SOURCES FOR PHENOLS AND CRESOLS IN URBAN AMBIENT AIR, MILAN (ITALY)

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INTRODUCTION: Nitrophenols and nitrocresols are produced by the oxidation of benzene and toluene with the main atmospheric oxidising agents (mainly [·OH] radical) in the presence of NO_x. Recent results from smog chamber experiments have shown that mixtures of benzene, toluene, and NO_x, irradiated with UV light, produce secondary organic aerosols where nitrophenol and nitrocresol derivatives have been abundantly identified and so thought to play an essential role as precursors of secondary organic aerosols (Bolzacchini E., 2004).

OBJECTIVE: Characterization of 19 phenols and cresols in the GAS PHASE and in the PARTICULATE PHASE present in
- Urban ambient air (Milan, Italy)
- emissions from vehicles

METHODS

Sampling gasoline and diesel engine exhausts, collected at the SSC ("Stazione Sperimentale dei Combustibili") : six in-use vehicles were tested as shown in the table. Three diesel fuels differed in sulphur content (G1= 240 mg/km S, G2= 50 mg/km S, G3= 10 mg/km S). Vehicle testing were performed on a chassis dynamometer with a constant volume sampler simulating typical Milan city traffic conditions (TI cycle, elaborated by SSC, mean velocity 11,4 km h-1; UDC European standard cycle, mean velocity 19,0 km h-1; EUDC, European standard cycle, mean velocity 62,6 km h-1).
• Particles were collected by a gravimetric system, in iso-kinetic conditions
• Gas phase (only phenol; 2-nitrophenol; 4-nitrophenol) were collected using silica gel cartridges

All samples were subjected to the same analytical procedure:
SAMPLE PREPARATION PROCEDURE: extraction in an ultrasonic bath using acetonitrile as solvent; filtration, evaporation and recovery in 1 ml by adding toluene
ANALISY BY GC-MS: double taper direct liner; HP-5MSsi column; pulsed pressure (25psi ; 1min)

Vehicle	A	B	C	D	E	F
Car Type	Fiat Punto TD	Alfa Romeo 156 1.9 JTD	Alfa Romeo 147 1.9 JTD	Fiat Ducato 14 (Van)	Fiat Stilo 1.6	Fiat Tipo 1.4
Homologation level	EUROI	EURO II	EURO III	EURO II	EURO IV	EURO I
Fuel	Diesel	Diesel	Diesel	Diesel	Gasoline	Gasoline
Catalytic converter	NO	YES	YES	YES	YES (TWC)	NO

Milan Campaign (17-27 May 2005) : the sampling site (Messina Street, Milan) is close to the city centre and representative of background pollution levels of the urban area of Milan. Six hours samples were collected (23h-05h; 05h-11h; 11h-17h; 17h-23h).

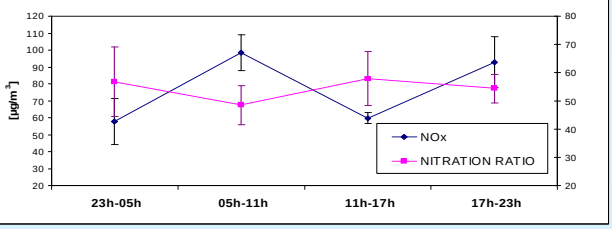
•The gas phase has been sampled using theTCR_Sky Post Gas sampler (1L/min; cartridges of XAD7)

•$PM_{2.5}$ and PM_{10} samples have been collected by LVS samplers (EN12341; 2.3 m^3/h; PTFE filters)

MILAN CAMPAIGN:
GAS PHASE: Results for the gas phase have shown a typical trend (figure 1) for the seven compounds quantified. Relative maximum concentrations have been found during the hours of highest photochemical activity (11 to 17 hours) as shown by ozone trend which is considered the principle photochemical index. This trend mostly indicates secondary formation.
PARTICULATE PHASE: In the particulate phase o-cresol, m- and p-cresol, 4-methyl-2-nitrophenol and 4-nitrophenol have been quantified. 4-nitrophenol is the most abundant (341,4±137,3 pg/m^3). This result is in good agreement with what a smog chamber showed: 4-nitrophenol is a low vapour tension substance which tends to aerosol phase.
PARTITION gas/PM: partition values between gas phase and particle phase for o-cresol, m-and p-cresol and 4-methyl-2-nitrophenol are in a range of 98,3-99,2% and they are in good agreement with literature (Pankow, 1985).

