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## Interpreting elevated space-borne HCHO columns over the Mediterranean Sea using the OMI and SCIAMACHY sensors

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### Abstract

Formaldehyde (HCHO) is an oxidation product of a wide range of volatile organic compounds (VOCs) and important atmospheric constituent found in both the polluted urban atmosphere and remote background sites. In this study, remotely sensed data of HCHO vertical column densities are analyzed over the Mediterranean Sea using the Ozone Monitoring Instrument (OMI). Data analysis indicates a marked seasonal cycle with a summer maximum and winter minimum confined to the marine environment during a three year period (2005–2007) examined. A possible retrieval artifact associated with Saharan dust transport over the region is explored by changing intensity of Saharan dust sources in GEOS-Chem following the recommendation of Generoso et al. (2008). Recalculated air mass factors (AMF), based on the new values of aerosol loadings, lead to a reduction of the summertime “hot spot” in OMI retrieval of HCHO columns over the Mediterranean Sea; however, even after the correction, enhanced values are still present in this region. To explain these values, marine biogenic sources of VOCs are examined. Calculations indicate that emissions of phytoplankton-produced isoprene and monoterpenes are not likely to explain the enhanced HCHO columns over the Mediterranean Sea.

To further understand spatial and seasonal variation of HCHO over the Mediterranean Sea, OMI HCHO columns are compared to those of the SCanning Imaging Absorption spectroMeter for Atmospheric CartographY (SCIAMACHY) sensor. Unlike OMI retrievals, over the Mediterranean Sea SCIAMACHY HCHO columns did not reveal clear seasonality during the three years and the two sensors did not agree within their retrieval uncertainty. Overall, comparison of OMI and SCIAMACHY HCHO columns were inconclusive. Moreover, retrievals of HCHO columns over other water bodies showed that the two sensors agree reasonably well over the Equatorial Pacific region, Gulf of Mexico, and the North Sea, but do not show similar magnitudes or seasonal variations over oligotrophic water bodies such as Mediterranean Sea, Northwestern and Southern Pacific Oceans. Model simulations in conjunction

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with measurements studies may be required to fully explore the complex mechanism of HCHO formation over the Mediterranean and its implications for the air quality in the region.

## 1 Introduction

5 Formaldehyde (HCHO) is one of the most abundant carbonyl compounds in both the polluted urban atmosphere and remote background sites (Ayers et al., 1997; Lee et al., 2001; Singh et al., 2001; Grosjean et al., 2002). Formaldehyde can be directly emitted from anthropogenic (automobile exhaust, industrial emissions, biomass burning) (Carlier et al., 1986; Sigsby et al., 1987; Stavrou et al., 2009a) and natural sources (vegetation) (Kesselmeier and Staudt, 1999; Seco et al., 2007) or photochemically produced through the oxidation of volatile organic compounds (VOCs) (Finlayson-Pitts and Pitts, 1997; Crutzen et al., 1999). The lifetime of HCHO in the atmosphere is controlled by two main sinks: photolysis and reaction with hydroxyl radical (OH). At low OH concentrations ( $5 \times 10^5$  molecule  $\text{cm}^{-3}$ ) and high OH concentrations ( $1 \times 10^7$  molecule  $\text{cm}^{-3}$ ), the lifetime of HCHO can be 60 h to 3 h respectively (Dufour et al., 2009). Although the photo-oxidation of methane ( $\text{CH}_4$ ) is the main source of HCHO in the background atmosphere, the additional oxidation of non-methane VOCs (e.g., monoterpenes and isoprene) can significantly contribute to local HCHO concentrations (Fehsenfeld et al., 1992; Fuentes et al., 2000). Shorter lived VOCs with higher HCHO yields (e.g., isoprene) can cause localized “hot spots” over certain regions (e.g., Southeastern United States) while the HCHO enhancement from the oxidation of longer lived VOCs will be spread over larger areas, causing a more uniform distribution. Based on this postulation, several studies have successfully used remotely sensed formaldehyde as a “top-down” approach to constrain terrestrial isoprene concentrations (Abbot et al., 2003; Palmer et al., 2003, 2006; Shim et al., 2005; Millet et al., 2008; Barkley et al., 2008; Stavrou et al., 2009a; Dufour et al., 2009; Curci et al., 2010).

