

1. Introduction

1.1 Background

Urban zones represent areas in which significant amounts of gaseous pollutants and particulate matter are released into the atmosphere. The Houston-Galveston Brazoria Area (HGB), located close to the Gulf of Mexico, is the fourth largest metropolitan area in the United States. Among major U.S. metropolitan areas, the HGB is the only one located in a subtropical region with extended hot and humid periods. Solar radiation is intense. Also, conditions with suppressed atmospheric mixing may occur. This specific climatology, along with strong emissions of primary species (carbon monoxide [CO], volatile organic compounds [VOCs] and nitrogen oxides [NO_x ; $\text{NO}_x = \text{NO} + \text{NO}_2$]) favor strong photochemical processes. In reactions involving ozone (O_3), hydroxyl (OH^\bullet) and nitrate (NO_3^\bullet) radicals, these primary emissions cause substantial formation of secondary species such as O_3 , peroxyacetylic nitric anhydrides (PANs) and other trace gases [Atkinson, 2000; Jenkin and Clemmshaw, 2000]. In these reactions peroxy radicals (RO_2) will be formed, which in turn will cause the conversion of NO to NO_2 and subsequently the formation of O_3 . With the degradation of VOCs, carbonyls will also be formed. These, in turn, may be photolyzed (e.g., formaldehyde) or oxidized by OH^\bullet and enhance PAN formation. Additionally, in the course of their oxidative degradation, the relatively volatile VOCs are transformed into higher boiling species that show a strong tendency to adhere to or to form particulate matter [Hoffmann *et al.*, 1997; Griffin *et al.*, 1999; Matsunaga *et al.*, 2003]. This secondary organic aerosol also activates atmospheric chemical feedback mechanisms, enhances cloud formation, and modifies the earth's radiation budget [Brasseur *et al.*, 1999].

The land-sea breeze system basically determines the distribution of trace gases in the HGB. In addition, the diurnal variation of the planetary boundary layer controls the accumulation of primary emitted species close to the surface and also decouples ozone enriched layers aloft during nighttime. Areas like HGB frequently suffer from severe loadings of a variety of air pollutants. High concentrations of primary toxic species and photooxidants in both the gas and particle phases can result in serious health effects, as well as ecological damage and economic losses. Photochemical smog episodes are common phenomena in the HGB. Comparisons with a number of other major US metropolitan areas indicate that while peak O_3 levels have decreased significantly in Los Angeles and also appreciably in the HGB over the last few years, it seems that little improvement in the number of exceedances of peak ozone levels has been observed in the HGB (see Fig. 1). Although several U.S. cities have higher particulate levels than does Houston, the higher levels of a number of hazardous pollutants may exacerbate the health effects of area particles.

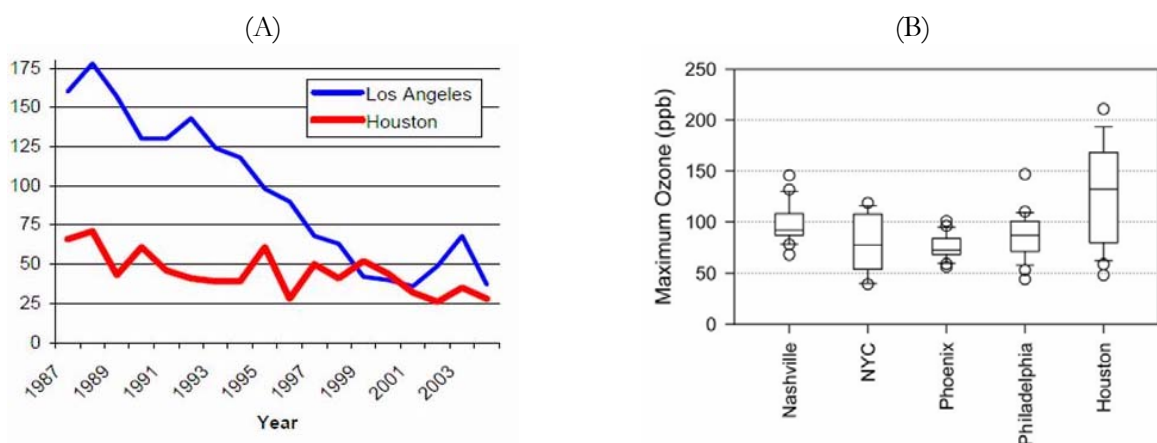


Figure 1: (A) Annual days exceeding federal one-hour ozone standard [HCPC, 2005]; (B) distribution for the peak ozone concentration observed on aircraft flights in five US cities [Kleinman *et al.*, 2002].

