this circulation, leading to build-up of emissions and reaction products, for example ozone (Tie et al. 2009).

Many MCCZ are located near mountains where slope/mountain circulation can further complicate the picture (e.g., Lima, Tokyo, Los Angeles) by interacting with the UHI and sea-breeze circulations. In the Los Angeles area, the presence of high mountains leads to a reverse flow at greater heights resulting in elevated pollution layers (Lu and Turco 1996). This complex and anthropogenically modified physical environment plays a critical role in the dispersion (or lack of it) of emissions from the MCCZ. Istanbul is affected by mountains as well as the complicated topography often leading to two sea-breeze cells over the European and the Asian part of the city which merge aloft. Strong accumulation of pollution is observed in sea-breeze events (see Kanakidou et al. 2011, and references therein). In regions with coastal upwelling, MCCZ are often affected by sea fog or low cloud decks (see Fig. 1, e.g., Lima and Los Angeles), which can also trap air pollution in the city as well as reducing incoming and outgoing radiation fluxes and changing local atmospheric dynamics. On the other hand, some pollutants might be scavenged by the fog/cloud droplets.

Thus, it is clear that regional air flow can influence the impact of emissions, but in megacities and especially in MCCZ the presence of the city profoundly affects the air flow and hence the distribution of pollutants as well as the microclimate/temperature. These various processes and the complex feedbacks between them therefore affect the habitability of the MCCZ.

Aerosol Sources and Radiative Forcing

Anthropogenic activities lead to the emission and production of very large amounts of aerosol particles. The enhanced aerosol amounts over megacities are not only due to enhanced emissions of primary particles (i.e., directly emitted particles) but also due to production of secondary aerosol (i.e., those formed in the atmosphere from gaseous precursors). MCCZ contribute 9.7 % to global black carbon emissions (based on data from Doering et al. 2009). In general, the effects of anthropogenic particle sources are more pronounced in regions with less pollution in the background air, which is relevant for coastal regions with lower particle loadings in marine air.

New particle formation has been observed in and downwind of megacities (e.g., Yue et al. 2009). The precursors for new particle formation (sulfuric acid, ammonia, and organics) have strong sources within megacities (e.g., Yue et al. 2009). Very strong new particle formation events in coastal regions have been shown to be due to biogenic release of iodine-containing gases, especially by macroalgae in intertidal areas (O'Dowd and Hoffmann 2005, see "Marine ecosystem responses" section). These events can occur under polluted conditions as well (McFiggans et al. 2010). The interaction of these different types of nucleation events has not been studied so far, but could lead to important influences on the unique atmospheric chemistry of MCCZ.

The aerosol in the atmosphere of megacities is a complex mixture containing components that are efficient at scattering solar radiation and others that absorb radiation. This so-called mixing state is highly variable in MCCZ and strongly dependent on local wind patterns which determine the relative importance of local pollution and long-range transport (Cheng et al. 2006).

The integral of the vertical column of aerosol can be quantified with the so-called aerosol optical depth. Ramanathan et al. (2007) found that satellite-determined aerosol optical depths in most of the world's megacities exceed 0.2 and can be as high as 0.8 on annual average compared with <0.1 over the Pacific Ocean and <0.2 over the North Atlantic (Kaufman et al. 2002). This results in a reduction of radiation reaching the surface (atmospheric dimming) which was estimated to be -20 to -60 W m^{-2} compared to an increase of radiation absorbed in the atmosphere (and hence heating) of $+20$ to $+40$ W m^{-2} (Ramanathan et al. 2007). This can change the thermal stability of the atmosphere and result in dramatic changes to the circulation patterns, which can impact regions over hundreds of kilometers including contaminant transport, cloud properties, and precipitation patterns and amounts (Chung et al. 2010) to monsoon circulations (e.g., Ramanathan et al. 2005) and alter the radiative forcings over the surrounding oceans by 10–30 % over areas extending over several thousand of kilometers (Guttikunda et al. 2002). This in turn has the potential to reduce the input of solar radiation into the oceans which can result in a decrease in surface evaporation, with important implications for regional climate (e.g., Ramanathan et al. 2007).

Hydrological Cycle

Megacity–coastal interactions may also impact the hydrological cycle through changes to the occurrence of fog, clouds, and precipitation in and around megacities and coastal areas. These changes are linked to alterations in circulation patterns (see above), and increases in the concentration of aerosol particles and are within the context of the potentially large humidity gradients that exist between the air over the ocean and inland.

The presence of aerosol particles, particularly cloud condensation nuclei (CCNs), profoundly impacts clouds, precipitation, and deposition and these effects are likely to be very strong in MCCZ due to the strong primary and secondary particle sources. An increase in CCN number may lead to more but smaller cloud droplets resulting in a higher cloud albedo, increasing cloud longevity and likely reducing precipitation (e.g., Stevens and Feingold 2009). On the other hand, so-called giant CCN (processed dust, sea salt, some anthropogenic particle classes) may enhance precipitation and also scavenge gases and smaller particles from the atmosphere (Rosenfeld et al. 2002) and provide a source of nutrients and contaminants to (coastal) oceans. However, the role of nonlinear feedbacks and "buffer" mechanisms in the aerosol–cloud-climate system were pointed out, leading to significant uncertainties and gaps in our knowledge (e.g., Stevens and Feingold 2009).

Several studies have shown that an UHI can have a significant influence on mesoscale circulations and resulting convection, e.g., warm seasonal rainfall was found to increase by 7–25 % within and 50–75 km downwind of megacities (Ohashi and Kida 2002; Shepherd 2005). There is increasing evidence that MCCZ, such as Tokyo and Houston, can influence weather (rainfall, lightning, etc.) through complex urban land use–weather–climate feedbacks (e.g., Ohashi and Kida 2002). Hence, rainfall patterns and location may change in and around a MCCZ compared to an uninhabited coastline, affecting local agriculture and fresh water supply for the city. The impacts of extreme precipitation events including flash floods may be much worse in a MCCZ because of the effects of the hardpaving and roofs providing little delay on water flows.

Atmospheric Composition: Air Quality and Greenhouse Gases

Overview

The composition of the atmosphere affects the habitability of MCCZ (human health, food production) and the ecological health of its surroundings both directly via air quality and via the emissions of greenhouse gases affecting climate (see also Fig. 1). Air pollution has long been recognized as a serious problem and a succession of air quality problems according to the development status of a megacity with a peak at intermediate development has been suggested (Mage et al. 1996). A recent ranking of global megacities according to a number of air quality parameters was published by Gurjar et al. (2008) to name but one of the many papers dealing with megacity air quality issues.

Air Quality

Of main concern for air quality are aerosol particles, ozone, NO_x and SO_2. The health impact of aerosol particles depends on their size and composition and aerosol can lead to detrimental effects already at low concentrations. Megacity emissions reflect the large range of emissions from urban and industrial sources within and around the city. Specifically for MCCZ, emissions from ships in urban waterways, ports, and upwind of MCCZ can be very significant additional pollution sources both for gases and particles (Kanakidou et al. 2011, see also Fig. 1). For example, Istanbul is divided by the Bosporus which is a major waterway and 17.6 and 9.5 % of SO_2 and NO_x emissions in this city, respectively, are from shipping (Kanakidou et al. 2011).

Interestingly, a first global three-dimensional modelling study (Butler and Lawrence 2009) accounting for complex, nonlinear responses in ozone and nitrogen chemistry, found both beneficial and negative impacts on air quality in megacities. They showed that compared to the fraction of anthropogenic emissions from megacities to the global total emissions many effects on local as well as global surface air quality, radiative forcing, and atmospheric oxidation capacity are disproportionately smaller than the proportion of anthropogenic emissions due to megacities. On the other hand, effects on reactive nitrogen, eventually impacting deposition patterns to the sea downwind of the megacities (see below), are disproportionally larger than expected.