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Past studies focusing on VOC emissions from Europe revealed remarkably high summertime HCHO mixing ratios over the Mediterranean Sea, that was not well simulated by chemical transport models (Lelieveld et al., 2002; Kormann et al., 2003; Ladstätter-Weißenmayer et al., 2003, 2007; Curci et al., 2010; Klippel et al., 2011). Since HCHO has a high solubility in water, with a Henry Law constant of  $\sim 6 \times 10^3$  mol  $\text{atm}^{-1}$  (Sander, 1999), it is generally assumed that there are no direct emissions from the ocean (Mopper and Stahovec, 1986). Therefore, formation of formaldehyde with marine sources is most likely from the photo-oxidation of phytoplankton-produced VOCs. Previous studies have shown that considerable amounts of isoprene and, to much lesser extent, monoterpenes can be produced by marine phytoplankton (Bonsang et al., 1992; Moore et al., 1994; Shaw et al., 2003; Broadgate et al., 2004; Yassaa et al., 2008; Shaw et al., 2010). It was proposed that incoming solar radiation and water temperature can significantly affect marine isoprene (Shaw et al., 2003; Gantt et al., 2009) and monoterpene (i.e.,  $\alpha$ - and  $\beta$ -pinene, Sabolis, 2010) emission rates, making dynamic marine areas (such as upwelling regions and estuaries) likely regions for higher marine biogenic VOC emissions compared to the global average. Although oxidation of marine VOCs can lead to the formation of HCHO, it is not clear if the rates of phytoplankton-produced VOCs are high enough to enhance HCHO signals above the background levels (determined by  $\text{CH}_4$  oxidation) and create the hot spots over marine environments large enough to be identified using remotely sensed techniques.

In this study, remotely sensed formaldehyde column densities from the Ozone Monitoring Instrument (OMI) and SCanning Imaging Absorption spectroMeter for Atmospheric CartographY (SCIAMACHY) satellite sensors for the years 2005–2007 are used to explore this potential marine source of VOCs in the region of the Mediterranean Sea. Previous work illustrated that such an approach can be effective when the parent VOC has a significant HCHO yield and sufficiently short lifetime to have local relationship between the emissions of the VOC and the retrieved HCHO columns (Palmer et al., 2003, 2006). Currently the origin for enhanced summertime concentrations of HCHO over the Mediterranean Sea is not clear and is suggested to be related

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to one or more processes such as summertime transport of polluted continental air masses, transport of Saharan dust, intense ship traffic, and changes in surface temperature and nutrient stratification, influencing marine biota (Curci et al., 2010). This study addresses following two questions: Do different satellite sensors consistently reveal enhanced HCHO columns over the Mediterranean Sea? If so, are they caused by retrieval errors or ocean biological sources (i.e., oxidation of marine VOCs)?

## 2 Data and methods

### 2.1 HCHO remote sensing

Data from two different space-borne sensors were used in this study for the retrieval of HCHO columns over the Mediterranean region. OMI is aboard NASA's Aura satellite with a sun-synchronous polar orbit and an equator crossing time of 13:38 local time. OMI has a 2600 km viewing swath, with pixel sizes ranging from  $13 \times 24$  km at nadir to  $26 \times 135$  km at the swath edges, allowing for almost daily global coverage (Millet et al., 2008). OMI is a nadir viewing UV/Vis sensor observing continuously from 270 to 500 nm (Kurosu et al., 2004). The SCIAMACHY sensor is aboard the ENVISAT satellite. The ENVISAT satellite has a sun-synchronous polar orbit with an equator crossing time of 10:00 local time (Bovensmann et al., 1999) and a 960 km viewing swath, allowing for global coverage every 6 days. SCIAMACHY has three viewing geometries (nadir, limb, and sun/moon occultation) and continuously observes from 240 to 1700 nm and in selected wavelengths between 1900 and 2400 nm (De Smedt et al., 2008).

Retrieval of HCHO columns start with the retrieval of slant column density (SCD), which essentially is the HCHO concentration integrated along the viewing path of the satellite. The retrieval algorithm for OMI HCHO SCD is based on a non-linear least-squares fitting, while the SCIAMACHY HCHO SCD uses differential optical absorption spectroscopy technique (DOAS) (De Smedt et al., 2008). OMI SCDs are determined

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by fitting measured radiances using a spectral window between 327.5–356.5 nm and consider molecular absorption cross sections (Cantrell et al., 1990), correction for Ring effect (Chance and Spurr, 1997) and effective albedo (Kurosu et al., 2004). Slant columns for SCIAMACHY are determined by fitting the measured radiances using a spectral window between 328.5–346 nm to avoid a known polarization peak around 350 nm in SCIAMACHY retrievals (De Smedt et al., 2008).

