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Variations and photochemical transformations of atmospheric constituents in North China

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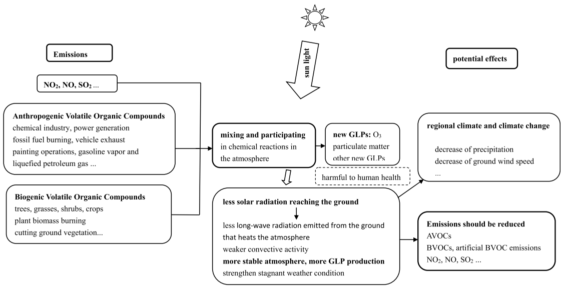
GRAPHICAL ABSTRACT



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ABSTRACT

To study air pollution and chemical transformation in North China, annual and seasonal variations of the concentrations of atmospheric constituents were analyzed for four representative sites in three different types of regions (two agricultural, Beijing and surroundings, atmospheric background) in North China during 2005–2015. Satellite-derived vertical column densities (VCDs) of NO_2, SO_2, O_3, HCHO, and aerosol optical depth (AOD) over the four sites were used together with ground-based radiation and meteorological measurements at each site and, at one of them (Xinglong), ground-based observations of NO_2, SO_2, O_3 and $PM_{2.5}$ concentrations. The temporal variations of UV loss in the atmosphere and VCDs of NO_2, SO_2, O_3 and HCHO were investigated together with the relations between these. Based on the analysis, a photochemical link relating the production of $PM_{2.5}$ and O_3 in North China was proposed and confirmed. In particular the role of volatile organic compounds (VOCs) in chemical and photochemical reactions is found to be prominent in the summer. Suggestions for air pollution control in North China are given, e.g., to reduce anthropogenic VOC emissions and to prevent artificial enhancements of biogenic VOC emissions.

1. Introduction

Heavy air pollution has been an important issue for Chinese people and the Chinese government, especially in recent years (e.g., Zheng, 2017). With the fast development of economy, transport and urbanization, more and more substances in the form of gases, liquids and particles (**GLPs**) are emitted and/or produced. The dominant GLPs are nitric oxide (**NO**), nitrogen dioxide (**NO_2**), sulphur dioxide (**SO_2**), ozone

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(O_3), anthropogenic volatile organic compounds (**AVOCs**), biogenic volatile organic compounds (**BVOCs**), primary aerosols such as dust, black carbon (**BC**) and organic carbon (**OC**), as well as secondary organic aerosols (**SOA**) and secondary inorganic aerosols (**SIA**). These species take part in chemical and photochemical reactions (**CPRs**) involving OH radical and H_2O (water and/or water vapor) initiated by solar ultraviolet (UV) and visible radiation (Bai, 2011, 2017a).

The CPRs result in complicated changes in the chemical composition of gases, liquids and particles and conversion between gas, liquid and particle phases. The reactive OH radical is mainly produced through O_3 photolysis ($O_3 + hv \rightarrow O_2 + O\ (^1D)$, $O\ (^1D) + H_2O \rightarrow 2OH$), and the photolysis of HNO_2, HNO_3, H_2O_2 by UV radiation. The OH radical is involved in almost all **CPRs** in the atmosphere. Molecules react with OH, but they do not consume UV energy directly. The products may be oxidized in the atmosphere and the second and third generation products may absorb UV radiation. Several recent studies show that water vapor absorbs near-UV radiation (Du et al., 2013; Wilson et al., 2016). Serving as both reactors and catalysts in atmospheric homogeneous and heterogeneous reactions, water and water vapor play important roles in continuous energy consumption and transfer, e.g., reacting with SO_2, NO_2, VOCs, formic acid (Luo et al., 2009), aerosols (Cheng et al., 2016), etc., and are recycled rapidly during daytime. For example, water is important as a catalyst in the reaction of HCOOH with OH radical, and as a reactor in aerosol water chemistry in northern China (Luo et al., 2009; Cheng et al., 2016). UV energy is absorbed directly by some GLPs, such as NO_2, SO_2, O_3, α-dicarbonyl compounds, ketone, benzaldehyde, NOCl, BC, and/or consumed by other GLPs (without direct UV absorption). During CPRs, these other GLPs, including various VOCs such as isoprene and monoterpenes, and aerosols, utilize UV energy or chemical energy from OH radicals, water and/or water vapor, and the GLPs mentioned above (Bai, 2009, 2011, 2017a, and references therein). Numerous VOCs and their oxidation products having different absorption spectra and different roles in CPRs have been reported (Bai, 2011). During these processes, OH, H_2O, BVOCs and AVOCs play a vital role in the variation of the concentrations of atmospheric GLPs, the intensity of UV radiation, and GLP/radiation interactions, which is the main reason for the interesting phenomenon that UV absorption is strongly correlated with "water vapor absorption" (Bai, 2009).

Formaldehyde (**HCHO**) is formed in the photochemical oxidation of methane and higher hydrocarbons of both natural and anthropogenic sources. It is an important atmospheric intermediate produced by the oxidation of BVOCs and AVOCs. It is also emitted by fossil fuel combustion and biomass burning (Gratien et al., 2007). Its subsequent decomposition by photolysis and reaction with OH radical serves as a source of HO_2 radical. The main loss processes for HCHO are photolysis by UV radiation ($<$ 370 nm) and reaction with OH radicals (Fried et al., 1997). Thus, UV radiation is an important energy source to trigger CPRs and the resulting changes in the concentrations of GLPs. In this paper, the intensity of UV radiation at the ground and the absorption and scattering by GLPs in the atmosphere are investigated together at four stations in North China.

