Science of the Total Environment 563–564 (2016) 40–52

Contents lists available at ScienceDirect

Science of the Total Environment

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

Ozone and carbon monoxide budgets over the Eastern Mediterranean

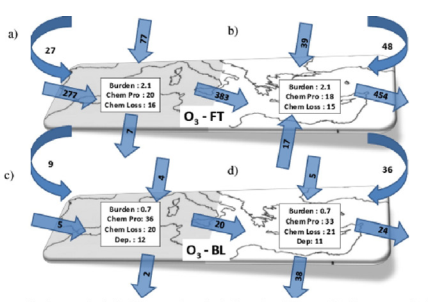
S. Myriokefalitakis [a,*], N. Daskalakis [a,b,1], G.S. Fanourgakis [a], A. Voulgarakis [c], M.C. Krol [d,e,f], J.M.J. Aan de Brugh [f], M. Kanakidou [a,*]

[a] Environmental Chemical Processes Laboratory (ECPL), Department of Chemistry, University of Crete, P.O. Box 2208, 70013 Heraklion, Greece
[b] Institute of Chemical Engineering, Foundation for Research and Technology Hellas (FORTH/ICE-HT), 26504 Patras, Greece
[c] Department of Physics, Imperial College London, London, UK
[d] Meteorology and Air Quality Section, Wageningen University, Wageningen, The Netherlands
[e] Institute for Marine and Atmospheric Research, Utrecht University, Utrecht, The Netherlands
[f] SRON Netherlands Institute for Space Research, Utrecht, The Netherlands

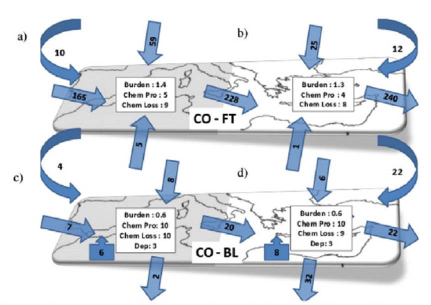
HIGHLIGHTS

- Eastern Mediterranean is a strong receptor of polluted air masses.
- The Free Troposphere is the most important pollution source for the boundary layer.
- Small impact of local sources on regional air quality has been computed.
- Projections reveal a CO increase and O_3 decrease over the Eastern Mediterranean.

GRAPHICAL ABSTRACT



O_3 annual budget analysis for Western (a,c; shaded area) and Eastern Mediterranean (b,d; non-shaded area) for a,b) the free troposphere (FT; upper figure) and c,d) the boundary layer (BL; bottom figure) including the burden, the chemistry, the deposition and the fluxes at each boundary. All budget terms and fluxes (Tg yr^{-1}) are annual totals; burdens (Tg) are annual averages. Straight arrows indicate N-S and W-E advection fluxes, while curved arrows indicate vertical fluxes from the upper troposphere to the FT and from the FT to the BL.



CO annual (budget analysis for Western (a,c; shaded area) and Eastern Mediterranean (b,d; non-shaded area) for a,b) the free troposphere (FT; upper figure) and c,d) the boundary layer (BL; bottom figure) including the burden, the emissions, the chemistry, the deposition and the fluxes at each boundary. Straight arrows indicate N-S and W-E advection fluxes, curved arrows indicate vertical fluxes from the upper troposphere to the FT and from the FT to the BL and box-arrows indicate CO emissions.

ARTICLE INFO

Article history:
Received 31 October 2015
Received in revised form 7 April 2016
Accepted 8 April 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Ozone (O_3)
Carbon monoxide (CO)
Eastern Mediterranean (EM)
Long-range transport (LRT)
Free Troposphere (FT)

ABSTRACT

The importance of the long-range transport (LRT) on O_3 and CO budgets over the Eastern Mediterranean has been investigated using the state-of-the-art 3-dimensional global chemistry-transport model TM4-ECPL. A 3-D budget analysis has been performed separating the Eastern from the Western basins and the boundary layer (BL) from the free troposphere (FT). The FT of the Eastern Mediterranean is shown to be a strong receptor of polluted air masses from the Western Mediterranean, and the most important source of polluted air masses for the Eastern Mediterranean BL, with about 40% of O_3 and of CO in the BL to be transported from the FT aloft. Regional anthropogenic sources are found to have relatively small impact on regional air quality in the area, contributing by about 8% and 18% to surface levels of O_3 and CO, respectively. Projections using anthropogenic emissions for the year 2050 but neglecting climate change calculate a surface O_3 decrease of about 11% together with a surface CO increase of roughly 10% in the Eastern Mediterranean.

