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Weekend/weekday differences of ozone, NOx, NMHC in São Paulo Metropolitan Region (MRSP)

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EXTENDED ABSTRACT

Ozone and inhalable particulate matter (PM_{10}) are the most important air pollutants in the Metropolitan Region of São Paulo (MRSP), Brazil (figure 01). The MRSP is located 23ºS and 46ºW, in the Southeastern portion of Brazil. It possesses an area of 8.051km² with a population of 17 million inhabitants and about 7 million registered vehicles. The urban area is placed, practically, in the Basin Sedimentary of São Paulo, whose main valley is of the River Tietê, guided in the direction east-west, with an average altitude of 720 meters and an extensive plain of flooding. This basin is surrounded to the north by the Mountain range of the Cantareira, also guided in the direction east-west and with altitudes that reach up to 1.200 meters and to the southeast for the reverse of the Mountain range of the Sea with altitudes that, in general, exceed the 800 meters. It is distant about 45km from the Atlantic Ocean (CETESB, 2005).

The formation of the ozone in the troposphere begins with the NO2 photolysis, and then the product of that, NO, reacts quickly with O3 to regenerate the NO2. In that way, the O3 stays in a stationary state that depends on the speed of NO2 photolysis and on the reason [NO2]/[NO]. If there isn't other process that transform NO in NO2, the concentration of ozone would not increase significantly. However, in the presence of the volatile organic compounds, the concentrations of ozone increase once NO is converted to NO2 due to the formation of radicals. The speed of ozone formation depends on the amount and of the reactivity of each one of those compounds (CETESB, 2002).

The ozone is not a pollutant emitted directly by the sources, but formed in the atmosphere through reaction among the volatile organic composites (VOCs) and oxide of nitrogen - NOx (where NOx = NO + NO2) in presence of solar light. Although beneficial in the stratosphere, where it constitutes a protecting layer against the harmful effects of the ultraviolet radiation, in the low troposphere it has toxicological effects when in contact with a living being. Besides the complexity of the system of chemical reactions, meteorological and topographical factors determine where it will occur the highest concentration of ozone, Many times the maximum concentration of ozone occur in a place without significant source of pollutants.(FINLAYSON-PITTS & PITTS, 1993, 1997).

The aerosols are solid or liquid particles in suspension in the atmosphere. The atmospheric aerosol particles are constituted by a mixture of primary origin (direct emission of the source) and secondary (transformation gas - particle) compounds. The aerosol particles possess sizes that vary of nanometers (nm) to the sets of ten of micrometers (μm) of diameter. The inhalabe particulate matter is divided in two modes: the fine mode with particles with aerodynamic diameter smaller than 2,5μm and the coarse mode, with particles greater than 2,5μm and smaller than 10μm (SEINFELD and PANDIS, 1998).

The aim of this work is to present an investigative study about the weekend effect on tropospheric ozone formation in MRSP. Ozone concentrations data were gathered from the Air Quality Monitoring Stations Network operated by the State of São Paulo Environmental Agency (CETESB, 2005). Levels of pollutants concentrations measured in a determined monitoring station, occurred due to several factors related to the location of this station and the emission sources that affect it. Among the factors that may influence the monitoring results, it is possible to remark the proximity of roadways, the use and occupation of the soil in near areas, etc. The station of Ibirapuera, IB,

was chosen to present usually ozone concentrations higher than the national air quality standard, and is localized approximately 50m from the main roads, that are streets of high traffic, and the Pinheiros Station (PN), that is close to a road of heavy vehicular traffic. The data base for HCNM was available only for the Sao Caetano do Sul air quality station (SCS), localized in thee MRSP. In the stations PN and IB are measured the following parameters: inhalable particles (PM10), sulfur dioxide, nitrogen oxides, ozone, carbon monoxide, wind direction and speed, relative humidity, temperature, atmospheric pressure and solar radiation (global and ultraviolet). The measurement methods of the parameters can be seen in Table 01. In SCS station are also measured the HCNM and CH4.