Vertical column densities (VCD) are then calculated by dividing slant columns over a calculated Air Mass Factor (AMF). The AMF takes into account atmospheric scattering, surface albedo, satellite viewing geometry, aerosols, clouds, and the vertical distribution of HCHO. The calculation of the AMF used for conversion of a SCD into a VCD has two parts: the use of a chemistry transport model (CTM) to generate the “shape factor” and a radiative transfer model within the CTM to generate “scattering weights” (see Palmer et al., 2001 and Martin et al., 2002 for details). OMI data products use the GEOS-Chem global 3-D chemical transport model (Bey et al., 2001; Palmer et al., 2001; Martin et al., 2002) and the LIDORT radiative transfer model for calculation of the AMF, while SCIAMACHY is using the TM4 model and the Doubling Adding KNMI (DAK) radiative transfer model with FRESCO cloud parameters (De Smedt et al., 2008). We use GEOS-Chem version 7.03 with GEOS-4 assimilated meteorological fields from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling Assimilation Office regridded to a horizontal grid resolution of  $2^\circ \times 2.5^\circ$  (latitude-longitude) and 47 vertical layers. In its full chemistry configuration, GEOS-Chem includes  $\text{H}_2\text{SO}_4$ - $\text{HNO}_3$ - $\text{NH}_3$  aerosol thermodynamics coupled to an  $\text{O}_3$ - $\text{NO}_x$ -hydrocarbon-aerosol chemical mechanism (Bey et al., 2001; Park et al., 2004). Sulfur compounds, carbonaceous aerosols, and sea-salt emission and chemistry are accounted for and described by Park et al. (2004), Heald et al. (2005), and Alexander et al. (2005). Supplement Table S1 summarizes the yields of HCHO from several different VOCs and their respective atmospheric lifetimes over Europe for summertime conditions.

For OMI retrievals we use Level 2 (v003) geolocated data products (<http://mirador.gsfc.nasa.gov/>), while for SCIAMACHY daily swath data (version 1.2) (<http://www.>

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temis.nl/airpollution/ch2o.html) are used. Clouds in the satellite viewing scenes have been identified as the primary source of error in the retrievals (Millet et al., 2006); therefore, both satellite data are gridded at a  $0.25^\circ \times 0.25^\circ$  resolution with data pixels of cloud fractions  $<20\%$ . The detection limit of OMI HCHO SCD is  $\sim 8 \times 10^{15}$  molecules  $\text{cm}^{-2}$  (Curci et al., 2010). The uncertainty on a single HCHO slant column ranges 40–100 % (Chance and Kurosu, 2008), while the uncertainty on the AMF calculated with GEOS-Chem is estimated to be about 30 % for cloud fractions less than 0.2 (Millet et al., 2006; Palmer et al., 2006). The total uncertainty of a single HCHO vertical column ranges from 50 to 105 % (Chance and Kurosu, 2008; Curci et al., 2010). For SCIAMACHY, with the SCD detection limit of  $6.5 \times 10^{15}$  molecules  $\text{cm}^{-2}$ , the systematic error in the SCD retrieval is  $\sim 2.5 \times 10^{15}$  molecules  $\text{cm}^{-2}$  in the tropics and increases to  $8 \times 10^{15}$  molecules  $\text{cm}^{-2}$  at increasing latitudes (De Smedt et al., 2008; Stavrou et al., 2009b). The total uncertainty on SCIAMACHY retrieved monthly mean HCHO vertical column ranges between 20 and 40 % (De Smedt et al., 2008). When considering regionally and temporally averaged columns, the random error on the slant columns of both satellite sensors is reduced by the square root of the number of observations included in the mean.

## 2.2 Biogenic sources

It has been well documented (both in laboratory and field studies) that phytoplankton can emit several types of biogenic VOCs, such as isoprene and monoterpenes (Bonsang et al., 1992; Shaw et al., 2003, 2010; Gantt et al., 2009). Owing to their short lifetime and relatively high HCHO yield (Palmer et al., 2003, 2006), these non-methane VOCs can potentially contribute to local HCHO columns. It is a common practice to characterize marine emissions of VOCs by using remotely sensed surface chlorophyll *a* concentration ([Chl-*a*]) as a proxy for the phytoplankton abundance in the surface layer. However, satellite based retrievals of [Chl-*a*] are not sufficient to describe the phytoplankton abundance in the Mediterranean Sea. Due to strong vertical mixing, nutrients accumulate at the surface throughout the winter months. With

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the springtime increase in sea-water surface temperatures and incoming solar radiation, these stored nutrients can fuel biological productivity in the upper water column (Marty et al., 2002). By the summertime, the nutrients get depleted and strongly-stratified oligotrophic (lacking essential nutrients to support primary productivity) surface waters can no longer sustain plankton growth. Under such conditions, phytoplankton in the Western and Eastern parts of Mediterranean Sea move lower in the water column at  $\sim 50$  m and  $\sim 100$  m, respectively (Crise et al., 1999) to the depth that is usually not sampled by the satellites. Due to the seasonal formation of this deep chlorophyll maximum, satellite retrieval of [Chl-*a*] may not be an accurate representation of the full water column biomass. Because of such difficulties in remotely sensed [Chl-*a*] retrievals in the Mediterranean Sea, to get an accurate representation of the biomass of marine organisms within the water column we use column integrated net primary production (NPP,  $\text{g C m}^{-2} \text{d}^{-1}$ ) as a proxy for a marine VOC source. This data product is based not only on satellite derived [Chl-*a*], but also on sea surface temperature, and cloud-corrected incident daily photosynthetically active radiation in conjunction with a Vertically Generalized Production Model (VGPM) (Behrenfeld and Falkowski, 1997) and therefore believed to be an accurate proxy for phytoplankton biomass in oligotrophic regions. The 8-day averaged NPP products are obtained from [www.science.oregonstate.edu/ocean.productivity/standard.product.php](http://www.science.oregonstate.edu/ocean.productivity/standard.product.php) and regridded from  $9 \text{ km} \times 9 \text{ km}$  to  $0.25^\circ \times 0.25^\circ$  resolution.