The air quality within a megacity is influenced by areas upwind as well as by activities within the megacity which has important implications for air quality management. In particular, several MCCZ especially in East Asia (for example, Seoul, Fukuoka, Tokyo and in recent years, Shanghai) are influenced by the inflow of soil dust aerosol which interacts with urban and regional pollutants. In the cities, this leads to a reduction in visibility and additional respiratory problems but, through uptake of gaseous air pollutants such as nitrogen oxides and SO_2 by dust, it can lead to a reduction in pollution (Zhu et al. 2010). As most dust particles are relatively large their lifetime is relatively short and these modified dust particles are deposited within the city and to the ocean off MCCZ (see "Marine ecosystem responses" section). Hence, the role of aerosol in air quality is strongly influenced by their size distribution. Trace metals such as arsenic, zinc, and selenium are released in many anthropogenic activities (e.g., fossil fuel combustion and cement production) and can become associated with dust (Chester et al. 1993b). Deposition of this material to the coastal ocean provides another source of contaminants to the ocean.

Another unique feature associated with MCCZ is the inflow of sea salt aerosol into coastal cities and its mixing with urban emissions. Subsequent deposition on buildings and structures can enhance corrosion and also lead to damage of cultural heritage. Furthermore, reactive halogens are released from sea salt aerosol (see Box, "Halogen chemistry"). Anthropogenic nitric acid is preferentially taken up on coarse sea salt particles, enhancing nitrogen deposition to the ocean (Song and Carmichael 1999, also see below). In addition for their role for the adsorption of nitric acid, dust and seasalt particles can also take up organic nitrogen compounds (Nakamura et al. 2006).

Ozone

Ozone (O_3) near the surface acts as a pollutant, it is harmful to humans, materials, and vegetation and can reduce crop yield and it is a short-lived greenhouse gas in the troposphere. Therefore, it is one of the main target compounds for air quality management. On the other hand, it plays a very important role for the so-called oxidation power—or "self-cleansing" capability—of the atmosphere, by reacting with chemicals and producing the highly reactive OH radical, which ensures the chemical removal of pollutants from the air. In the troposphere, O_3 is only produced by catalytic reaction cycles involving sunlight, volatile organic compounds (VOCs), and nitrogen oxides (NO_x); and in the suburbs and the outflow of the megacities strong O_3 production occurs because high concentrations of these precursors (VOCs, NO_x) are emitted. Furthermore, ship traffic is an additional important source of NO_x. Halogen compounds can be released from sea spray aerosol and depending on the conditions can lead to enhanced ozone production or destruction, for details (see Box "Halogen chemistry"). The fact that MCCZ are in close proximity to the oceans fundamentally alters the atmospheric chemical cycles within MCCZ (due to sea salt being transported into the MCCZ) but also in air masses that are transported from the megacity out over the ocean. Thus, ozone management strategies must consider these marine–atmospheric interactions if they are to succeed.

In MCCZ—compared to unpopulated coastal regions—we expect O_3 production to be higher in the city suburban regions and near-city outflow. However, the net effect of O_3 production and destruction in the outflow further away from the city remains unclear and will likely depend on the existing chemical and meteorological conditions. The impacts can be present in the outflow for several days (see Box "Halogen chemistry") which translates to transport distances of several hundred kilometers and possibly even thousands of kilometers.

Greenhouse Gases

The large-scale use of energy within megacities means that they are inevitably large sources of greenhouse gases (including CO_2, CH_4, N_2O, and O_3); they are responsible, for example, for 12 % of the global CO_2 emissions (Collins 2009). But they also offer locations where mitigation strategies might be concentrated (see also "Discussion" section). In addition to energy sources, greenhouse gases, especially nitrous oxide (N_2O) and methane (CH_4), are released from water treatment, landfill sites, some industrial processes, low oxygen zones of estuaries and coastal areas etc. (e.g., Hashimoto et al. 1999), all of which are concentrated in MCCZ. The combined effects of pressures described in the "Marine ecosystem responses" section can make these limited areas relatively important sources of CH_4 and nitrous oxide (Nirmal Rajkumar et al. 2008). Ozone and CH_4 are the only greenhouse gases destroyed within the troposphere; the chemistry of O_3 specific to MCCZ was discussed above. The key chemical sink for CH_4 is the reaction with the OH radical but chlorine atoms react very quickly with CH_4 as well, so that the photochemical sink of CH_4 might also be affected by halogens (see Box on "Halogen chemistry"). Recent measurements in the Pearl River Delta showed that OH was 3–5 × higher than expected from known chemistry implying large gaps in our knowledge (Hofzumahaus et al. 2009). Hence, the impacts of MCCZ on greenhouse gas fluxes, their concentrations and the associated climate forcing need to be better evaluated, particularly for CH_4.

Box: Halogen Chemistry

Chlorine compounds are known to be the main reason for the destruction of O_3 in the stratosphere. However, chlorine atoms also react very quickly with VOCs, thereby producing organic peroxy radicals which in the presence of NO_x lead to O_3 formation. Nitryl chloride ($ClNO_2$) is formed in the reaction of nitrogen oxides on chloride-containing aerosol (such as sea spray aerosol, see Fig. 2) and has been measured in large amounts in the outflow of Houston, TX, USA (Osthoff et al. 2008). MCCZ as well as ship plumes are a "perfect" combination of pollutants and sea salt (von Glasow 2008) so one would expect this chemistry (and other reactions leading to chlorine release from sea spray) to be active both in the inflow and outflow of MCCZ. In the outflow, the large amounts of acidity lead to further release of chlorine and also bromine from sea salt aerosol. Chorine atoms react very quickly with the greenhouse gas CH_4 and thereby reduce its lifetime (see Fig. 2).

Due to the short lifetime of NO_x and the lack of strong marine sources of NO_x other than shipping, the atmospheric boundary layer over most ocean regions is a net sink for O_3. However, the outflow of air from MCCZ onto the ocean can transform O_3 depleting regions into O_3 producing regions. In addition, the high levels of gas-phase acids (organic acids, HNO_3, H_2SO_4) in the outflow of MCCZ will lead to enhanced chlorine and bromine release from sea salt aerosol. Under low-NO_x conditions both lead to the destruction of O_3. The multiphase cycling of halogens ensures a long lifetime (order of several days) of the gaseous halogen species even after the NO_x and acids have been removed from the air (e.g., Lawler et al. 2009).

In addition, in the outflow of MCCZ the deposition of O_3 onto the ocean surface followed by photosensitized reaction can lead to the release of iodine and chlorine compounds (e.g., Martino et al. 2009, see Fig. 1) which can react quickly and effectively to destroy O_3, resulting in a negative feedback on O_3.