All these factors determine the representative scale of the station that should be considered concerning the monitoring objectives. The temporal distributions suggest that maximum ozone concentrations occur between August and October (figure 03). The typical daily duration of high ozone concentrations is short, usually between 1:00 and 4:00 pm. The weekend effect of higher observed ozone concentrations when compared to values observed on weekdays, may be related to the relatively low concentrations of ozone precursors such as nitrogen oxide ($NOx=NO+NO_2$) and volatile organic compounds (HCNM) at weekends. This behavior has been reported in some areas in America since the 1970s (CLEVELAND et al., 1974; LEBRON, 1975; ELKUS and WILSON, 1977). This phenomenon has caused general interest because the weekend effect presents results related to a natural atmospheric experiment for ozone precursor chemicals (ALTSHULER et al., 1995). The weekend effect combined with change of emission inventories of ozone precursors might imply whether ozone formation was NOx or HCNM control limited. Several recent studies on the weekend effect have tried to analyze the causes of the weekend effect and to find effective ozone control strategies. Weekend/weekday differences of ozone, ozone precursors and PM_{10} concentrations, traffic rush time and afternoon peak ozone time were compared. The possible causes for the weekend effect were discussed. The analysis of ozone in Pinheiros Air Quality Station showed that the concentrations at weekend were about 24% higher than those on weekdays while the concentrations of O_3 precursors and PM_{10} were higher at weekday in MRSP (figure 03), as observed in the air quality monitoring stations. HCNM sensitivity for ozone formation and a decrease in NOx emissions at weekend can explain the weekend effect in MRSP. Less scatter of sunlight due to lower fine particle concentration at weekend can be another possible cause to the enhanced in ozone formation.

The hourly variation of CO can be used as a tracer of the vehicular emissions (figure 02) in São Paulo where more than 90% of the pollutant is due to emission associated to the fossil fuel burning.

In Figure 04 is shown the inversely proportional relationship between the NO and O3 during the weekday and weekend periods. Larger concentrations of ozone occurred in the Ibirapuera station (figure 04a) for the two periods in comparison with Pinheiros station (figure 04b), explained by the smallest concentration of NO that was observed in the Ibirapuera station. For the period of the week a characteristic increase in the concentration of NO happened at 08 am and at 7 pm explained by the increase of the flow of self-driven vehicles that are the main sources of NO, and the meteorological conditions. For the period of days of the week the concentration of NO is on average 27% larger than that on the weekend that affects the concentrations of O3 whose medium values were 24% larger than the concentrations that happened in the weekend period.

Opposite to what happened in Pinheiros station, that presented a decrease in the concentration of O3 for the weekend, the Ibirapuera station didn't present significant difference between the weekday periods and weekend. An explanation for the non existence of that difference among the periods is attributed to the fact that the Ibirapuera station is more distant of the sources of pollutants precursors for the formation of ozone (it isn't near streets of high traffic). With a detailed analysis of Figure 04, it can be observed that the ozone average cycle presents a peak during the weekday period at 2 pm with $74.5 \mu g.m^{-3}$ (Pinheiros peak at 2 pm with $55.2 \mu g.m^{-3}$). During the weekend period the concentration is

smaller and the peak of ozone happened at 3 pm with 71.3µg.m^{-3} (Pinheiros peak at 3 pm with 59,7µg.m^{-3}).

In Figure 05 can be observed a smaller concentration of NO2 and a larger concentration of O3 for Ibirapuera station (figure 05a) in comparison to Pinheiros station (figure 05b), what reinforces the hypothesis of the atmosphere to be cleaner. A strong decrease in the NO2 concentration in the first hours of the day was observed, associated to the decrease of the vehicular traffic. The concentrations of NO2 during the week were on average 20% larger (with two characteristic peaks at 10 am with 72.1µg.m^{-3} and at 7 pm with 75.4µg.m^{-3}) in comparison to the weekend for the Pinheiros station.

An explanation for the fact that the concentration of O3 was on average 24% higher during the weekend is based on the existence of the precursors of ozone formation in ratios different from that found during the weekdays, for the Pinheiros and Ibirapuera station. The NO2 presented smaller concentratios (in the order of 30µg.m^{-3} less), but there was a decrease more accentuated in the concentration of NO (of the order of 50µg.m^{-3}). Due to the proximity of the issuing source of NOx the ozone that is produced is quickly consumed by the high concentration of NO. With the decrease of the NOx concentration in the weekend and the atmosphere being cleaner due to decrease of the concentrations of the PM10 and CO, it may happen an increase in the photolysis of NO2 and consequently an increase in the concentration of O3.