The Texas Air Quality Study 2000 campaign (TexAQS 2000) provided a wealth of data about the unique air chemistry and meteorological conditions that prevail in the Houston area. These studies revealed that the HGB often encounters critical loadings of a variety of species [Roberts *et al.*, 2001, 2003; Karl *et al.*, 2003; Ryerson *et al.*, 2003; Berkowitz *et al.*, 2004; Stutz *et al.*, 2004]. Investigations mainly focused on the rapid O_3 formation processes, which appear to be associated with releases of highly reactive VOCs from industrial facilities [Kleinman *et al.*, 2002 and 2004; Daum *et al.*, 2003; Ryerson *et al.*, 2003; Daum *et al.*, 2004; Berkowitz *et al.*, 2005; Springston *et al.*, 2005], and on the related HGB meteorological conditions that promote O_3 formation [Berkowitz *et al.*, 2004; Banta *et al.*, 2005]. These findings were supported by numerical modeling [Jiang and Fast, 2004]. A few recent publications address the formation of secondary species other than O_3 . For example, Wert *et al.* [2003] and Dasgupta *et al.* [2005] discuss measurements of oxygenated hydrocarbons, and Russell and Allen [2005] carried out the first modeling studies of the formation of SOA due to biogenic hydrocarbon precursors.

The objective of the TRAMP (TexAQS II Radical Measurement Project) is to support the TexAQS II field experiment with a selected ground-based supersite which will bring together a broad suite of instrumentation to collect a comprehensive data set which will allow to elucidate fast radical chemistry occurring under high pollution events typical for the HGB. The study will be accomplished by an analysis of radical sources and sinks (and production and loss rates) as identified by a steady-state time dependent photochemical box model.

1.2 Project Goals

The project addresses the determination and quantification of sources and sinks for radicals in the urban atmosphere of Houston during the TexAQS II field campaign 2006. This is important for a better understanding of the formation processes of secondary species in the Houston area.

Fig. 2 describes in principle the fast reaction cycles involved in the formation of secondary species as well as the removal mechanisms from those cycles for nitrogen and carbon containing species. The hydroxyl radical (OH) is the most important oxidant in the atmosphere and controls the atmospheric lifetimes of most trace gases. OH is produced in photolysis processes of ozone (O_3), formaldehyde (HCHO) and nitrous acid (HONO). OH initiates oxidation reactions with NO_x , CO,

