

## The Management of Devaluated Autocats and Air Quality Variation in Athens

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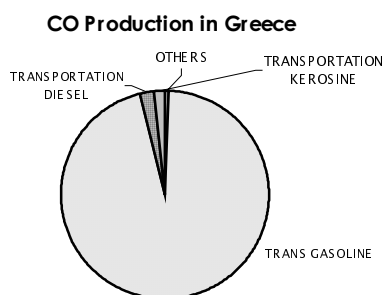
### 1 Introduction

Athens, being a city of about 4,000,000 inhabitants, faces air pollution problems as most big cities in the world. The rapid increase of population in conjunction with the continuously increasing motorized fleet, has resulted in high pollution levels during the last 25 years. Until the mid 80's the main pollutants in the Greater Athens Area (GAA) were sulphur dioxide and smoke. Photochemical pollution followed pollution from primary pollutants and resulted in the Athens photochemical smog. In recent years, European Union (EU) and World Health Organisation (WHO) air quality standards are frequently exceeded in the GAA, especially concerning CO, O<sub>3</sub> and NO<sub>x</sub> (Ziomas et al., 1995; Viras et al., 1996). The variability of the physiographic characteristics and the complex topography of the GAA cause the formation of local atmospheric circulations that negatively affect the pollutant transportation and dispersion. The GAA is located in Attica peninsula and includes the Athens basin, the Thriassion Plain and the area of Mesogia. A detailed description of the Athens area may be found in various publications (e.g. Viras et al., 1996).

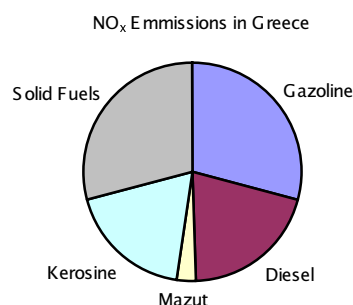
The Greek authorities, in an effort to protect the environment from a serious air pollution problem, imposed the substitution of gasoline powered vehicles with three-way catalyst vehicles. It should be noted that the vast majority of the vehicle substitution took place mainly during the period 1989-1993. The application of this regulation was initially found to be a satisfactory solution, especially for the heavily polluted urban areas. However, after some years, the efficiency of catalysts is remarkably decreasing, therefore, their replacement is becoming essential (Kaldellis et al., 2000).

### 2 Position of the problem

In summer 1983, a network was established by the Ministry of the Environment, Physical Planning and Public Works (MEPPPW) in order to measure -by automatic stations- CO, NO, NO<sub>2</sub>, SO<sub>2</sub> and O<sub>3</sub> concentrations. The data obtained by the MEPPPW network has been analysed in the past by various researchers (Lalas et al., 1987; Moussiopoulos et al., 1993; Ziomas et al., 1995; Viras et al., 1996; Paliatsos, 1998, among others). The first automatic station ("Patission") -starting operating in 1986- was situated at the headquarters of the public service responsible for the air pollution monitoring system. This station is located at a heavily polluted urban site in the centre of Athens, at the edge of a high-traffic street. The station "Maroussi" -starting operating in 1989- is located in the north east of Athens, about 7 km from the centre of Athens. Nearby -about 300 m- is one of the biggest GAA avenues. Around the station, a few-storied houses with open spaces and some small gardens and greens are situated.



**Figure 1** CO Production according to fuel used.



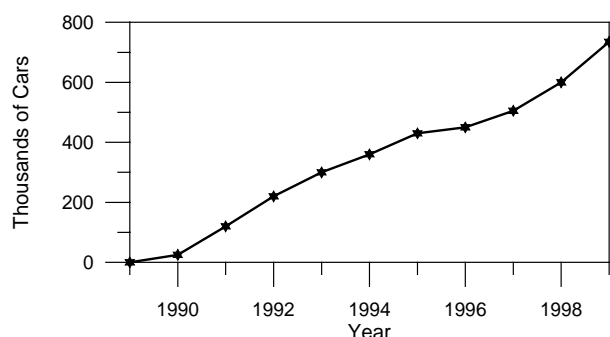
**Figure 2** NO<sub>x</sub> production according to fuel used.

Take into account that gasoline-powered private cars are by far (Figures 1 and 2) the most important factor, contributing to the increased concentration of several primary air pollutants (Kaldellis and Konstantinidis, 1995; Viras and Siskos, 1992). It is also important to note the rapid evolution of private catalytic vehicles (Figure 3) encountered in Athens during 1989-1999 (GAMVM, 1999).

