Chlorinated organics in the air of Taranto, southern Italy

Ettore Guerriero¹, <u>Angelo Cecinato¹</u>, Leda Occhipinti¹, Patrizia Di Filippo²

¹CNR IIA ²ISPESL

Introduction

Due to the duty pollution levels and the variety of emission sources, Taranto, a city of Southern Italy, represents an interesting case study of urban pollution. Indeed, both downtown and surrounding areas suffer heavily of the presence of big industry quarter running 24-h a day (a steel factory, a petrol refinery, a cement plant and related harbour activity), where control strategies for toxic emissions do not seem to run fine. In addition, ambient pollution is there implemented by rush motor vehicle circulation (over 50,000 cars for 250,000 inhabitants) and shape and size of the city, characterized by long and thin canyon streets lying between high building lines. Finally, meteo-climatic conditions dominating the region seems to promote both accumulation of pollutant and development of photochemical processes.

By consequence, in the air of Taranto national concentration limits for atmospheric pollutants result often exceeded for coal- or petroleum originated species (e.g., suspended particulates, PAH, nitrogen oxides, benzene), while sea waters and sediments are rich of hydrocarbon and metal matter. Recently, Taranto has been provided with an air pollution monitoring network, covering both the city and province territory and City Authority has scheduled several actions and strategies to reduce drastically the health impact of industrial emissions. In addition, a program has been launched by Italian Ministry of Health, with the purpose of assessing the true emission rates of toxic pollutants with the corresponding fallout onto the province territory, and the relative contribution of sources to ambient pollution of Taranto.

Experimental

During 2004 two intensive campaigns (in winter and summer) were carried out, aimed to monitor toxic organic components of the atmosphere at three locations in the Taranto countryside, which appeared exposed to different emission impacts. The sites were *Tamburi*, a quarter in downtown Taranto located just close to the biggest steel plant in Europe, *Statte*, a town 20 km N of the city, lying usually below the emission plume coming from industrial quarter, and *Palagiano*, a rural site kept as representative of background pollution.

Concurrently to study of suspended particulates (discussed elsewhere), also the semi-volatile fraction of the atmosphere was investigated, with special attention for organic chlorinated compounds OCC, e.g. chlorinated biphenyls PCB, dioxins PCDD and furans PCDF. Our concern was addressed to acquire the concentration levels reached by OCC and identify the respective distribution profiles (i.e. group fingerprints), to attempt the source assessment with respect to ambient pollution level.

For this purpose, three *high-volume* equipments were used, collecting PM₁₀ air particles onto quartz filter

membranes QFMs and, backflow, semi-volatile gaseous species onto polyurethane cartridges PUFs¹. Solventextractable organics were recovered from loaded filters by applying accelerated solvent extraction with toluene, and from cartridges by soxhlet refluxing with *n*-hexane/acetone (2:1). After solvent reduction close to 200 mL, a former chromatography through a silicagel/sulphuricacid column was applied to cut off most of interferents while OCC passed unaltered. Then, a second elution through a multi-layer column allowed to clean chlorinated analytes and separate PCB from PCDD&PCDF by basic alumina column (a Pasteur pipet)². Finally, analyses were run by GC-MS or GC-MS/MS. Several ¹³C-marked isotopes were spiked at different steps of procedure: before the extraction , before the clean-up and before the instrumental determination in order to account for sample losses and detector variability.

Results and discussion

PCDD&PCDF aerial concentrations (both in gas and particulate phase) recorded during the winter and summer campaigns at the Orsini and Statte sites are shown in Figures 1 and 2, respectively. In winter, the prolonged measurements allowed to distinguish two sampling periods, which showed very different profiles of pollutants (see Figure 3).

The two sites presented different profiles for PCDD and PCDF. In fact, in winter more than 50% of OCC were associated to particulate phase at Orsini, and in gas phase at Statte. Many PCDD/F congeners were found at Orsini in the winter time, whilst only H_7CDD and O_8CDD could be determined in summer and at Statte. At the Palagiano station, neither PCDD nor PCDF reached the quantification limits of the procedure adopted. So, it was confirmed as "background pollution site" for the province of Taranto with respect to particulate organics (this finding was in agreement with results obtained for PAH). In all site, the STEQ concentration where also evaluated. They reached 17-

References

1. J. I. Baker and R.A. Hites "Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in the remote North Atlantic marine atmosphere" *Environ. Sci. Technol.* **1999**, *33*, pp 14-20

2. M.L.Molinelli, A. Sbrilli, E. Guerriero, M.Bianchini, M. Rotatori and A. Cecinato. "PAHs, N-PAHs and PCDD/PCDF in the urban atmosphere of Milan". Chemistry for a sustaining world. *Environmental Science and Pollution Research - Special Issue 3 –***2002**pp 159-160

3. USEPA, 1989. Interim procedures for estimating risks associated with exposures to mixtures of chlorinated dibenzo-p-dioxins and dibenzofurans (CDDs and CDFs) and 1989 update, EPA/625/3-89/016, US Environmental Protection Agency, Risk Assessment Forum, Washington, DC

Figure 1. Average PCDD/PCDF concentrations recorded at the Orsini site in Taranto.



57 fg/m³ TEQ at Orsini and 7-19 fg/m³ TEQ at Statte. ³

Figure 2. Average PCDD/PCDF concentrations recorded at the Statte site.



Figure 3. PCDD/PCDF concentrations found at the Orsini site in the two winter samplings.