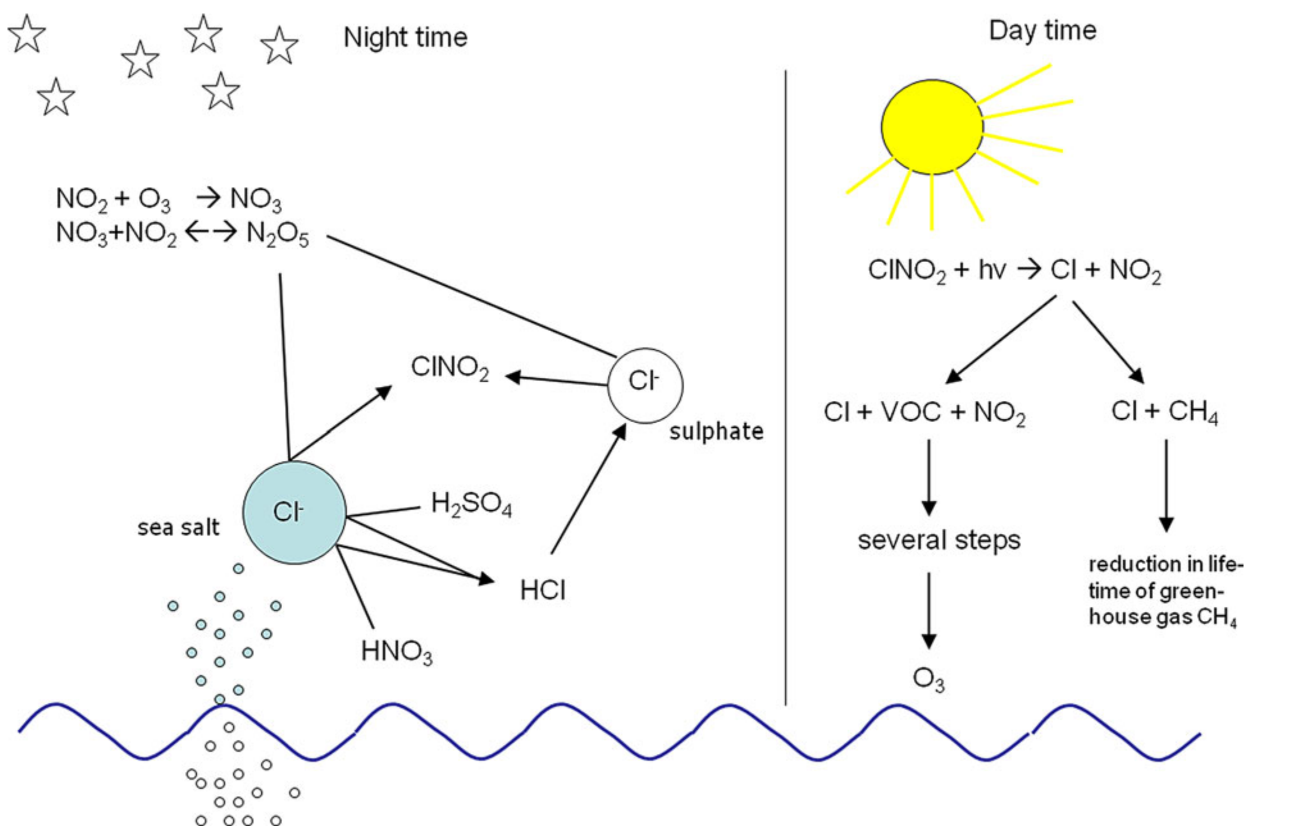

Fig. 2 Schematic of the multiphase reactions leading to the production of $ClNO_2$ at night. During daytime $ClNO_2$ can lead to O_3 formation and contribute to the reduction of the lifetime of the greenhouse gas CH_4. For details see boxed text and Osthoff et al. (2008). Figure modified from von Glasow (2008)

Marine Ecosystem Responses

Overview

Emissions from megacities can impact coastal ecosystems and potentially compromise the many ecosystem services they provide. The loss of intertidal, salt marsh, and mangrove habitats to provide environmental services such as coastal defense, carbon/nitrogen storage, and fisheries is a likely consequence of megacity development in coastal areas where pressure for land is acute and future sea-level rise will exacerbate this problem (Nicholls and Cazenave 2010). Emissions from the coastal zone can also impact on air quality within MCCZ and in air advecting from the megacity over the ocean. All of these impacts are driven by the effects of MCCZ emissions and deposition of toxins and nutrients in coastal waters on marine ecosystems and particularly on primary production. We therefore begin by considering the nature of key inputs, then discuss their effects on algal productivity in general before considering the special case of harmful algal blooms. Finally, we consider the feedbacks arising from the emissions of marine biogenic trace gases.

Input of Nutrients and Pollutants

An important by-product of human activity and waste disposal in MCCZ is an increase in the flux of the key phytoplankton nutrients, fixed nitrogen and phosphorus, to coastal waters. The impacts of such discharges are known, but the key point about MCCZ is that the localized scale of discharge relative to local dilution capacity is often particularly large with the potential for nonlinearities in the ecosystem response (Middleburg and Levin 2009).

Phosphorus has essentially no volatile phase, so most of the enhancement of phosphorus discharge is via the fluvial system. In the case of nitrogen, the situation is more complex and inputs arise from both NO_x emissions from fuel combustion and ammonia emissions from waste disposal and intensive agriculture. There are also emissions of nitrogen via fluvial systems from activities such as waste disposal, as well as from agriculture and the deposition of atmospheric emissions within the fluvial catchment. While in terrestrial systems atmospheric nitrogen transport occurs via gaseous transport of nitric acid and ammonia gas and ammonium nitrate aerosol, in the coastal environment, the interactions of nitric acid and seasalt form coarse mode aerosol sodium nitrate (and potentially some other substances) which is subject to relatively rapid deposition due to its large particle size. Hence, one feature of the interaction of megacities and the coastal zone is enhanced deposition of nutrients to coastal waters (Spokes and Jickells 2005), in addition to riverine inputs. In many coastal regions, downwind of megacity conurbations atmospheric nitrogen deposition inputs are comparable to fluvial inputs [e.g., North Sea (Spokes and Jickells 2005); East China Sea (Uno et al. 2007)]. The overall effect of atmospheric deposition of nitrate and sulfate is also to increase acidification pressure on marine waters (Doney et al. 2007), although it has been argued that the effects are rather small (Hunter et al. 2011). Industrial activities and shipping within megacities and their vicinity can also result in the discharge of trace metals and potentially toxic organic compounds (Islam and Tanaka 2004). The atmospheric transport of these contaminants is relatively efficient compared to fluvial transport due to estuarine trapping of fluvial inputs (e.g., Church et al. 1988) or low fluvial flow due to limited precipitation and hence in a region such as the North Sea or the East Mediterranean, atmospheric inputs may rival fluvial inputs (e.g., Chester et al. 1993a; Krom et al. 2004).

On a global basis, atmospheric nitrogen deposition to the open ocean seems to provide a modest stimulus to primary production (Duce et al. 2008), but in coastal systems the effects are somewhat different. Increasing fluxes of nitrogen and phosphorus lead to increases in primary production rates in coastal ecosystems with various deleterious effects (Conley et al. 2009), which we consider below. The impacts of trace metals and toxic organic compounds are less certain, although they can lead to accumulation of some metals and toxins in biota, damaging the biota and their potential as a food resource (Islam and Tanaka 2004; Sekovski et al. 2012). The potential for environmental damage from atmospheric inputs of copper has recently been discussed (e.g., Paytan et al. 2009). Copper inputs have been linked specifically to changes in phytoplankton speciation (Moffett et al. 1997) and high local concentrations can arise particularly from antifouling paints from shipping. In addition, in the recent past, the release of the antifouling agent tributyl tin TBT from shipping has caused significant environmental damage (Islam and Tanaka 2004; Sekovski et al. 2012), emphasizing the multiple stresses imposed on coastal zones.

In the following, we highlight three particular ecosystem responses to these inputs that we suggest are particularly important for MCCZ.

Nutrients and Hypoxia

The impacts of enhanced fluvial and atmospheric nutrient fluxes will act together to increase algal productivity and potentially the overall productivity of the system and food production. However, there are also potential deleterious impacts including changes in algal species composition and problems arising from the bacterial decomposition of the increased biological carbon load (Jickells 1998). One effect of this can be the development of low oxygen (hypoxia), a phenomenon that appears to be increasing worldwide (Middleburg and Levin 2009). However, it should be noted that the impact of enhanced nutrient inputs on a particular coastal sea is highly dependent on the physical environment, as illustrated by contrasting the Baltic and North Sea, adjacent large coastal seas receiving large atmospheric and fluvial nutrient inputs from large urban zones of Northern Europe. The Baltic is subject to chronic hypoxia (Conley et al. 2009) while the North Sea has until recently shown little evidence of hypoxia (Queste et al. 2012), with the difference attributable in large part to the short residence time of waters within the North Sea relative to flushing with open North Atlantic waters, compared to the Baltic. The estimated residence time in the Baltic is more than 20 years with slow vertical mixing (Meier et al. 2006), whereas in the North Sea it is about 1 year with seasonal or shorter time scale vertical mixing of the water column (Jickells 1998). The more rapid mixing in the North Sea disperses inputs and reoxygenates the water more effectively compared to the Baltic.