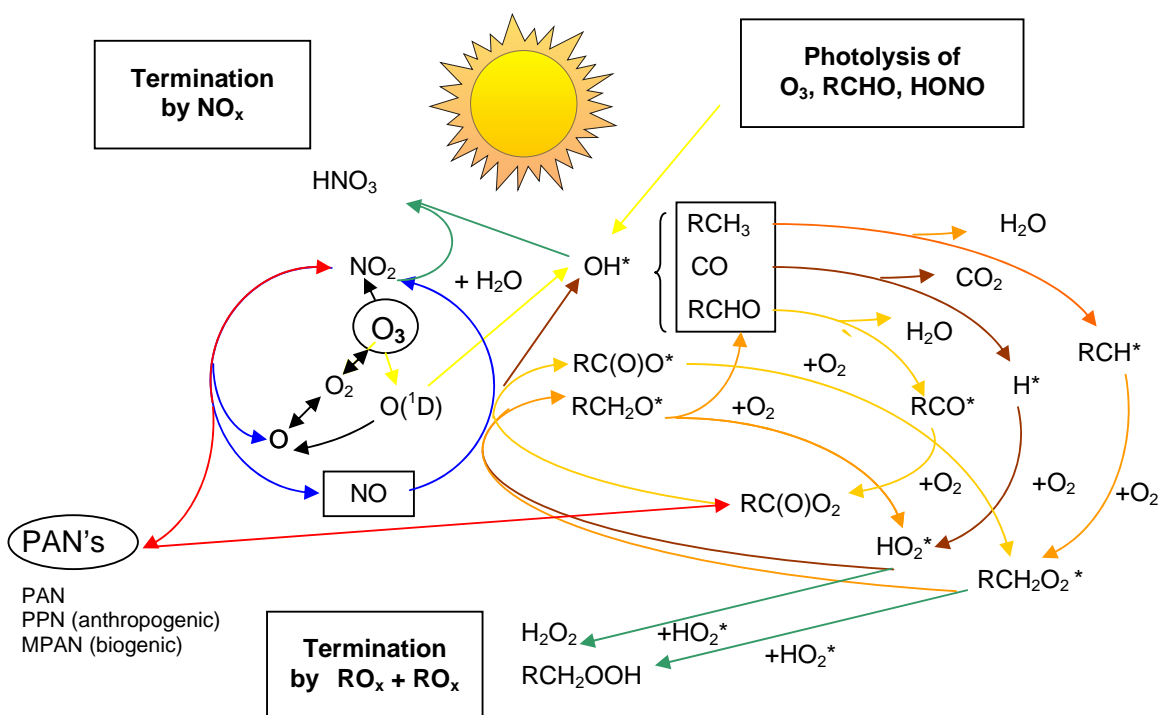


Figure 2: Daytime photochemical Processes

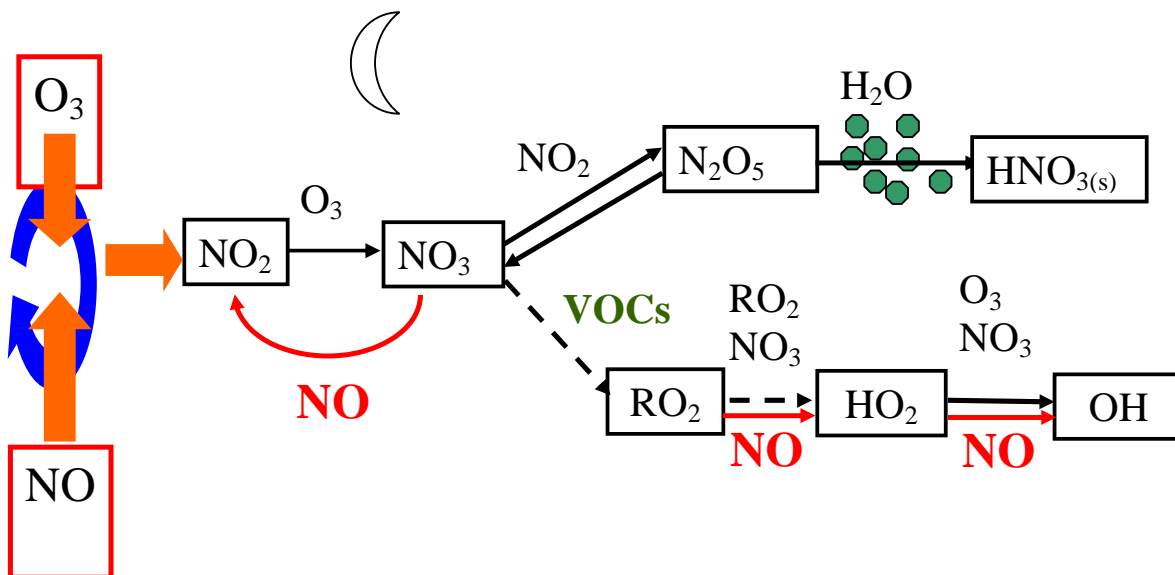


Figure 3: Nighttime radical chemistry.

anthropogenic and biogenic VOCs. These reactions form peroxy radicals (RO_2) which in turn will cause the conversion of NO to NO_2 and subsequently the formation of O_3 . Within the degradation of VOC also carbonyls will be formed which either may be photolyzed (e.g. formaldehyde) or oxidized by OH and finally contribute to the formation of peroxyacetic nitric anhydrides (PANs). Loss mechanisms for OH involve reactions between peroxy radicals leading to hydrogen peroxide (H_2O_2) and organic peroxides, e.g. methylhydroperoxide (MHP) and hydroxymethylhydroperoxide (HMHP), and reactions with NO_2 leading to nitric acid (HNO_3) and PAN.

Figure 3 describes radical chemistry occurring during nighttime conditions. The main starting point in the absence of solar radiation is the formation of NO_3 through the conversion of NO to NO_2 and subsequently to NO_3 in reactions involving O_3 . NO_3 may either react with NO_2 or a suite of VOCs including aldehydes, alkanes, short lived alkenes, and fast reacting terpenes. This way either nitrogen compounds may be removed through formation of HNO_3 on particles or OH radicals can be produced which in turn interact in fast reactions described in Figure 2.

The TRAMP project is designed to determine photochemical processing which is representative for the urban boundary layer area of Houston and to study the following research issues:

- What are the main sources and sinks for radicals in the urban air of Houston?*
- What processes determine the radical budget in the urban air of Houston?*
- What are the impacts with regard to the formation of secondary species?*
- What are the anthropogenic vs biogenic contributions in photochemical processes?*

In order to address these research issues a ground-based measurement system was set up for the TexAQS II intensive in August and September 2006. This site was equipped with state-of-the-art techniques to collect a comprehensive data set covering meteorological parameters, gas-phase chemistry using in-situ and long path instrumentation, physical and chemical aerosol properties including analysis of inorganic and organic aerosol content, and highly resolved measurements of the atmospheric radiation field including a wide range of photolysis rates which are critical for photochemical processes. This field experiment will be accomplished by an analysis of radical sources and sinks (and production and loss rates) as identified by a steady-state time dependent photochemical box model.