In the figure 06 is presented the variation of HCNM and O3, with the available data of the São Caetano do Sul station. There are two characteristic peaks observed about 08 am and an increase starting from 6 pm, associated with the flow of vehicles.

In general it is observed that the concentration of O3 was larger in the weekend period in the Pinheiros station (about 24% larger), and for the Ibirapuera station the concentration of O3 didn't present significative difference between the weekday and weekend periods. The differences are associated with the characteristics of the local measurements, especially with the proximity of roads of high traffic. Similar results were found by QIN, et al. (2004), in a study realized in the south of California in the USA, showing the existence of different concentrations of O3 in the weekday and weekend periods, being the weekend concentration larger than during the week.

The formation of ozone presents a strong relationship with the meteorological conditions. Considering the great urban centers, great emissions of precursors of ozone formation exist associated with the burning of fossil fuels by the light and heavy-duty vehicles. The atmosphere suffers with high concentrations of ozone that is harmful to the human health and to the vegetation.

The distance from the road traffic determined the behavior of ozone average concentrations.

The Ibirapuera station (distant from the traffic road), presented a larger number of ozone air quality violations. In Pinheiros station (nearby a traffic road) the concentrations of NO is higher, consuming the ozone.

The station of Pinheiros presented larger concentrations during the period of the weekend, associated to the decrease of the flow of vehicles and consequently a relationship of VOC and NOx more favorable to the ozone formation.

ACKNOWLEDGMENTS

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FIGURE LIST

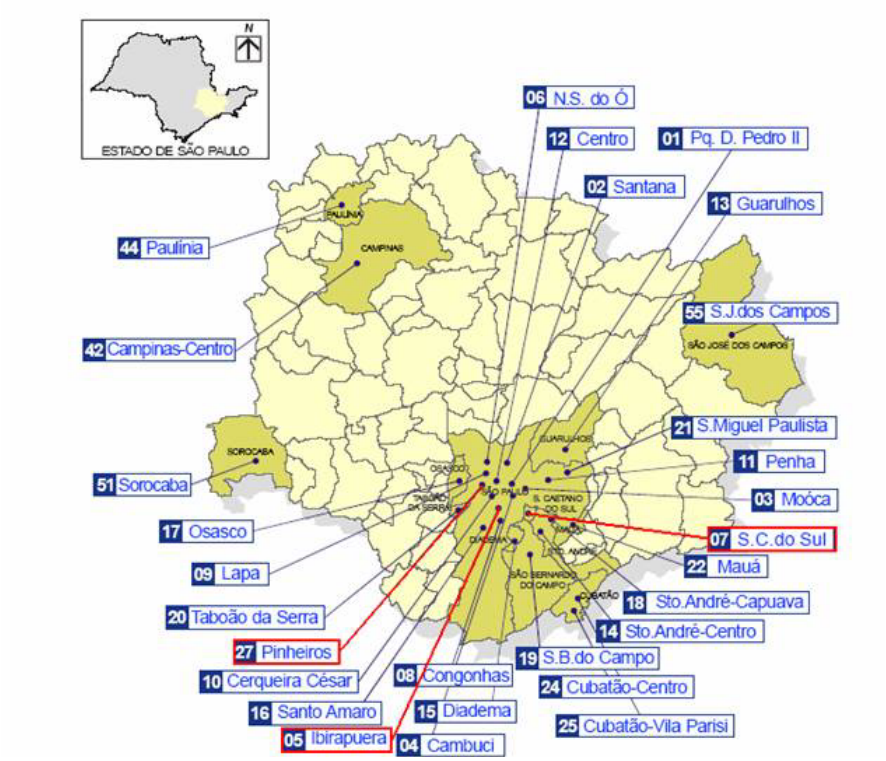


Figure 01: Localization of the Air Quality Monitoring Stations from the State Environmental Protection Agency of São Paulo (CETESB).