Hence, it is impossible to generalize the impacts of enhanced nutrient fluxes as the physical environment of the coastal system adjacent to the megacity will be a key factor. Hypoxia has a very direct effect on ecosystems including the loss of benthic fauna and hence fisheries, potentially affecting biodiversity, tourism, and food supply in the coastal seas around megacities (Middleburg and Levin 2009). Hypoxic pressures are likely to increase around megacities with increasing temperatures which tend, at least seasonally, to lead to stronger stratification and therefore limiting vertical mixing resulting in reduced dissolved oxygen concentrations, in addition to increased bacterial breakdown of organic matter as water temperatures rise. There can then be a positive feedback with hypoxia in sediments increasing some nutrient fluxes and stimulating further productivity (Middleburg and Levin 2009).

Harmful Algal Blooms

The principles of nutrient enhancement encouraging high biomass algal blooms (eutrophication) and consequent deterioration of aquatic ecosystems are now reasonably well understood. However, in addition to the general issue of eutrophication pressures, a small number of algal species under certain circumstances can be toxic to other marine species or even to humans. These are referred to as harmful algal blooms (HABs, see Figs. 1, 3) and are another key issue that potentially couples coastal systems and megacities. Whilst there is no direct evidence of nutrient enhancement encouraging the biogeographical expansion of toxin-producing plankton, more subtle alterations in nutrient conditions contribute to the development of toxic episodes such as domoic acid production by *Pseudo-nitzschia* which seems to produce the toxin under most nutrient limitations, with the exception of nitrogen (e.g., Hagström et al. 2011). Of greater relevance to megacities are modifications in the coastline which can arise from the developments relating to commercial (docks), recreational (marinas), or other activities. These can alter circulatory patterns and locally influence stratification, which can encourage blooms of toxin- producing phytoplankton (Gentien et al. 2008). Inlets created can have low flushing which will promote the development of dinoflagellates, and chronic infestations will arise for species which have a dormant sedimentary cyst stage in their life cycle, such as *Alexandrium*.

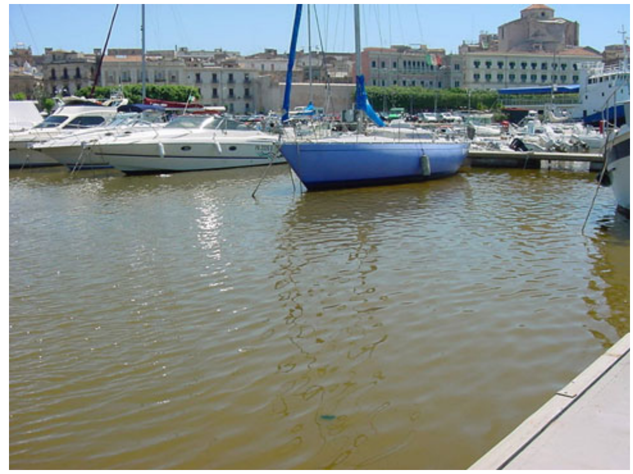

Fig. 3 An exceptional plankton bloom with cell densities high enough ($\leq 10^6\ L^{-1}$) to cause discolored water in the marina of Syracuse Harbor, Sicily on the Mediterranean coast. The bloom comprised the toxin-producing dinoflagellates *Alexandrium minutum* and *Lingiulodinium polyedrum* (Photo courtesy Mariagrazia Giocobbe). Harmful blooms of this nature will become more common as we continue to modify the coast to our own purpose

Blooms of several species from this genus produce highly potent neurotoxins called saxitoxins and occur annually in bays and harbors which are not well flushed (e.g., Ní Rathaille and Raine 2011). The impacts of blooms of toxin-producing phytoplankton on aquaculture such as harvest closures of contaminated shellfish, fish kills etc. are well established (Anderson et al. 2000). Less well understood is their effect on the marine ecosystem. In addition, the deleterious effect on human populations caused by potent neurotoxins escaping into the atmosphere via aerosol cannot be ignored. Brevetoxin-containing aerosol resulting from red tides of *Karenia brevis* along the Florida coast are known to cause harmful respiratory effects (Fleming et al. 2007) and recent similar events in the Mediterranean caused by palytoxins produced by *Ostreopsis* have been documented (Brescianini et al. 2006).

Modifications in the coastal habitat around megacities could further encourage similar episodes.

Trace Gas Emissions by Marine Biota

In addition to the greenhouse gases discussed above, the coastal zone is a source of a wide range of other climatically active biogenic gases including dimethyl sulfide (DMS), the volatile halogens, non-methane hydrocarbons (NMHC) such as ethene and isoprene and oxygenated volatile organic compounds (OVOC) including acetone and methanol (e.g., Liss 2007). Changes in coastal ecosystem composition and functioning associated with megacity development are likely to alter biogenic trace gas emissions with resultant impacts on atmospheric acidity, aerosol formation, and ozone cycling. Predicting the impacts of environmental change on emissions is not straightforward as biogenic gas concentrations are a complex function of a variety of production and loss processes the rates of which vary between biological species (Carpenter et al. 2000) and are subject to environmental controls (e.g., Hughes et al. 2011). Whilst dedicated case studies and greater process understanding will be needed to assess how megacity development will impact emissions, some generalisations can be made for specific scenarios.

Studies have shown that these marginal coastal zones are a source of volatile halogens (I_2, CH_2I_2, CH_3I, CH_3Cl, $CHBr_3$) to the atmosphere due to production by seaweeds (Carpenter et al. 2000; Küpper et al. 2008) and salt-marsh plants (Manley et al. 2006). Disturbance or pollution of these coastal environments is likely to alter the supply of volatile halogens to the local atmosphere with potentially important implications for ozone cycling (Vogt et al. 1999) and secondary aerosol formation (McFiggans et al. 2004), see also "Atmospheric composition: air quality and greenhouse gases" section.

Another potential consequence of megacity development that would be expected to have a major impact on biogenic trace gas emissions from the MCCZ is the more frequent occurrence of high biomass algal blooms. For example, the occurrence of mass blooms of green seaweeds known as "green tides" has increased over the last four decades as a result of nutrient overloading and aquaculture expansion (Morand and Merceron 2005). It is anticipated that the extremely high seaweed biomass levels (up to 10^2 kg wet weight m^{-2}, Morand and Merceron 2005) associated with these events would result in large pulses in the release of a range of biogenic gases including volatile halogens (Carpenter et al. 2000), DMS (Van Alstyne 2008), and NMHC (e.g., Broadgate et al. 2004) during active growth. The co-emission of these different trace gases could have wide-ranging impacts on atmospheric chemistry. In addition, "green tide" decay is known to be associated with the production of noxious gases such as hydrogen sulfide (H_2S) with potentially important implications for human health during clean-up and disposal (Morand and Merceron 2005).

Sea weed from aquaculture or massive algal blooms drying on land may lead to the release of halogenated and other trace gases (such as H_2S) with potential implications for health, tropospheric, and stratospheric chemistry and climate. The magnitude of this has yet to be quantified.

An alteration in biogenic trace gas emissions from the coastal zone in response to megacity development is clearly a route by which anthropogenic activities could indirectly impact atmospheric chemistry, but further research is needed to determine the nature and magnitude of the effects.