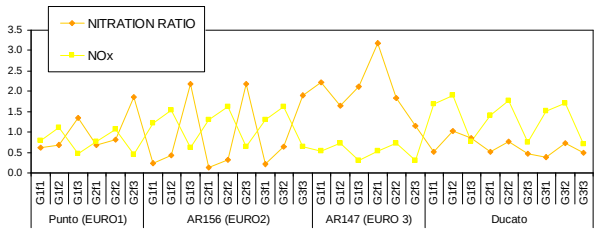
RESULTS

Figure 3: gas phase, Milan Campaign 17-27 May 2004



NITRATION RATIO: The "nitration ratio" is considered an index of nitration level for phenols. It has been calculated as follows:
([phenol])/([4-nitrophenol]+[2-nitrophenol])
Figures 3 and 4 show the relation between nitration and NO_x has been observed both in gas exhausts and in the troposphere of Milan.

Figure 4: gas exhaust SSC tests (correlation = 0,97)



VEHICLES EMISSIONS:
GAS PHASE: phenol, 2-nitrophenol and 4-nitrophenol were quantified within the emission factors range of 0,0-7,5 µg/Km.

PARTICULATE PHASE: As shown in figure 2, phenols and cresols are primarily emitted by diesel cars. Significant variations of emission factors have been observed for different engine technologies (EURO1 to EURO4) but not for different guide cycle or fuel. The 4-nitrophenol results to be the most abundant (0,35 to 2,62 µg/Km).

PARTITION gas/PM: Partition value between particle phase and gas phase for 4-nitrophenol is 66,02±5,10%. It confirms that 4-nitrophenol is mostly distributed into particle phase.

Figure 1: gas phase daily trend, Messina street (MI) 17-27 Maggio 2004

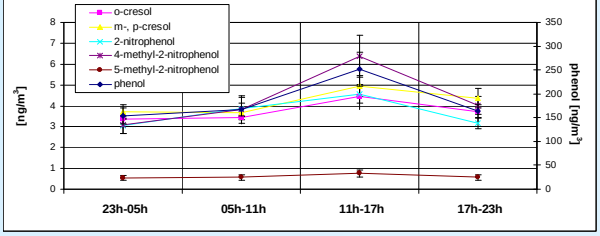
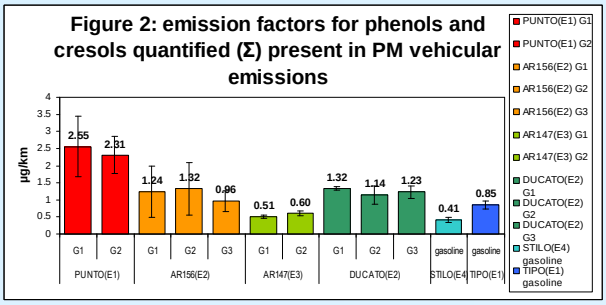


Figure 2: emission factors for phenols and cresols quantified (Σ) present in PM vehicular emissions



CONCLUSIONS:

•In the urban ambient air of Milan mainly secondary formation is confirmed for the seven quantified phenols and cresols as shown by their daily trend

• Emission factors for phenols and cresols are mostly influenced by the engine technology levels

•The main partition in the particle phase for 4-nitrophenol is in agreement with the hypothesis that this compound plays an essential role in secondary aerosol formation

•A relation between nitration and NOx has been observed both in exhaust gases and in the urban troposphere of Milan. If that relation would be confirmed, it could likely suggest a possible correlation between nitration processes and SOA.

REFERENCES: Bolzacchini, E., et al (2004).Nitrophenols in Milan atmosphere and urban particulate. Chemistry Division, Siena, 8-11 June 2004.
Pankow, J. F. *et al*, (1985). Mechanisms for Phenols in Urban Air and Rain, *Env. Sci. Technol.*, Vol. 19, No. 11.

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