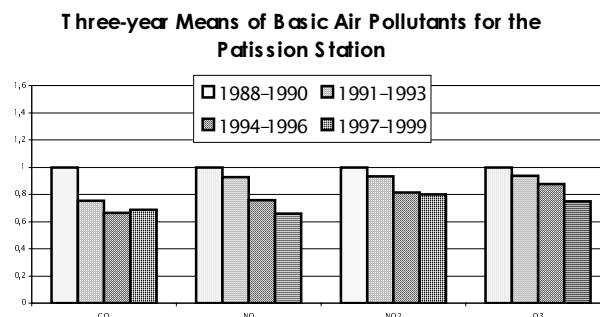
In order to more precisely estimate the air quality variation in Athens before and after pollution abatement measures, the basic pollutants (CO, NO, NO<sub>2</sub> and O<sub>3</sub>) three-year averages (1988-1990, 1991-1993, 1994-1996 and 1997-1999), for the "Patisision" and "Maroussi" stations, were compared. These averages are presented in Table 1 (see also Figures 4 and 5), while the changes (%) between the successive three-year means are presented in Table 2.

**Table 1** Three-year means of basic air pollutants for "Patisision" and "Maroussi" stations.

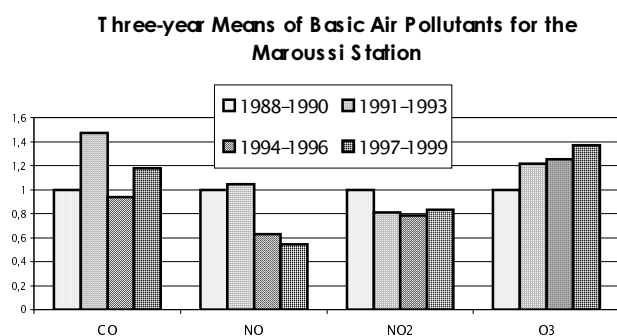
Period	CO (mg/m <sup>3</sup> )	NO (µg/m <sup>3</sup> )	NO <sub>2</sub> (µg/m <sup>3</sup> )	O <sub>3</sub> (µg/m <sup>3</sup> )
1988-1990	7.7 / 1.7	198 / 46	119 / 42	32 / 51
1991-1993	5.8 / 2.5	184 / 48	111 / 34	30 / 62
1994-1996	5.1 / 1.6	150 / 29	97 / 33	28 / 64
1997-1999	5.3 / 2.0	130 / 25	95 / 35	24 / 70



**Figure 3** Evolution of catalytic vehicles in Athens.



**Figure 4** Time evolution of basic air pollutants for "Patisision" station (relative values).



**Figure 5** Time evolution of basic air pollutants for "Maroussi" station (relative values).

According to the existing data, the NO and NO<sub>2</sub> levels -examined at both stations- demonstrate a decelerated reductive trend, almost zeroed during the last three years. The ozone increase at "Maroussi", during the period examined, may be attributed to the NO levels reduction at the same site (Figures 4 and 5).

Although a gradual CO levels degradation at "Patisision" was recorded, late measurements indicate quite the opposite. This fact might be attributed to the corresponding variation observed in the three-year mean percentage values of 8-h carbon monoxide concentrations (MEPPPW, 2000), that are higher than the WHO long term goal (10 mg/m<sup>3</sup>) for the period 1988-1999 (Table 3).

**Table 2** Counterbalanced changes (%) of basic air pollutants for GAA.

Period	CO	NO	NO <sub>2</sub>	O <sub>3</sub>
1988-1990				
	-5.8	-2.6	-5.3	6.5
1991-1993				
	-10.1	-12.7	-5.4	0.1
1994-1996				
	4.2	-2.3	0.1	1.0
1997-1999				

**Table 3** mChanges (%) of CO concentrations that are higher than 10 mg/m<sup>3</sup> in "Patisision".

Period	1991-1993	1994-1996	1997-1999
1988-1990	-73.7		
1991-1993		-89.7	
1994-1996			17.0

Recapitulating, one may conclude that during the first six years of the previous decade, a remarkable decrease of several air pollutants has been recorded, before this situation being inverted during the last four years (Kaldellis et al., 2000).

### 3 Environmental Behaviour of Spent Catalysts

What has really happened? One of the most rigid explanations for this significant change is that after some years of service, the three-way catalysts of cars imported after 1990 lose their activity, either due to thermal impacts or poisoning by contaminants in exhaust. These effects result in gradual decrease of the autocats efficiency. On the other side, the owners of old autocats do not substitute them (Figure 6) by new ones, mainly due to their replacement cost, contributing thus to a remarkable deterioration of

the air quality level. This situation is going to worsen, taking into account the gradual degradation of the already existing 1,500,000 autocats in Greece.