DISCUSSION

Scale of Influence

What is the scale of the environmental impacts specific to MCCZ? This seemingly simply question can be answered on very different levels. The influence of the megacity on the atmosphere encompasses the outflow over the ocean where effects are discernible for several hundred or even thousand kilometers (Lawrence and Lelieveld 2010). Deposition onto the ocean not only can cause changes in trace gas fluxes from the ocean to the atmosphere which can extend the "reach" of MCCZ even further but can also affect air quality in MCCZ. For long-lived greenhouse gases emitted by the megacity this influence becomes a global one. Air being transported into the MCCZ can be influenced by upwind natural and anthropogenic sources. East Asian MCCZ are for example influenced by European air pollution and desert dust, both stemming from regions thousands of kilometers away, whereas the air quality in Los Angeles can be affected by Asian pollution and dust that was transported across the Pacific (Uno et al. 2009).

The extent of the impact of a MCCZ on the marine environment is also large (hundreds of kilometers), but less than atmospheric transport and governed by local hydrographic patterns. The local hydrogeography is key in determining whether inputs of a MCCZ is mixed quickly or might be recirculated. In some regions, river plumes can remain distinct from the surrounding waters for hundreds of kilometers (e.g., Rhine plume in North Sea). Many estuaries are tidal so that the impacts of a MCCZ can be trapped within complex estuarine hydrodynamics leading to large local impacts on intertidal systems such as salt marshes and mangrove forests. The threats from the loss of such habitats were highlighted earlier.

Table 2 Spatial scales on which the MCCZ processes that are discussed in the article are of importance

	10s km	100s km	1000s km
Atmospheric circulation	Sea breeze, UHI, mountain winds, surface roughness, coastal fog	Sea breeze, mountain winds, coastal fog	Poss. circulation changes due to aerosol-heating-stability interactions
Atmospheric composition	Air quality, toxins from HAB, aerosol, marine trace gas emissions, ship emissions, coastal fog	Aerosol, O_3 budget, marine trace gas emissions, GHG, coastal fog	Long-range transport of pollutants into and from MCCZ, O_3 budget, aerosol, GHG
Climate	UHI, aerosol–cloud-precipitation effects, coastal fog	Greenhouse gases, aerosol radiative effects, precipitation changes, coastal fog	Greenhouse gases, aerosol radiative effects
Ocean biogeochemistry	Atmospheric input (gas/aerosol), fluvial input, estuarine processes, trace gas emissions, changes in productivity, HAB, hypoxia	Atmospheric input (gas/aerosol), trace gas emissions, changes in productivity, hypoxia	If local hydrogeography allows: changes in productivity, transport of pollutants, large-scale changes in ocean circulation, climate change
Economic reach	Supply of food, water, energy	Supply of food, water, energy, migration	Supply of food, migration, global economic changes
Health	Air quality, toxins from HAB, water quality	Air quality, long-range transport	Long-range transport

UHI urban heat island, *GHG* greenhouse gases, *HAB* harmful algal blooms

The economic reach of a MCCZ is extensive as well because food, water, and energy have to be provided and this often involves long- range transport into the megacity. For example, water and energy for Los Angeles is sourced from the Sierra Mountains and the Colorado River, hundreds of kilometers away from Los Angeles and as noted earlier the impacts of MCCZ on weather patterns and air pollution (particularly ozone) has the potential to create complex feedbacks. Food transport impacts, of course, become global (Galloway et al. 2008).

Another way to look at scales is to consider the recovery timescale of the perturbed domains. In the atmosphere, this timescale is on the order of days to weeks for the removal of aerosol particles and reactive gases, but on the order of months for less reactive gases. Greenhouse gases have lifetimes of hundreds and thousands of years. In coastal waters, although the timescales of individual blooms or eutrophication events is days, the recovery timescale for ecosystems is on the order of tens to hundreds of years (Middleburg and Levin 2009). See Table 2 for a summary of the various spatial scales.

Impact of Global Change on MCCZ and Vice Versa

MCCZ are impacted by a changing climate and are also contributing to this change. Rising sea levels put MCCZ in a particularly precarious situation compounding the issues we discuss here (Nicholls and Cazenave 2010). Shifts in precipitation patterns can either inhibit the water supply to the city or lead to precipitation events that result in flooding, which the sewage system may not be able to cope with leading potentially, for example, to HABs. In the future, projections suggest most of the world's megacities will remain to be located in the coastal zone, being impacted by global change and contributing to it at the same time. Anticipated climate changes will greatly amplify risks to coastal populations. By the end of the century, increases in the rates of global and local sea-level rise could lead to inundation of low-lying coastal regions, including wetlands, more frequent flooding due to storm surges, and worsening beach erosion. Saltwater could penetrate further up rivers and estuaries and infiltrate coastal aquifers, thereby contaminating urban water supplies (Horton and Rosenzweig 2010). Globally, the size of the population and wealth exposed to 100-year floods is expected to rise up to threefold by 2070 under projected socio-economic and climate change sea-level rise and increased storminess (Nicholls et al. 2008). Other vulnerabilities include water security, food security, health effects, and vulnerability to natural hazards.

The way these interactions impact the people who live in megacities and the ecosystems around them will depend in large part on the local conditions and physical environment. This will not only include the geographic setting but also the manmade-physical environment which alters the air and water flows, as we have discussed, and which in turn profoundly affect the biogeochemical functioning of the system. In the same way, the responses of the physical, chemical, and biological environments will be different for each MCCZ.

Sporadic events, for example storms causing strong runoff through the megacity into the oceans or even tsunamis washing contaminants from the land into the coastal ocean, can cause high stress on ecosystems, for example triggering

HABs which might impact on the megacity. These could push an ecosystem such as a coral reef area over a tipping point from which no (quick) recovery might be possible.

MCCZ are potentially very vulnerable as many people are dependent on a complex physical and social infrastructure which can be subject to nonlinear environmental effects that we urgently need to understand. Hence, effective environmental management is critical to the habitability of MCCZ and this needs to recognise the importance of land–air–sea interactions.

Compared to more rural areas or urban "sprawl,', megacities have a number of benefits. Megacities are, per capita, generally more energy efficient and require less transport. Megacities are at the frontline of change—especially in positive sense, for example regarding air pollution regulation and environmental management and in general, energy use, transportation, education, innovation etc. Changes (in the direction of improving quality of living etc) can be implemented more easily than elsewhere (Parrish and Zhu 2009). A good example is Los Angeles where ozone levels dropped substantially even though the population almost doubled in number (Parrish and Zhu 2009). Greenhouse gas emissions per capita are generally lower for megacities compared to the national average due to more efficient use of resources (Hoornweg et al. 2011).

As megacities pass through several stages of development they often undergo an evolution of patterns and regulation. Older megacities have come up with solutions for many environmental problems and could be used as guidelines for the development of younger and future megacities. The world's MCCZ are in different stages of development and have administrations of varying effectiveness. Learning from good practice in one can greatly benefit other MCCZs. MCCZ could become examples in terms of mitigation of global change and a large potential for co-benefits for air pollution and climate (e.g., de-carbonisation of economy) exists and is already being realised in some cases.

RESEARCH NEEDS FOR POLICY DEVELOPMENT

In our investigations, we have been surprised by the paucity of research information on MCCZ. Much of the advances have been focused on quick fixes with an engineering approach. These take the form of a linear approach that focus on a predetermined end point, for example construction of sewage treatment plants to achieve a perceived decreased level of eutrophication. Much less has been done to study or address the more prevalent complex or "wicked" problems that have no clear solutions and require value-based decisions. Some examples lead to inevitable and unpopular or politically untenable tradeoffs such as discharge limits or cap and trade metrics based on monetary evaluation (Jentoft and Chuenpagdee 2009; Mee 2012).