## 3 Results

### 3.1 OMI AMF correction

Analysis of remotely sensed data reveals that the HCHO hot spot typically appears over the Mediterranean during the warmer seasons. Figure 1 shows that during January, the magnitude of HCHO VCD is low in all areas over the Mediterranean region ( $\sim 3 \times 10^{15}$  molecules  $\text{cm}^{-2}$ ) and is below the OMI detection limit. However, during the

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summer months VCDs are greatly enhanced over the western Mediterranean Sea particularly at the beginning of summer. Figure 1 also shows some spatial variations: the western part of the Mediterranean displays higher summertime HCHO columns compared to the eastern region. One of the possible reasons for such enhanced summertime HCHO columns could be the presence of mineral dust in a viewing path of the satellite. Due to its proximity to the Sahara Desert, there are frequent intrusions of large dust in the Mediterranean Sea area. Although dust events are largely variable, climatological records indicate a seasonal cycle coinciding with the dry season; specifically, a maximum occurs during spring in the Eastern Mediterranean and during summer in the Western Mediterranean (Moulin et al., 1998). Moreover, persistent dust haze conditions (typically lasting 1–3 days) impact the Western Mediterranean more frequently than the eastern part (Pye, 1992). Therefore, to understand enhanced HCHO columns over the Mediterranean Sea, we first examine the possible retrieval artifacts associated with Saharan dust transport over the region.

Figure 2a shows time series of 8-day averaged OMI AMF generated using GEOS-Chem and the LIDORT radiative transfer model. In this figure there is a pronounced reduction of AMFs from March to June for all three years examined. The AMF values depend on atmospheric scattering and the vertical distribution of the species. Therefore the presence of aerosols in the vertical atmospheric column should lead to a strong decrease of the AMF. When satellite retrieved HCHO SCDs are divided by the reduced AMF values, higher values for VCDs are attained (see Fig. 2b, c). However, it has recently been reported that GEOS-Chem may overestimate dust abundance for Saharan dust sources (Generoso et al., 2008). Such overestimation of dust AOD could cause excessive reduction in AMF values and increases in HCHO VCDs. Here we have followed recommendation of Generoso et al. (2008) and reduced Saharan dust emissions by a factor of three. Figure 2c shows that these corrected AMF values yield considerably lower OMI HCHO VCDs for the all three years. Figure 3 shows that corrected AMFs lead to significant reduction of the OMI retrieved HCHO columns for both the western and the eastern parts of the Mediterranean Sea. Comparison of Figs. 1

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and 3 shows that when the new AMF values are employed, HCHO column densities are lowered by ~40 % in June and by ~10 % in July and August. It should be noticed however, that despite the reduction in the original HCHO hot spot, there is still an enhancement in the HCHO columns confined over the water. This is a robust result with column values roughly a factor of 2 higher than the detection limit over the large areas of the Mediterranean Sea.

### 3.2 Possible marine biogenic sources of HCHO over the Mediterranean Sea

The Mediterranean is naturally oligotrophic (i.e., low nutrients and therefore low productivity), with an increase to ultraoligotrophic waters in the eastern section (Pedrós-Alió et al., 1999; Turley, 1999). However, during the winter, surface waters cool leading to a breakdown in the thermohaline circulation. This breakdown allows for vertical mixing between the deep-nutrient rich waters and the oligotrophic surface waters (Turley, 1999; Pedrós-Alió et al., 1999; Turley et al., 2000), especially in the North-western Mediterranean. Nutrients upwelled in winter facilitate primary production in the surface waters reaching highest levels in April, before decreasing again in summer. Figure 4 shows that in June, the western Mediterranean has a considerable amount of productivity ( $\sim 1300 \text{ mg C cm}^{-2} \text{ day}^{-1}$ ) while the Eastern part is fairly sparse ( $\sim 400 \text{ mg C cm}^{-2} \text{ day}^{-1}$ ). The enhancements of marine biological productivity in the Mediterranean and Atlantic Ocean (i.e., the Bay of Biscay, off the coast of Portugal, the coast of Italy and at the mouth of the Nile River Delta) viewed in June are diminished by August (see Fig. 4), leading to an ultraoligotrophic environment. Comparison with Fig. 3 shows that there is little correlation (either spatial or temporal) between the net primary productivity in the Mediterranean Sea and the atmospheric column concentrations of HCHO.