* Corresponding authors.
E-mail addresses: stelios@uoc.gr (S. Myriokefalitakis), mariak@uoc.gr (M. Kanakidou).
[1] Now at: LATMOS, Laboratoire Atmosphères, Milieux, Observations Spatiales, UPMC/UVSQ/CNRS, Paris, France.

http://dx.doi.org/10.1016/j.scitotenv.2016.04.061
0048-9697/

1. Introduction

Tropospheric O_3 and CO are atmospheric pollutants both generated from natural and anthropogenic sources depending on numerous physical and chemical processes (e.g. Lelieveld and Dentener, 2000). They significantly affect the oxidizing capacity of the troposphere, climate (IPCC, 2013) and human and ecosystem's health (e.g. Jimoda, 2012; Ainsworth et al., 2012; Yue and Unger, 2014). Therefore, much attention is been paid to limit exceedances of threshold air pollution levels set by environmental policy directives (e.g. DIRECTIVE 2008/50/EC Annex VII). Attribution of air pollution to sources is a prerequisite for designing measures to be taken to comply with such instructions. Pollution within urban agglomerations can build-up both locally (via local emissions and chemistry) and regionally (via transport from other regions) (e.g. Parrish et al., 2011). In the outflow of pollution centers, oxidation of volatile organic compounds (VOCs) and CO fosters the formation of secondary pollutants such as O_3 (Molina and Molina, 2002), which is produced during the oxidation of VOCs in the presence of nitrogen oxides (NO_x) (Crutzen, 1974; Derwent et al., 1996; Monks et al., 2009) following non-linear chemical processes. Therefore, it is particularly important to know whether actions on national level or coordinated actions on regional, or even global scale, are needed to limit air pollution in a region.

In this respect, Colette et al. (2012) analyzed atmospheric pollutant surface observations in Europe to derive trends over the past decade and compared them with multi-model chemistry-transport simulations. They found robust decreases of NO_x throughout Europe except in South-Eastern France and North Italy and pointed out much larger model uncertainty over the Mediterranean than elsewhere. Over the Eastern Mediterranean (EM), they calculate a decrease in non-methane volatile organic compounds (NMVOC) to NO_x ratio indicating a shift in the chemical regime in the area. Beekmann and Vautard (2010) have shown that the Mediterranean atmosphere is a NO_x sensitive regime, while North-Western Europe is always VOC sensitive. Furthermore, modeling studies simulate high O_3 concentrations in the summer, in agreement with the observed northern hemisphere summertime O_3 maxima (Zanis et al., 2014). They also predict higher O_3 levels in parts of the European continent as a result of a warmer climate in the near future (Langner et al., 2012; Zanis et al., 2014) and an increase in regional biogenic emissions, both of which lead to a summertime regional O_3 increase by 1 ppb $°C^{-1}$ (Im et al., 2011). Within large agglomerations of the EM, O_3 is significantly depressed through reaction with NO, followed by HNO_3 formation, in particular during wintertime (Im and Kanakidou, 2012).

The Mediterranean is among the most climatically sensitive regions of Europe, often exposed to multiple stresses, such as simultaneous water shortage and air pollution exposure (IPCC, 2013). It is also a characteristic region of a strongly coupled atmosphere–ocean system, composed by two basins that differ in air circulation patterns (Millán et al., 2005; Kallos et al., 2007) — the eastern and the western part. EM is affected by several large agglomerations, including the two megacities (http://www.newgeography.com): Istanbul (13.6 M; Turkey) at the northeastern edge, Cairo (17.8 M; Egypt) at the southern edge of the basin, and one agglomeration, Athens, which gathers 40% (4 M) of Greece's total population. The rapid urbanization and the unique location of the EM as a crossroad of air masses affected by various pollution sources has turned air pollution into a challenging environmental problem in the area. Air masses from upwind locations carrying anthropogenic emissions, mainly from Europe, the Balkans and the Black Sea, meet with biomass burning (Sciare et al., 2008), biogenic (Liakakou et al., 2009) and other natural emissions (Gerasopoulos et al., 2011) from surrounding regions under sunny and warm conditions that enhance photochemical build-up of pollutants (Lelieveld et al., 2002; Kanakidou et al., 2011).