Source: CETESB, 2005

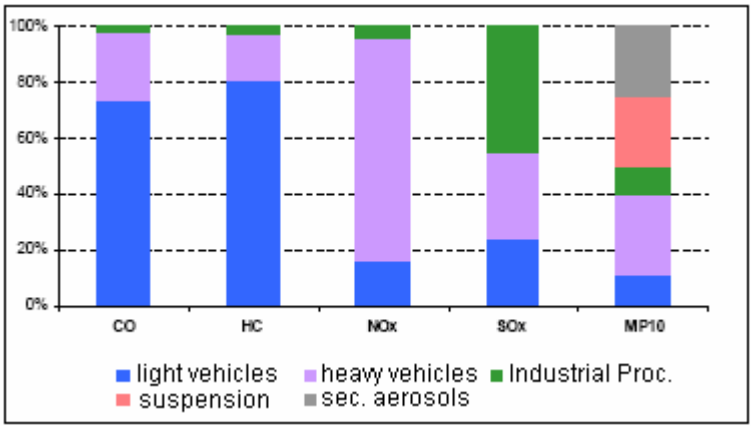


Figure 02 – Contributions of different sources to the total emission of pollutants in São Paulo Metropolitan Área in 2004 year.
Source: CETESB, 2005

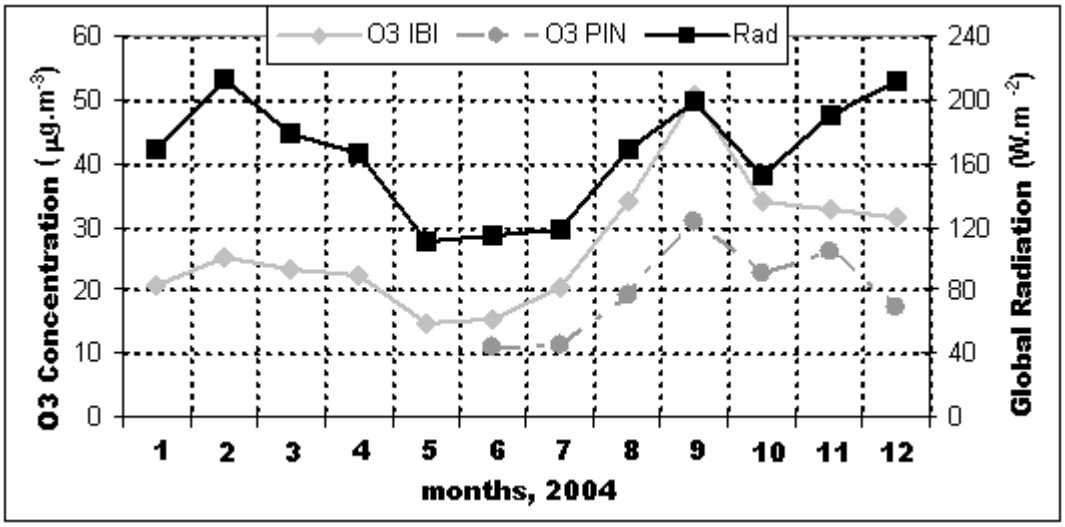
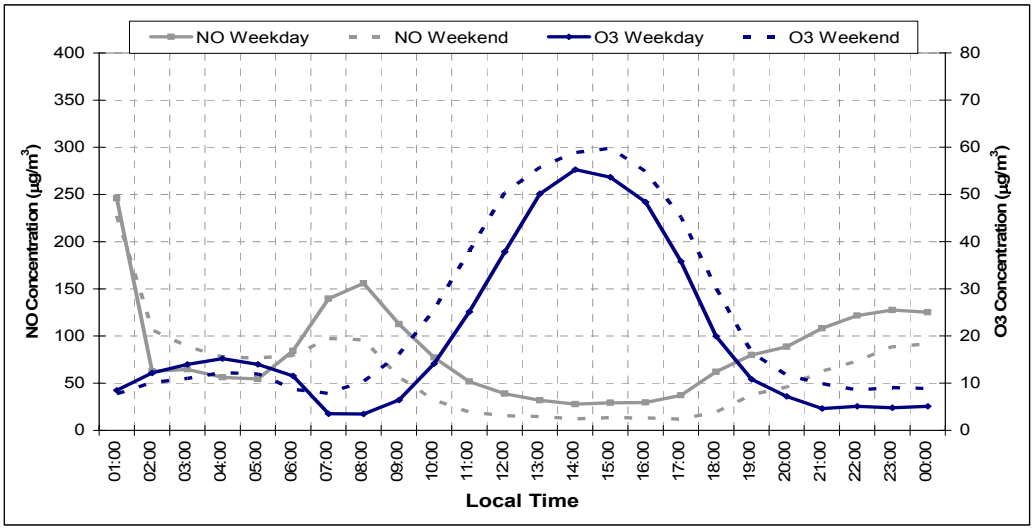
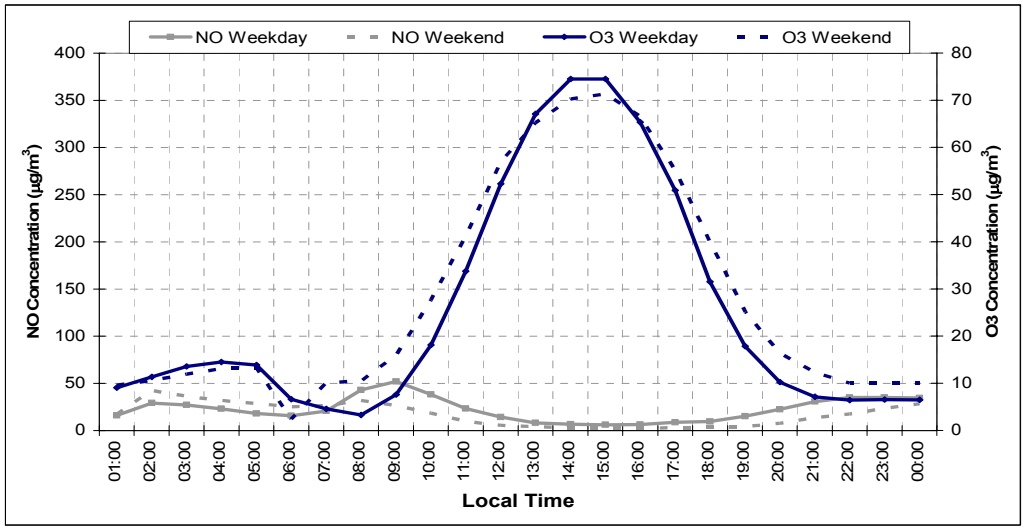