In order to estimate the impact of aged autocats on the evolution of atmospheric pollution, the definition (Konstantinidis and Kaldellis, 1997) concerning the environmental efficiency " $\eta$ " of an autocat (A/C) is hereby used, expressed as:

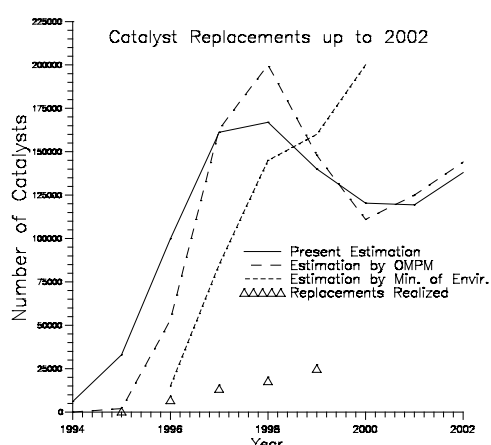
$$\eta = \sum w_i \cdot \eta_i \quad (1)$$

Keep in mind that " $\eta_i$ " is defined as:

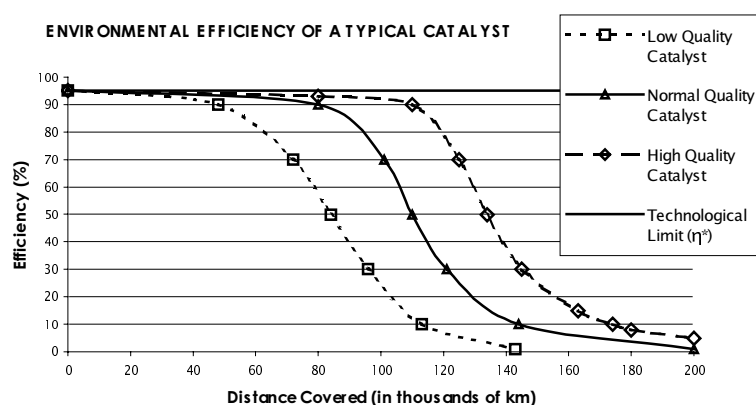
$$\eta_i = 1 - \frac{\text{quantity of pollutant (i) at the outlet of A/C}}{\text{quantity of pollutant (i) at the inlet of A/C}} \quad (2)$$

and " $w_i$ " is the corresponding weight factor related to the air pollutant "i". The " $w_i$ " depends firstly on the mass flow rate and secondly on the toxicity factor of each pollutant, produced by an internal combustion engine. A typical new catalyst converts approximately 96% of total hydrocarbons "THC", 90% of carbon monoxide "CO" and 96% of nitrogen oxides "NO<sub>x</sub>" produced by the engine into less harmful carbon dioxide "CO<sub>2</sub>", nitrogen and water vapour.

Using the available experimental data from several sources (e.g. Summers and Thompson, 1980; MHPPEN, 1996) one may conclude that the environmental efficiency of a commercial catalyst is decreased; gradually in some cases, more rapidly in others. Therefore, the distribution of a typical commercial autocat (Figure 7) is proposed by the authors. For example, according to this semi-empirical profile, the environmental efficiency of an autocat after an 80,000 km distance covered is between 0.55 and 0.94, while the minimum (EU-2000 limits) environmental acceptable efficiency " $\eta_{\min}$ " is 0.8.



**Figure 6** Estimated and realized number of autocats replacements.



**Figure 7** Proposed efficiency distribution of a typical commercial autocat.

#### 4 Conclusions

Air quality data -obtained by the Athens air pollution monitoring system, from the twelve-year period started in 1988- are investigated in order to determine time variations of selected air pollutants, mainly attributed to the transportation sector of the economy. According to the proposed analysis, the amelioration of the air pollution situation, taken place during the 1990-1996 period, is practically inverted, especially as far as the CO and NO<sub>x</sub> emissions are concerned.

One of the main factors explaining this negative evolution is the low replacement rate of spent catalysts from the unleaded gasoline-powered vehicles. In fact, an integrated statistic analysis model is under development, in order to establish a quantitatively relation between air pollution changes and gradual degradation of existing autocats. Taking into account all above information, we believe that the local authorities have the necessary data to determine the future of spent autocats in our country, in view of the encountered air quality variations in the GAA.

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