The role of scientists in managing "wicked" problems is to support policy makers' understanding of trade-offs and alternative solutions. By applying a systems thinking approach, a better linkage between science and policy can be developed. This can be through such means as proposing and validating models of the coupled social-ecological system, clarifying causality, understanding temporal and spatial scales, postulating or simulating alternative future scenarios, examining the effects of natural variability, co-developing (with stakeholders) potential solutions to identified problems and quantifying trade-offs. In doing this, it must be recognized that the coupled social-ecological systems involving large coastal agglomerations operate across a number of scales from local to global and some of the issues result from the legacy of the past and may be difficult to resolve (Mee 2012). A city that decides to place high-value properties at or below sea level (e.g., London, New Orleans, Rotterdam) is committing successive generations to major investments in sea defenses, irrespective of scientific logic.

To serve the needs of policy makers and apply strategies such as Integrated Coastal Zone Management or Adaptive Management, scientists need reliable and transparent data and process studies and our work has shown these to be generally deficient. The establishment of water and air monitoring networks with advanced technology that can provide real time data are critical to the implementation of these strategies. A successful example are those in the Los Angeles basin that over the past decades have led to vastly improved air and coastal water quality. In many MCCZ, including those in developed countries, emission inventories are poor for example and do not provide the evidence baseline needed to observe change. As an example of process studies, we need to address uncertainties in marine ecosystem response to atmospheric deposition of contaminants and nutrients which, depending on the situation, might lead to an increase or decrease of trace gas or particle emissions to the atmosphere. This need goes beyond the atmosphere/sea interaction we have focussed on; we have a very poor understanding of the synergistic and antagonistic effects of multiple inputs of contaminants. For example, specific organic pollutants in the form of human hormone or drug treatments in sewage may have deleterious effects that impair trophic structures in the food chain of coastal ecosystems. Another is the expanded footprint of the MCCZ in extended deposition of nutrients that impact coastal fisheries. Given the scale of likely megalopolis city development in our coastal zones, we suggest that a dedicated international program should be established to tackle knowledge gaps that must be bridged before integrated environmental management programs can become a practical reality.

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REFERENCES

Anderson, D.M., P. Hoagland, Y. Kaoru, and A.W. White. 2000. Estimated annual economic impacts from harmful algal blooms in the United States. Technical Report WHOI-2000-11, Woods Hole Oceanog. Inst.Tech. Rept.

Bloss, W.J., M.J. Evans, J.D. Lee, R. Sommariva, D.E. Heard, and M.J. Pilling. 2005. The oxidative capacity of the troposphere: Coupling of field measurements of OH and a global chemistry transport model. *Faraday Discussions* 130:425–436.

Brescianini, C., C. Grillo, N. Melchiorre, R. Bertolotto, A. Ferrari, B. Vivaldi, G. Icardi, L. Gramaccioni, et al. 2006. Ostreopsis ovata algal blooms affecting human health in Genova, Italy, 2005 and 2006. Euro Surv., 11:3040.

Broadgate, W.J., G. Malin, F.C. Küpper, A. Thompson, and P.S. Liss. 2004. Isoprene and other non-methane hydrocarbons from seaweeds: A source of reactive hydrocarbons to the atmosphere. *Marine Chemistry* 88:61–73.

Butler, T.M., and M.G. Lawrence. 2009. The influence of megacities on global atmospheric chemistry: A modelling study. *Environmental Chemistry* 6:219–225.

Carpenter, L.J., G. Malin, P.S. Liss, and F.C. Küpper. 2000. Novel biogenic iodine-containing trihalomethanes and other short-lived halocarbons in the coastal East Atlantic. *Global Biogeochemical Cycles* 14:1191–1204.

Cheng, Y.F., H. Eichler, A. Wiedensohler, J. Heintzenberg, Y.H. Zhang, M. Hu, H. Herrmann, L.M. Zeng, et al. 2006. Mixing state of elemental carbon and non-light-absorbing aerosol components derived from in situ particle optical properties at Xinken in Pearl River Delta of China. *Journal of Geophysical Research* 111:D20204. doi:10.1029/2005JD006929.

Chester, R., G.F. Bradshaw, C.J. Ottley, R.M. Harrison, J.L. Merrett, M.R. Preston, A.R. Rendell, M.M.Kane, and T.D. Jickells. 1993a. The atmospheric distribution of trace metals, trace organics and nutrients over the North Sea. *Philosophical Transactions of the Royal Society of London A* 343:543–556.

Chester, R., K.J.T. Murphy, F.J. Lin , A.S. Berry, G.A. Bradshaw, and P.A. Corcoran. 1993b. Factors controlling the solubilities of trace metals from non-remote aerosols desposited to the sea-surface by the dry deposition mode. *Marine Chemistry* 43:107–126.

Chung, C.E., V. Ramanathan, G. Carmichael, S. Kulkarni, Y. Tang, B. Adhikary, L.R. Leung, and Y. Qian. 2010. Anthropogenic aerosol radiative forcing in Asia derived from regional models with atmospheric and aerosol data assimilation. *Atmospheric Chemistry and Physics* 10:6007–6024.

Church, T.M., J.M. Tramontano, J.R. Scudlark, and S.L. Murray. 1988. Trace metals in the waters of the Delaware estuary. In *Ecology and restoration of the Delaware river basin*, eds. Majumdar, S.K., E.W.Miller, and L.E. Sage. Philadelphia: The Philadelphia Academy of Sciences.

Colle, B.A., J.B. Olson, and J.S. Tongue. 2003. Multi season verification of the MM5. Part I: Comparison with the Eta model over the central and eastern United States and impact of MM5 resolution. *Weather and Forecasting* 18:431–457.

Collins, W.J. 2009. Global radiative forcing from megacity emissions of long-lived greenhouse gases. Technical Report 09-01, MEGAPOLI Project Scientific Report.

Conley, D.J., C. Humborg, L. Rahm, O.P. Savchuk, and F. Wulff. 2009. Hypoxia-related processes in the Baltic Sea. *Environmental Science & Technology* 43:3412–3420.

Costanza, R., R. d'Arge, R. de Groot, S. Farber, M. Grasso, B. Hannon, K. Limburg, S. Naeem, et al. 1997. The value of the world's ecosystem services and natural capital. *Nature* 387:253–260.

Doering, U., J. van Aardenne, S. Monni, V. Pagliari, L. Orlandini, and F. San Martin. 2009. CIRCE report D8.1.3 Update of gridded emission inventories, addition of period 1990-2005 and the years 2010, 2015, 2050. Technical report, Project FP6: 6.3—No. 036961—CIRCE.

Doney, S.C., N. Mahowald, I. Lima, R.A. Feely, F.T. Mackenzie, J.-F. Lamarque, and P.J. Rasch. 2007. Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system. *Proceedings of the National Academy of Sciences of the United States of America* 104:14580–14585.

Duce, R.A., J. LaRoche, K. Altieri, K.R. Arrigo, A.R. Baker, D.G. Capone, S. Cornell, F. Dentener, et al. 2008 Impacts of atmospheric anthropogenic nitrogen on the open ocean. *HortScience* 320:893–897.

Fleming, L.E., B. Kirkpatrick, L.C. Backer, J.A. Bean, A. Wanner, A. Reich, J. Zaias, Y.-S. Cheng, et al. 2007 Aerosolized red tide toxins (brevetoxins) and asthma. *Chest* 131:187–194.

Freitas, E.D., Christopher M. Rozoff, William R. Cotton , and Pedro L. Silva Dias. 2007. Interactions of an urban heat island and sea-breeze circulations during winter over the metropolitan area of São Paulo, Brazil. *Boundary Layer Meteorology* 122:43–65.