To estimate the possible contribution of marine biota to the remotely sensed HCHO VCD signal over the Mediterranean Sea, we use the method similar to Palmer et al. (2003) and estimated the amount of ocean-derived isoprene required to explain the retrieved column concentrations of formaldehyde. According to Palmer et al. (2006)

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HCHO yields from oxidation of pinenes are only about one third those of isoprene and have minor contribution to HCHO columns. Assuming a background HCHO concentration is due to methane oxidation and longer-lived VOCs, the HCHO VCD ( $\Omega_{\text{HCHO}}$ ) can be calculated as  $\Omega_{\text{HCHO}} = S \times E_{\text{iso}} + B$ , where  $S$  is the linear slope corresponding to HCHO yield from isoprene ( $1.9 \times 10^3$  s),  $E_{\text{iso}}$  is the isoprene emission rate, and  $B$  is the background HCHO concentration (Palmer et al., 2003). The remotely sensed  $\Omega_{\text{HCHO}}$  can be used to back-calculate the isoprene emission necessary for the observed HCHO. Palmer et al. (2003) showed that the assumption is valid in summer at midlatitudes for a high HCHO-yield and reactive (lifetime 30 min) parent VOC (i.e., isoprene). For the background HCHO concentration we use the lowest OMI-retrieved value ( $\sim 3.5 \times 10^{15}$  molecules  $\text{cm}^{-2}$ ) over the Mediterranean during the month of January. By solving the equation for  $E_{\text{iso}}$  we estimate that the lowest isoprene emission required to explain summertime maxima in the observed OMI HCHO column is  $\sim 10^{12}$  atoms  $\text{C cm}^{-2} \text{ s}^{-1}$ . This isoprene emissions rate is  $\sim 2$  to 3 orders of magnitude higher than recent estimates of marine isoprene emissions in the Mediterranean Sea (Liakakou et al., 2007) and outside the range of uncertainty due to variability in [Chl- $a$ ] and laboratory measured isoprene emission rates (Shaw et al., 2003, 2010; Palmer and Shaw, 2005; Gantt et al., 2009; Sabolis et al., 2010). Although this simplified approach is in no way revealing the actual marine isoprene emissions over the Mediterranean, it does provide a rough estimate of the contribution needed in order for primary productivity to be the major source of the remotely sensed HCHO VCD over the Mediterranean Sea. Therefore, based on the comparison of laboratory measured isoprene emission rates and the ones estimated using remotely sensed data, we conclude that marine primary productivity in the Mediterranean Sea is not likely to be an important source of the retrieved summertime vertical column densities of HCHO.

### 3.3 Comparison with the previous results

The summertime Mediterranean basin is directly under the descending branch of the Hadley circulation, driven by deep convection in the Inter-Tropical Convergence Zone

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(Lelieveld et al., 2002). Owing to cloud-free conditions and higher solar radiation intensity, VOCs in the air masses transported from the surrounding regions (e.g., Central Europe, Balkans) and distant areas (e.g., Asia and North America) are subject to intense photochemical degradation. The large-scale subsidence also limits upward dispersion of pollutants (Ladstätter-Weißmayer et al., 2003), causing strongest anthropogenic influence to be detected in the lower 4 km over the Mediterranean basin (Lelieveld et al., 2002). Previous in situ measurements and remotely sensed data revealed remarkably high HCHO mixing ratios over the Mediterranean (Lelieveld et al., 2002; Kormann et al., 2003; Ladstätter-Weißmayer et al., 2003, 2007; Klippel et al., 2011). In general, reported HCHO concentrations were highest in the marine boundary later (up to 1500 ppt) and decreased with increasing altitude (Kormann et al., 2003). GOME (Global Ozone Monitoring Experiment) satellite retrieved HCHO VCD averaged over July and August, 2001 was  $6.4 \times 10^{15}$  molecules  $\text{cm}^{-2}$ , with occasional enhanced values of  $1.1 \times 10^{16}$  molecules  $\text{cm}^{-2}$  in the Eastern Mediterranean (Ladstätter-Weißmayer et al., 2003). Over Crete (South East Mediterranean), monthly averaged HCHO VCD columns from GOME for 1996–2002 also showed highly enhanced monthly mean summertime values between  $4 \times 10^{15}$  and  $8 \times 10^{15}$  molecules  $\text{cm}^{-2}$  (Ladstätter-Weißmayer et al., 2007). Although previously reported data cannot be directly compared to the results of current study, it shows general consistency for highly elevated summertime concentrations of HCHO over the Mediterranean basin.