To quantify the impact of anthropogenic sources on air-quality of the region as the EM, the inter- and the intra- continental transport have to be considered and distinguished from the impact of the regional sources (HTAP, 2011). Such analysis remains challenging, due to the chemical complexity of atmospheric composition and the significant seasonal and interannual variability of meteorological conditions that affect transport patterns (e.g. driven by the North Atlantic Oscillation; Pausata et al., 2012). Thus, large-scale chemistry-transport models (CTMs) are more appropriate tools for studying LRT (e.g. HTAP, 2011) than mesoscale models in which inter-/intra-continental transport procedures are strongly driven by the imposed boundary conditions. Satellite observations of tropospheric O_3, NO_2 and aerosol optical thickness (AOT) over the Mediterranean clearly show the regional tropospheric O_3 column maximum over the Mediterranean sea as well as the high NO_2 columns in the urban pollution centers that surround the basin (Kanakidou et al., 2011). Ground-based and satellite observations and numerical modeling reviewed by Kanakidou et al. (2011) point out that air pollution transported to the area is of similar importance to local sources for the background air pollution levels in the EM. Indeed, Drori et al. (2012) calculated that transport of air masses from Eastern Europe and Turkey to the EM can contribute up to 50% of surface CO in the area. Gerasopoulos et al. (2005) analyzing observations provided evidence that the main mechanism controlling the high background tropospheric O_3 levels in the EM is the long-range transport (LRT) from the European continent (mainly during summer) and the local photochemical O_3 build-up (especially under western flow and stagnant wind conditions). In line with these findings, Zanis et al. (2014) attributed the characteristic summertime tropospheric O_3 pool over the EM to enhanced downward transport from the upper troposphere and lower stratosphere that characterize the summertime circulation over this region.

In the present study we investigate the contribution of LRT on O_3 and CO budgets in the Mediterranean basin, using a global CTM, the TM4-ECPL, to conduct a source attribution of atmospheric composition changes. The relative impacts of regional anthropogenic, biomass burning and natural emissions to the air quality in the EM are evaluated. First, the model set-up and methodology followed are described. Then simulated O_3 and CO levels are compared with in-situ observations and satellite retrievals on a European and global level and model deficiencies are discussed. The importance of regional emissions and the strength of LRT for air quality are investigated based on sensitivity simulations and budget analysis. Projected changes resulting from anthropogenic emissions scenarios for 2050 are also discussed.

2. Materials and methods

2.1. Global model set-up

The global CTM TM4-ECPL (Daskalakis et al., 2015 and references therein) is able to simulate oxidant chemistry, accounting for NMVOCs, as well as all major aerosol components, including inorganic aerosols such as sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+) using the ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007) and secondary organic aerosols (SOA). Compared to its parent TM4 model (van Noije et al., 2004), the present version includes a description of glyoxal and other oxygenated organics (Myriokefalitakis et al., 2008) and organic aerosols (Myriokefalitakis et al., 2010). The model also accounts for multiphase chemistry in clouds and aerosol water that affects SOA formation (Myriokefalitakis et al., 2011) and dust solubility (Myriokefalitakis et al., 2015). TM4-ECPL has been previously evaluated for its ability i) to compute atmospheric composition and uncertainties associated with the use of different biomass burning emissions (Daskalakis et al., 2015), ii) to reproduce distributions of tropospheric O_3 and its precursors, as well as aerosols over Asia in summer 2008 as seen by satellite and by in-situ observations (Quennehen et al., 2015), iii) to simulate the concentrations of sulfate, black carbon (BC) and other aerosols in the Arctic (Eckhardt et al., 2015) and iv) to evaluate the air quality impacts of short-lived pollutants based on current legislation for the recent past and present (Stohl et al., 2015).

For the present study, year 2008 anthropogenic emissions of NMVOC, NO_x, CO, SO_2, NH_3, OC and BC developed within the EU-FP7 ECLIPSE project (Stohl et al., 2015) have been used to drive the