Figure 03: Annual Cycle of the ozone concentration and solar radiation, in Ibirapuera(IBI) and Pinheiros(PIN) stations.

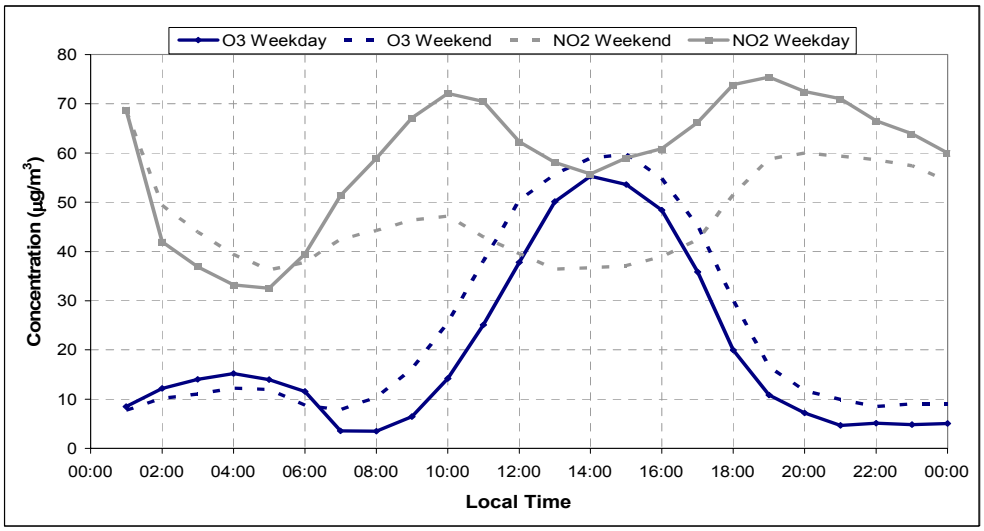


(a)