The exact reasons for such enhanced HCHO concentrations over the Mediterranean summer conditions (factor of 4 to 5 higher compared to pacific background troposphere, Lelieveld et al., 2002) are not well understood. The model simulations consistently underestimate HCHO mixing ratios over the Mediterranean Sea (Ladstätter-Weißmayer et al., 2003; Klippel et al., 2011). The discrepancy between model-predicted and measured HCHO concentrations over the Mediterranean region was suggested to be associated with the missing terpene chemistry (Ladstätter-Weißmayer et al., 2003) and/or incomplete characterization of air mass trajectories (Kormann et al., 2003; Ladstätter-Weißmayer et al., 2007; Scheeren et al., 2003).

However, recent airborne campaign covering an area from the Mediterranean region in the south up to the subpolar regions north of Norway revealed homogeneous distribution of formaldehyde everywhere, except over the Mediterranean, where strongly elevated summertime levels of HCHO were reported (Klippel et al., 2011). In fact, large discrepancies between model-predicted and measured HCHO concentrations over the marine boundary layer have been previously identified (Jacob et al., 1996). Although some measurement campaigns reported very low (50–250 pptv) HCHO mixing ratios over marine boundary layer, often without clear diurnal variation (Lowe and Schmidt, 1983; Mackay et al., 1996; Heikes et al., 1996), others report mixing ratios between 300 to 1000 ppt with a distinct diurnal cycle (Zafirou et al., 1980; Arlander et al., 1990, 1995; Ayers et al., 1997; Zhou et al., 1996; Weller et al., 2000; Singh et al., 2001; Fried et al., 2002). Such high mixing ratios (factor of 2 to 4 above what is typically predicted by photochemical models considering methane ( $\text{CH}_4$ ) as the only source, Logan et al., 1981), point to a possible missing HCHO source in marine boundary layer. Potential new mechanisms for the enhanced production of HCHO such as reaction of methylperoxy ( $\text{CH}_3\text{O}_2$ ) with hydroperoxyl radical ( $\text{HO}_2$ ) (Ayers et al., 1997; Weller et al., 2000; Elrod et al., 2001) were shown not to be sufficiently important to explain measurement-model discrepancies (Fried et al., 2003). Results of our study, based on the comparison of laboratory measured ocean-isoprene emission rates and the ones estimated using remotely sensed data, suggest that contribution of ocean-derived terpenes (Ayers et al., 1997) is also not likely to be a main source of HCHO in marine boundary layer. Nevertheless, it should be noted that today very large discrepancies (factors of 30 for isoprene and 2000 for  $\alpha$ -pinene) exist for marine VOC emission rates estimates based on the ambient measurements and laboratory data (Luo and Yu, 2010).

### 3.4 OMI and SCIAMACHY retrievals over different water bodies

As both OMI and SCIAMACHY sensors have been operational since 2005, a comparison of two different HCHO VCD data products for three years is possible. Figure 5 shows a time series of OMI and SCIAMACHY 8-day mean HCHO VCDs over the open

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ocean and isolated/semi-isolated water bodies. There is a consistent discrepancy between OMI and SCIAMACHY retrievals of HCHO columns in terms of magnitude, with OMI usually having higher values. This is especially true for pristine regions with oligotrophic waters (e.g., northwest and southern Pacific Ocean) where the sensor differences are often beyond the retrieval uncertainty. Compared to SCIAMACHY, OMI HCHO columns display greater seasonality in isolated/semi-isolated water bodies such as the Mediterranean Sea, Gulf of Mexico, and Black Sea near anthropogenic pollution and terrestrial biogenic sources. Assuming that there are no retrieval artifacts in either sensor, the most likely reason for this difference is the equatorial overpass times of the sensors, ~13:30 for OMI and 10:00 for SCIAMACHY. As HCHO is photochemically-produced, afternoon higher values are expected. Retrievals of HCHO SCDs from OMI and SCIAMACHY (see Supplement Fig. S1) display behavior similar to VCDs; however, as discussed in Sect. 2.1, slant columns are derived for the two satellite sensors using different spectral windows and retrieval algorithms.

The difference in seasonality between the two sensors shown in Fig. 5 is particularly evident over the Mediterranean Sea region, where the corrected OMI HCHO columns are higher than SCIAMACHY in the summer and lower in the winter. As the measurement data and model results of HCHO and VOC over marine regions are sparse, further research is needed to better constrain SCIAMACHY and OMI retrievals of HCHO columns and identify the reason for the discrepancies over different water bodies.

## 4 Conclusions

In this study, we use the Ozone Monitoring Instrument (OMI) and SCanning Imaging Absorption SpectroMeter for Atmospheric CartograpHY (SCIAMACHY) remotely sensed formaldehyde (HCHO) vertical column densities (VCD) for the years 2005–2007 to explore unexpectedly high concentrations of HCHO observed over different parts of the Mediterranean Sea. The summertime enhancement of HCHO columns in OMI retrievals is considerably diminished when Saharan dust sources in GEOS-Chem

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are reduced by a factor of three following the recommendation of Generoso et al. (2008). The new values of aerosol loadings and the corrected air mass factors (AMFs) lead to a reduction of the summertime “hot spot” in OMI retrievals of HCHO over the Mediterranean Sea; however, even after the correction enhanced HCHO columns over the Mediterranean are still present. Future studies should examine OMI HCHO columns when GEOS-Chem model is driven by the Goddard Earth Observing System Model, Version 5 (GEOS-5) assimilated meteorological fields.