Galloway, J.N., A.R. Townsend, J.W. Erisman, M. Bekunda, Z. Cai, J.R. Freney, L.A. Martinelli, S.P. Seitzinger, et al. 2008. Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. *HortScience* 320:889–892.

Gedzelman, S.D., R. Austin, S. Cermak, N. Stefano, S. Partridge, and S. Quesenberry. 2003. Mesoscale aspects of the urban heat island around New York city. *Theoretical and Applied Climatology* 75:29–42.

Gentien, P., B. Reguera, H. Yamazaki, L. Fernand, E. Berdalet, and R. Raine. 2008. Harmful algal blooms in stratified systems. Technical Report EOHAB Core Research Project 4, IOC and SCOR, Paris and Newark.

Gurjar, B.R., T.M. Butler, M.G. Lawrence, and J. Lelieveld. 2008. Evaluation of emissions and air quality in megacities. *Atmospheric Environment* 42:1593–1606.

Guttikunda, S.K., G.R. Carmichael, G. Calori, C. Eck, and J.-H. Woo. 2002. The contribution of megacities to regional sulfur pollution in Asia. *Atmospheric Environment* 37:11–22.

Hagström, J., E. Granéli, M.O.P. Moreira, and C. Odebrecht. 2011. Domoic acid production and elemental composition of two Pseudo-nitzschia multiseries strains, from the NW and SW Atlantic Ocean, growing in phosphorus- or nitrogen-limited chemostat cultures. *Journal of Plankton Research* 33:297–308.

Hashimoto, S., K. Gojo, S. Hikota, N. Sendai, and A. Otsuki. 1999. Nitrous oxide emissions from coastal waters in Tokyo Bay. *Marine Environmental Research* 47:213–223.

Hidalgo, J., V. Masson, A. Baklanov, G. Pigeon, and L. Gimeno. 2008. Advances in urban climate modelling. Trends and directions in climate research. *Annals of the New York Academy of Sciences* 1146:354–374.

Hofzumahaus, A., F. Rohrer, K. Lu, B. Bohn, T. Brauers, C.C. Chang, H. Fuchs, F. Holland, et al. 2009. Amplified trace gas removal in the troposphere. *HortScience* 324:1702–1704.

Hoornweg, D., L. Sugar, and C.L. Trejos Gómez. 2011. Cities and greenhouse gas emissions: Moving forward. *Environment and Urbanization* 23:207–227.

Horton, R., and C. Rosenzweig. 2010. Climate risk information. In *Climate change adaptation in New York city: Building a risk-management response: New York City Panel on Climate Change*, 147–228, Vol. 1196. New York: Annals of the New York Academy of Sciences.

Hughes, C., D. Franklin, and G. Malin. 2011. Iodomethane production by two important marine cyanobacteria: *Prochlorococcus marimus* (CCMP 2389) and Synechococcus sp. (CCMP 2370). *Marine Chemistry* 125:19–25.

Hunter, K.A., P.S. Liss, V. Surapipith, F. Dentener, R. Duce, M. Kanakidou, N. Kubilay, N. Mahowald, et al. 2011. Impacts of anthropogenic SO_x, NO_x and NH_3 on acidification of coastal waters and shipping lanes. *Geophysical Research Letters* 38:L13602. doi:10.1029/2011GL047720.

Ichinose, T., K. Shimodozono, and K. Hanaki. 1999. Impact of anthropogenic heat on urban climate in Tokyo. *Atmospheric Environment* 33:3897–3909.

Islam, M.S., and M. Tanaka. 2004. Impacts of pollution on coastal and marine ecosystems including coastal and marine fisheries and approach to amanagement: A review and synthesis. *Marine Pollution Bulletin* 48:624–629.

Jentoft, S., and R. Chuenpagdee. 2009. Fisheries and coastal governance as a wicked problem. *Marine Policy* 33:553–560.

Jickells, T.D. 1998. Nutrient biogeochemistry of the coastal zone. *HortScience* 281:217–222.

Kanakidou, M., N. Mihalopoulos, T. Kindap, U. Im, M. Vrekoussis, E. Gerasopoulos, E. Dermitzaki, A. Unal, et al. 2011. Megacities as hot spots of air pollution in the East Mediterranean. *Atmospheric Environment* 45:1223–1235.

Kaufman, Y.L., D. Tanré, and O. Boucher. 2002. A satellite view of aerosols in the climate system. *Nature* 419:215–223.

Krom, M.D., B. Herut, and R.F.C. Mantoura. 2004. Nutrient budget for the Eastern Mediterranean: Implications for P limitation. *Limnology and Oceanography* 49:1582–1592.

Küpper, F.C., L.J. Carpenter, G.B. McFiggans, C.J. Palmer, T.J. Waite, E.-M. Boneberg, S. Woitsch, M. Weiller, et al. 2008. Iodide accumulation provides kelp with an inorganic antioxidant impacting atmospheric chemistry. *Proceedings of the National Academy of Sciences of the United States of America* 105:6954–6958.

Lawler, M.J., B.D. Finley, W.C. Keene, A.A.P. Pszenny, K.A. Read, R. von Glasow, and E.S. Saltzman. 2009. Pollution-enhanced reactive chlorine chemistry in the eastern tropical Atlantic boundary layer. *Geophysical Research Letters* 36:L08810. doi: 10.1029/2008GL036666.

Lawrence, M.G., and J. Lelieveld. 2010. Atmospheric pollutant outflow from southern Asia: A review. *Atmospheric Chemistry and Physics* 10:11017–11096.

Liss, P.S. 2007. Trace gas emissions from the marine biosphere. *Philosophical Transactions of the Royal Society of London A* 365:1697–1704.

Lu, R., and R.P. Turco. 1996. Ozone distributions over the Los Angeles basin: Three-dimensional simulations with the SMOG model. *Atmospheric Environment* 24:4155–4176.

Mage, D., G. Ozolins, P. Peterson, A. Webster, R. Orthofer, V. Vandeweerd, and M. Gwynne. 1996. Urban air pollution in megacities of the world. *Atmospheric Environment* 30:681–686.

Manley, S.L., N.-Y. Wang, M.L. Walser, and R.J. Cicerone. 2006. Coastal salt marshes as global methyl halide sources from determinations of intrinsic production by marsh plants. *Global Biogeochemical Cycles* 20:GB3015. doi:10.1029/2005GB002578.

Martino, M., G.P. Mills, J. Woeltjen, and P.S. Liss. 2009. A new source of volatile organoiodine compounds in surface seawater. *Geophysical Research Letters* 36:L01609. doi:10.1029/2008GL036334.

McFiggans, G., H. Coe, R. Burgess, J. Allan, M. Cubison, M.R. Alfarra, R. Saunders, A. Saiz-Lopez, et al. 2004. Direct evidence for coastal iodine particles from Laminaria macroalgae—linkage to emissions of molecular iodine. *Atmospheric Chemistry and Physics* 4:701–713.

McFiggans, G., C.S.E. Bale, S.M. Ball, J.M. Beames, W.J. Bloss, L.J. Carpenter, J. Dorsey, R. Dunk, et al. 2010. Iodine-mediated coastal particle formation: An overview of the reactive halogens in the marine boundary layer (RHaMBLe) Roscoff coastal study. *Atmospheric Chemistry and Physics* 10:2975–2999.

Mee, L. 2012. Between the devil and the deep Blue Sea: The coastal zone in an era of globalisation. *Estuarine, Coastal and Shelf Science* 96:1–8.

Meier, M.H.E., R. Feistel, J. Piechura, L. Arneborg, H. Burchard, V. Fiekas, N. Golenko, N. Kuzmina, et al. 2006. Ventilation of the Baltic Sea deep water: A brief review of present knowledge from observations and models. *Oceanologia* 48(S):133–164.