The objective of this paper is to investigate some of the basic mechanisms that produce air pollution and the primary substances that should be controlled to reduce severe air pollution in China. This challenging issue is addressed by analyzing trace gases and solar radiation at four representative stations in North China. The loss of UV energy in the atmosphere associated with the absorption and scattering by trace gases (anthropogenic and natural) and aerosols at these sites is studied using ground-based and satellite observations of GLP concentrations and UV radiation during a period of 10 years. Their year-to-year variations provide information on CPRs in which these GLPs are involved. Suggestions are made to contribute to the reduction of current severe air pollution events, in particular the concentrations of particulate matter (**$PM_{2.5}$**) and O_3 in North China.

Table 1
Observational periods for solar radiation at 4 stations in North China.

Stations	1st	2nd	3rd	4th
YC	2005/07/08–07/17	2005/12/12-12/26	2006/04/03–04/17	2006/10/01–10/17
LC	2005/07/19–07/28	2005/11/27–12/11	2006/04/18–05/03	2006/09/14–09/30
XH	2004/09/12–2005/07/12		2005/09/12–2006/10/31	
XL	2005/09/10–11/11	2006/02/19–03/23	2006/05/12–07/04	2006/08/11–09/02

2. Measurements and methods

During 2005, 2006, measurements of solar radiation (including UV, visible, global, direct, etc.) and meteorological (temperature and humidity) parameters were carried out at 4 stations in North China, namely, Yucheng (**YC**: 36.83N, 116.57E, 23.0 m asl), Luancheng (**LC**: 37.89N, 114.68E, 50.1 m asl), Xianghe (**XH**: 39.78N, 116.95E, 95.0 m asl) and Xinglong (**XL**: 40.38N, 117.58E, 960.0 m asl) (The map is shown in Bai, 2013). Each of these stations is operated by different institutes of the Chinese Academy of Sciences (**CAS**) (Bai, 2013, 2017a, see Table 1). The stations are representative for agricultural conditions (YC and LC), Beijing and its surroundings (XH), and clean atmosphere (mountain) (XL). At the Xinglong site, an atmospheric background station in North China, solar radiation, surface concentrations of trace gases (NO, NO_2, SO_2, O_3) and **$PM_{2.5}$**, and meteorological parameters have been routinely measured since 2005 (Bai et al., 2015a). Solar global radiation (285–2800 nm) and UVB were measured using a CMP21 Pyranometer and a UVS-B-T UV Radiometer (280–315 nm) (Kipp & Zonen Company, the Netherlands) since January 2007 and July 2007, respectively. Monthly AOD and vertical column densities (**VCDs**) of HCHO, NO_2, SO_2, and O_3 at the four stations were derived from satellite data. The trace gas VCDs for the period from January 2005 to December 2015 were obtained from the Ozone Monitoring Instrument (**OMI**). Monthly O_3 VCDs were calculated from averaged OMI observations (http://www.temis.nl/protocols/o3col/overpass_omi.html) within 100 km around each station. HCHO and NO_2 VCDs obtained from OMI were averaged monthly on a grid of 0.25° resolution, considering measurements for solar zenith angle (SZA) $<$ 70° and cloud fraction (CF) $<$ 40% (De et al., 2015). Monthly OMI SO_2 VCDs were averaged over an area within a radius of 50 km around each station, SZA $<$ 65° and CF $<$ 30% (Theys et al., 2015). The absorption cross section of formaldehyde is from Meller and Moortgat (2000). The absorption cross sections of NO_2, SO_2 and O_3 are from the HIgh-resolution TRANsmission molecular absorption database (HITRAN, http://hitran.iao.ru/home). Monthly aerosol optical depth **(AOD)** was derived from the L2 AOD data retrieved from the AATSR (Advanced Along Track Scanning Radiometer) on the European Space Agency (**ESA**) environmental satellite ENVISAT. AOD L2 is the default AOD product retrieved from AATSR L1 data using FMI's AATSR Dual View (ADV) algorithm (Kolmonen et al., 2016; Sogacheva et al., 2017) with a resolution of $10 \times 10\,km^2$ on a sinusoidal grid (L2) for cloud-free conditions. The L2 product includes per-pixel uncertainty estimates (Popp et al., 2016). ADV-retrieved AOD data (version 2.31) used in the current study are available for the period from January 2005 until April 2012, when contact to the satellite was lost and its mission ended.

Absorption and scattering by GLPs in the atmosphere can be separated by considering the various UV radiation measurements at the ground, as described in Bai (2017a). The total UVA and UVB (290–400 nm) radiation under all sky conditions is described by:

$$UV = (A_1 e^{-kWm} + A_2 e^{-S/Q} + A_0)\cos Z \tag{1}$$

where k is the average absorption coefficient of water vapor (0.70–2.845 μm). W is the total water vapor content in the atmospheric column (cm), $W = 0.021E$, E is water vapor pressure at the ground