In addition to AMF corrections due to the presence of mineral dust over the Mediterranean Sea, possible sources associated with local photochemical production of HCHO are also explored. Marine biological sources of VOCs such as phytoplankton production of isoprene and monoterpenes do not seem to be probable sources for the enhanced HCHO concentrations over the Mediterranean Sea. The back-calculations show that marine isoprene emissions rates required for explaining the observed HCHO columns are several orders of magnitude larger than previously estimated in laboratory experiments. It is unlikely that oligotrophic waters of the Mediterranean are capable of supporting such high emission rates.

Downwind from polluted continental regions, satellite retrievals of OMI HCHO columns show a defined seasonal cycle with a winter minimum and summer maximum. Although this finding points to a photochemical production of HCHO over water bodies (e.g., Mediterranean Sea) likely involving continental sources, based on this study alone such a relationship cannot be ascertained. Detailed studies with chemical transport models in conjunction with measurements may be required to fully explore the complex mechanism of HCHO formation over the Mediterranean and its implications for the air quality in the region.

Comparisons of OMI and SCIAMACHY HCHO columns are also inconclusive; the data analyses showed that OMI and SCIAMACHY agree fairly well over highly productive upwelling regions. In contrast, a large discrepancy between the two satellite sensors was found over oligotrophic water bodies and regions near anthropogenic pollution sources. The discrepancy between OMI and SCIAMACHY was particularly large

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for the Mediterranean Sea, which is both oligotrophic and near anthropogenic pollution sources in Europe. We suggest that future research is needed to improve the quantification of the satellite retrievals of the HCHO column concentrations, particularly over the marine environments.

**Supplementary material related to this article is available online at:**  
<http://www.atmos-chem-phys-discuss.net/11/17913/2011/acpd-11-17913-2011-supplement.pdf>.

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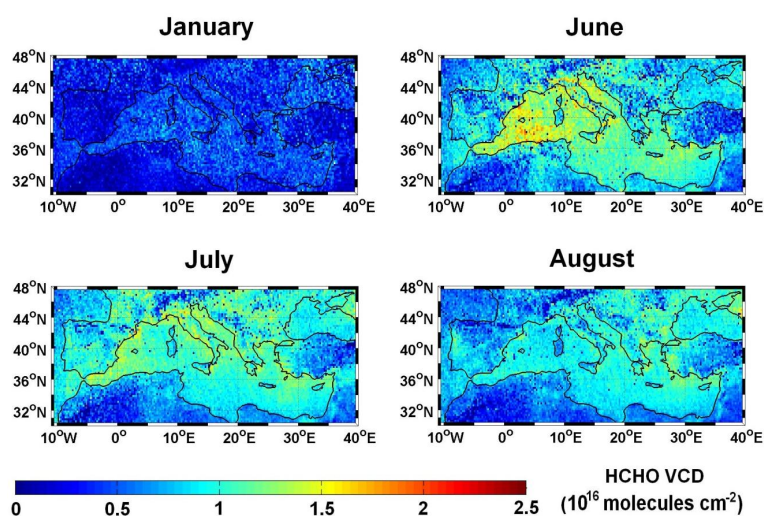
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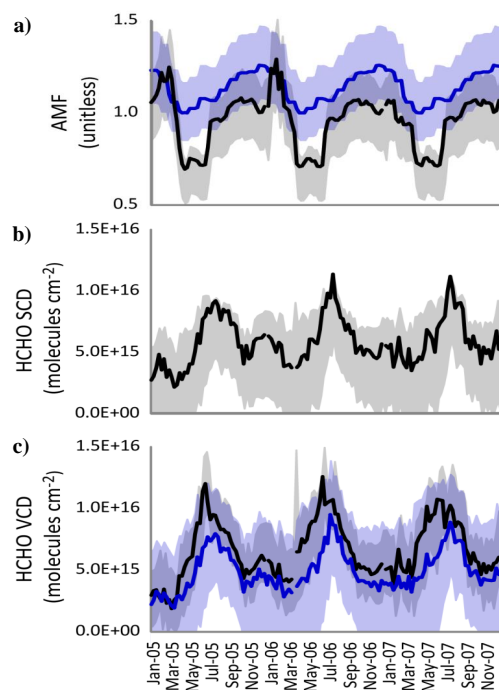
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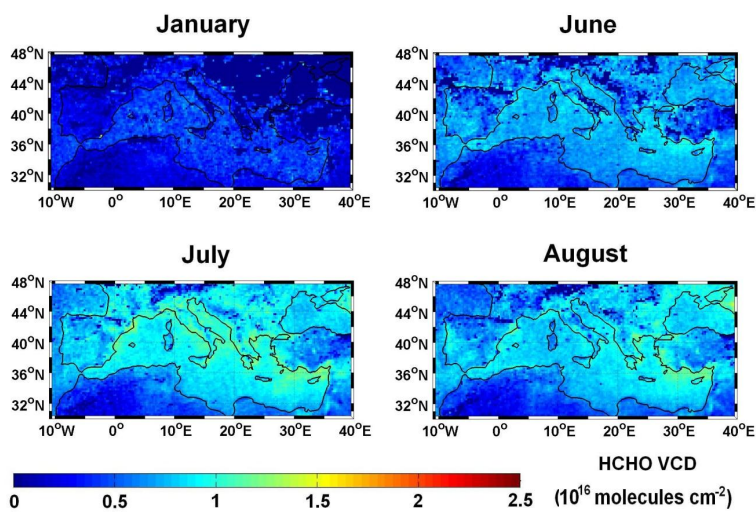
**Fig. 1.** Monthly averaged (from 2005 to 2007) OMI retrieved formaldehyde vertical column densities.