Mestayer, P.G., P. Durand, P. Augustin, S. Bastin, J.M. Bonnefond, B. Bénech, B. Campistron, A. Coppalle, et al. 2005. The urban boundary layer field experiment over Marseille, UBL/CLU-ESCOMPTE: Experimental set-up and first results. *Boundary Layer Meteorology* 114:315–365.

Middleburg, J.J., and L.A. Levin. 2009. Coastal hypoxia and sediment biogeochemistry. *Biogeosciences* 6:1273–1293.

Moffett, J.W., L.E. Brand, P.L. Croot, and K.A. Barbeau. 1997. Cu speciation and cyanobacterial distribution in harbours subject to anthropogenic Cu inputs. *Limnology and Oceanography* 42:789–799.

Morand, P., and M. Merceron. 2005. Macroalgal population and sustainability. *Journal of Coastal Research* 21:1009–1020.

Nakamura, T., H. Ogawa, D.M. Kumar, and M. Uematsu. 2006. Contribution of water soluble organic nitrogen to total nitrogen in marine aerosols over the East China Sea and western North Pacific. *Atmospheric Environment* 40:7259–7264.

Nicholls, R.J., and A. Cazenave. 2010. Sea-level rise and its impact on coastal zones. *HortScience* 328:1517–1520.

Nicholls, R.J., S. Hanson, C. Herweijer, N. Patmore, S. Hallegatte, J. Corfee-Morlot, J. Chateau, and R.M. Wood. 2008. Ranking port cities with high exposure and vulnerability to climate extremes: Exposure estimates. Technical report, OECD Environment Working Papers, No. 1, OECD Publishing.

Ní Rathaille, A., and R. Raine. 2011. Seasonality in the excystment of *Alexandrium minutum* and *Alexandrium tamarense* in Irish Coastal waters. *Harmful Algae* 10:629–635.

Nirmal Rajkumar, A., J. Barnes, R. Ramesh, R. Purvaja, and R.C. Upstill-Goddard. 2008. Methane and nitrous oxide fluxes in the polluted Adyar River and estuary, SE India. *Marine Pollution Bulletin* 56:2043–2051.

O'Dowd, C.D., and T. Hoffmann. 2005. Coastal new particle formation: A review of the current state-of-the-art. *Environmental Chemistry* 2:245–255.

Ohashi, Y., and H. Kida. 2002. Local circulations developed at the vicinity of both coastal and inland urban areas: A numerical study with a mesoscale atmospheric model. *Journal of Applied Meteorology* 41:30–45.

Osthoff, H.D., J.M. Roberts, A.R. Ravishankara, E.J. Williams, B.M. Lerner, R. Sommariva, T.S. Bates, D. Coffmann, et al. 2008 Unexpectedly high $ClNO_2$ mixing ratios in the polluted subtropical marine boundary layer. *Nature Geoscience* 1:324–328.

Parrish, D.D., and T. Zhu. 2009. Clean air for megacities. *Science* 326:674–675.

Paytan, A., K.R.M. Mackey, Y. Chen, I.D. Lima, S.C. Doney, N. Mahowald, R. Labiosa, and A.F. Post. 2009. Toxicity of atmospheric aerosols on marine phytoplankton. *Proceedings of the National Academy of Sciences of the United States of America* 106:4601–4605.

Pullen, J., J. Ching, D. Sailor, W. Thompson, B. Bornstein, and D. Koracin. 2008. Progress towards meeting the challenges of our coastal urban future. The seventh conference on coastal atmospheric and oceanic prediction and processes and the seventh symposium on the urban environment. *Bulletin of the American Meteorological Society* 89:1727–1731.

Queste, B.Y., L. Fernand, T.J. Jickells, and K.J. Heywood. 2012. Spatial extent and historical context of North Sea oxygen depletion in August 2010. *Biogeochemistry*. doi:10.1007/s10533-012-9729-9.

Ramanathan, V., C. Chung, D. Kim, T. Bettge, L. Buja, J.T. Kiehl, W.M. Washington, Q. Fu, et al. 2005. Atmospheric brown clouds: Impacts on South Asian climate and hydrological cycle. *Proceedings of the National Academy of Sciences of the United States of America* 102:5326–5333.

Ramanathan, V., F. Li, M.V. Ramana, P.S. Praveen, D. Kim, C.E. Corrigan, H. Nguyen, E.A. Stone, et al. 2007. Atmospheric brown clouds: Hemispherical and regional variations in long-range transport, absorption, and radiative forcing. *Journal of Geophysical Research* 112:D22S21. doi:10.1029/2006JD008124.

Rosenfeld, D., R. Lahav, A, Khain, and M. Pinsky. 2002. The role of sea spray in cleansing air pollution over ocean via cloud processes. *Science* 297:1667–1670.

Sekovski, I., A. Newton, and W.C. Dennison. 2012. Megacities in the coastal zone: Using a driver-pressure-state-impact-response framework to address complex environmental problems. *Estuarine, Coastal and Shelf Science* 96:48–59.

Shepherd, J.M. 2005. A review of current investigations of urban-induced rainfall and recommendations for the future. *Earth Interactions* 9:1–27.

Song, C.H., and G.R. Carmichael. 1999. The aging process of naturally emitted aerosol (sea-salt and mineral aerosol) during long range transport. *Atmospheric Environment* 33:2203–2218.

Spokes, L.J., and T.D. Jickells. 2005. Is the atmosphere really an important source of reactive nitrogen to coastal waters? *Continental Shelf Research* 25:2022–2035.

Stevens, B., and G. Feingold. 2009. Untangling aerosol effects on clouds and precipitation in a buffered system. *Nature* 461:607–613.

Thompson, W.T., T. Holt, and J. Pullen. 2007. Investigation of a sea breeze front in an urban environment. *Quarterly Journal of the Royal Meteorological Society* 133:579–594.

Tie, X., Fuhai Geng, Li Peng, Wei Gao, and Chunsheng Zhao. 2009. Measurement and modeling of O_3 variability in Shanghai, China: Application of the WRF-Chem model. *Atmospheric Environment* 43:4289–4302.

UN. 2010. World urbanization prospects: The 2009 Revision. Technical Report, United Nations Department of Economic and Social Affairs/Population Division.

Uno, I., M. Uematsu, Y. Hara, Y.J. He, T. Ohara, A. Mori, T. Kamaya, K. Murano, et al. 2007. Numerical study of the atmospheric input of anthropogenic total nitrate to the marginal seas in the western North Pacific region. *Geophysical Research Letters* 34:L17817. doi:10.1029/2007GL030338.

Uno, I., K. Eguchi, K. Yumimoto, T. Takemura, A. Shimizu, M. Uematsu, Z. Liu, Z. Wang, et al. 2009. Asian dust transported one full circuit around the globe. *Nature Geoscience* 2:557–560.

Van Alstyne, K.I. 2008. Ecological and physiological role of dimethylsulponiopropionate and its products in marine macroalgae. In *Algal chemical ecology*, ed. Amsler, C.D., 173–194. Heidelberg:Springer.

Vogt, R., R. Sander, R. von Glasow, P. Crutzen. 1999. Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: A model study. *Journal of Atmospheric Chemistry* 32:375–395.

von Glasow, R. 2008. Pollution meets sea salt. *Nature Geoscience* 1:292.

Yue, D., M. Hu, Z. Wu, Z. Wang, S. Guo, B. Wehner, A. Nowak, P. Achtert, et al. 2009. Characteristics of aerosol size distributions and new particle formation in the summer in Beijing. *Journal of Geophysical Research* 114:D00G12. doi:10.1029/2008JD010894.

Zhu, S., T. Butler, R. Sander, J. Ma, and M.G. Lawrence. 2010. Impact of dust on tropospheric photochemistry over polluted regions: A case study of the Beijing megacity. *Atmospheric Chemistry and Physics* 10:3855–3873.

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