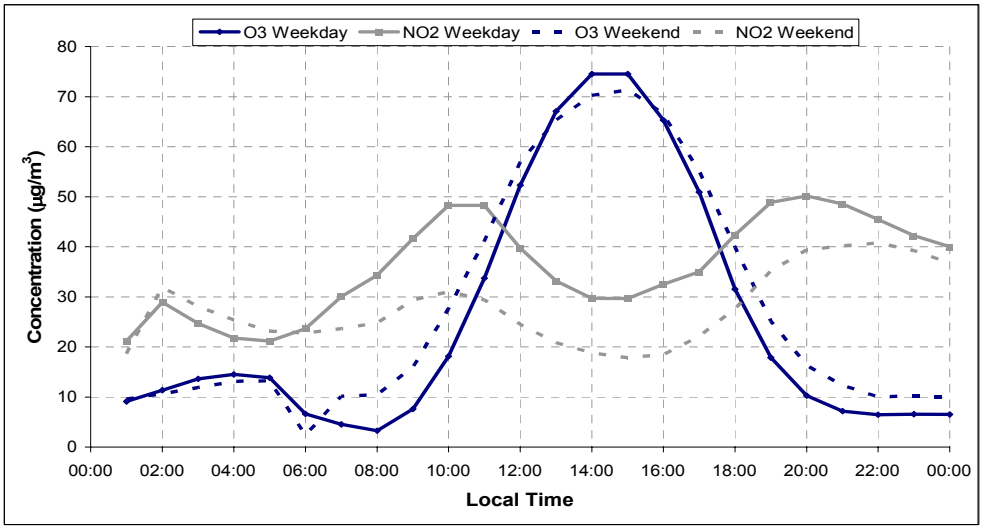


(b)

Figure 04: Daily average cycle of the NO and O3 concentrations during the weekday and weekend periods, Pinheiros (a) and Ibirapuera (b) stations, year 2004.



(a)



(b)

Figure 05: Daily average cycle of NO2 and O3 concentrations in weekday and weekend periods, Pinheiros (a) and Ibirapuera (b) stations, year 2004.

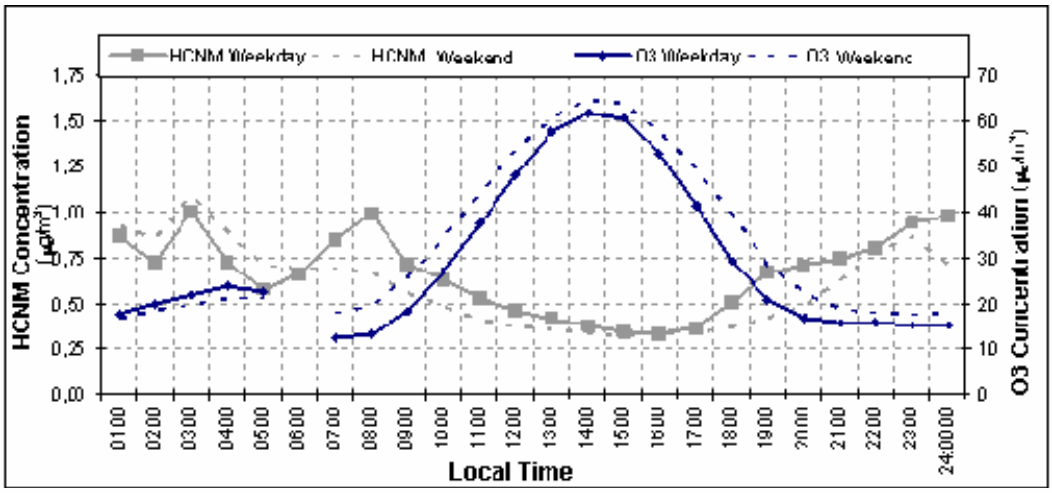


Figure 06: Daily Average cycle of HCNM and O3 concentrations for weekday and weekend periods, São Caetano do Sul station, year 2004.

TABLE LIST

Table 01: Measurements methods for the pollutants in the air quality monitoring stations.

PARAMETERS	METHODS
Inhalable particles (PM10)	*β Radiation*
Sulfur dioxide	*Fluorescence of pulse (ultraviolet)*
Nitrogen oxides	*luminescence-chemical*
carbon monoxide	*not dispersive infrared*
Hydrocarbons	*gaseous chromatography/ionization of flame*
Ozone	*ultraviolet*

Source: CETESB, 2005