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**Fig. 2.** Time series of 8-day averaged OMI HCHO (a) air mass factor, (b) slant column, density, and (c) vertical column density from January 2005 to December 2007 for the standard (black) and corrected (blue) datasets. The data was averaged over entire Mediterranean Sea. Shaded area represents one standard error about mean observation.

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**Fig. 3.** Monthly averaged (from 2005 to 2007) retrieved formaldehyde vertical column densities. The VCDs are recalculated using corrected AMF values. See text for more details.

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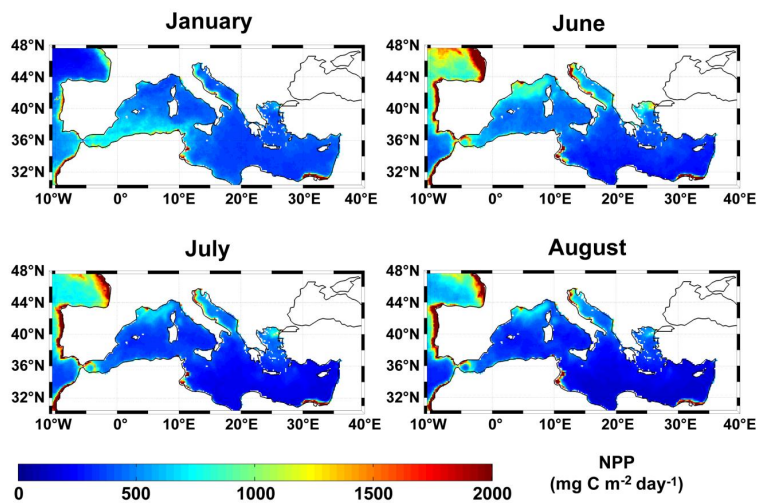


Fig. 4. Monthly averaged (from 2005 to 2007) net primary production (NPP).

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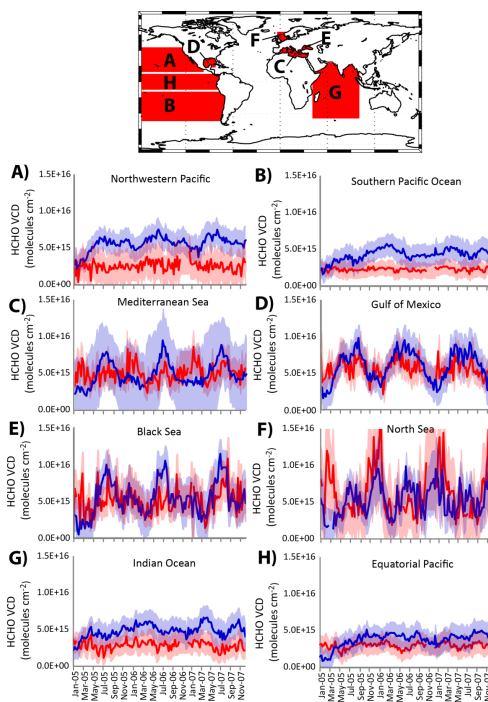


Fig. 5. Time series of 8-day averaged HCHO VCD from SCIAMACHY (red) and OMI (blue) for January 2005 to December 2007. Shaded area represents one standard error about mean observation. The areas selected are highlighted in red in the top two panels: (A) northwestern Pacific Ocean, (B) southern Pacific Ocean, (C) Mediterranean Sea, (D) Gulf of Mexico, (E) Black Sea, (F) North Sea, (G) Indian Ocean, and (H) equatorial Pacific Ocean. Note that the OMI VCD time series in (C) uses the corrected values.

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