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SUPERSITE PROJECT
PROJET SUPERSITE
PROGETTO SUPERSITO

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Abstract

The project is focused on a detailed study of some chemical, physical and toxicological parameters and on health, epidemiological and environmental assessment by interpretative models, in the atmosphere of Emilia-Romagna (Italy). The project rises from the necessity to improve knowledge about environmental and health aspects of fine and ultrafine particles, in primary and secondary components, in the atmosphere. The project, structured in 7 workpackages, is organized in two measurement programmes: the routine one that has a mainly daily time resolution, and the intensive one with high time resolution and a higher chemical speciation than the routine one. The sampling sites are five: three in urban areas (Bologna, Parma and Rimini), one in a rural area (San Pietro Capofiume) and one in a remote area (Monte Cimone). Parallel to outdoor studies, a workpackage is planned for indoor studies and chemical composition analysis with the outdoor/indoor ratio for characterizing indoor human exposure to outdoor pollution.

Key-words: *fine particles chemical speciation**;** nanoparticles size distribution; air quality models;, toxicological and epidemiological studies*

Résumé

Le projet consiste en une étude détaillée des paramètres chimiques, physiques et météorologiques et une évaluation sanitaire, épidémiologique et l'environnementale (grâce à des modèles), dans l'atmosphère de la région Emilie-Romagne. L'objectif du projet est le progrès des connaissances sur les aspects environnementaux et sanitaires des particules fines et ultra-fines en composants primaires et/ou secondaires dans l' atmosphère. Le projet, articulé en 7 lignes directrices, est organisé en deux programmes de mesures: un programme de routine avec une fréquence temporelle surtout quotidienne et un programme intensif avec une fréquence temporelle èlevée et un éventail plus large de l'analyse. Les sites de mesure sont au nombre de cinq: trois dans la zone urbaine (Bologne, Parme et Rimini), un dans la zone rurale (San Pietro Capofiume) et un dans une région reculée (Monte Cimone). Parallèlement, une ligne directrice se concentre sur l'étude du rapport intérieur/extérieur des composants de la qualité de l'air dans

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les bâtiments, pour caractériser l'exposition humaine à la pollution extérieure lorsque les sujets son à l'intérieur. .
Mots-clés: *spéciation chimique des particules fines; distribution de la taille des nano-particules; modèles de qualité de l'air; études d'épidémiologie et de toxicologie.*

Riassunto

Lo scopo del progetto è la realizzazione di uno studio integrato dell'inquinamento dell'atmosfera in Emilia-Romagna attraverso misure di parametri chimici, fisici, tossicologici e valutazioni sanitarie, epidemiologiche ed ambientali mediante modelli interpretativi. Il progetto nasce dalla necessità di migliorare le conoscenze relativamente agli aspetti ambientali e sanitari del particolato fine ed ultrafine, nelle componenti e/o secondarie, presente in atmosfera. Il progetto, strutturato in 7 linee progettuali, è organizzato in due programmi di misure: uno routinario in cui sono previsti campionamenti giornalieri ed uno intensivo in cui è prevista una speciazione più dettagliata con maggiore risoluzione temporale. I siti di campionamento sono 5: 3 in area urbana (Bologna, Parma e Rimini), 1 in area rurale (San Pietro Capofiume) e 1 in area remota (Monte Cimone). Contestualmente agli studi outdoor è prevista una linea progettuale che si occupa dello studio del particolato, della sua composizione chimica nel rapporto qualità dell'aria outdoor/indoor e della caratterizzazione dell'esposizione della popolazione in ambienti indoor agli inquinanti tipici dell'ambiente outdoor.
Parole chiave: *speciazione chimica; distribuzione dimensionale nano particelle; modelli qualità aria*

Introduction

The aim of Supersite Project is to realize in Emilia-Romagna region a detailed study about some chemicals, physical and toxicological parameters of the atmosphere and to get health, epidemiological and environmental evaluations by interpretative models. The project takes into account international and consolidated experiences of Augsburg (Munich, D) and USA "Supersites". The project main value is the close integration among environmental data and health and epidemiological information. Many epidemiological studies have already demonstrated the correlation between air particulate and higher morbidity and mortality. Besides, European Commission, in September 2009, decided not to allow exceptions to Emilia-Romagna Region about the obligation of PM10 limit values observance in air quality. Therefore it's necessary to improve the knowledge about atmospheric aerosol to achieve a better governance of themes related to atmospheric and health protection. Specific objectives are:

- Chemical mass balance estimated using a detailed fine aerosol speciation data (EC/OC, ions, metals, organic compounds),
- Size distribution of nanoparticles with high time resolution;
- Characterization of PBL (Planet Boundary layer) and SEB (Surface Energy

Balance) meteorology during crustal particles transport and ultrafine particles nucleation events,

- Evaluation of growth and formation events of inorganic and organic secondary aerosol,
- Use of high resolution meteorological modelling (COSMO) and chemistry-transport models (Chimere) to simulate chemical species of epidemiological interest,
- Source apportionment by receptor models using chemical speciation data,
- In compliance to Directive 50/2008 with regard to organic/elemental carbon and ions in PM2.5 in different areas of the region and to D. Lgs. 183/2004 about ozone precursors in air in a rural area,
- Toxicology evaluation of health dangerous substances, elements and compounds or mixture in aerosol,
- Realization of epidemiologic assessments by means of studies of remarkable health events:

- short term studies, by correlation among informative flows (hospital schedule, pharmaceutical database, etc..) about diseases linked to exposure of pollutants and the values of some aerosol compounds;
- long term studies, by analysis of informative sources as cancer and mortality registry and values of some aerosol chemical species;

- Risk assessment by elaborations of chemical parameters and toxicological observations and by comparisons with epidemiological analysis of short and long term events;
- Improvement of population exposure evaluation by indoor air quality studies about fine and ultrafine particles.

The sampling site are five: n. 3 in urban area, Bologna (main site, MS), Parma (US1) and Rimini (US2), n. 1 in rural area, San Pietro Capofiume (RS3) and n. 1 in remote area, Monte Cimone (RS4). The project is organized in 7 workpages, summarized below. Sampling period lasts 3 years (2011-2013) in which routine and intensive activities are planed: routine samplings are principal daily and intensive ones have a more detailed speciation.

WorkPackage 1: Sampling, chemical analysis and aerosol size distribution. Routine measures program. The main goal is to provide data fluxes about chemical composition of PM2.5 in atmosphere on long term (3 years). Second aim is to study the size distribution of submicron particles to understand the reactions happening and driving particle transformations and growth. Moreover WP1 studies chemical and physical conditions that govern particles formation and destruction in urban and rural areas. The planned activities are management and execution of aerosol (PM2.5) samplings and chemical-physical analysis in "main site", "satellite sites" of Parma and Rimini and in the rural site of San Pietro Capofiume.

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Sampling times and methods are different among sites. The analysed parameters are:
- organic and elemental carbon by means of termo-optic analyzer (MS,US1,US2,RS3)
- ions by means of ion chromatography (all sites)
- metals by means of Inductively Coupled Plasma - Mass Spectrometry (MS,US1,US2,RS3).

Analysis results represent both database for epidemiological evaluation of WP6 and answers to requests of Directive 50/ 2008.
Furthermore in main and rural site PM1, 2.5 hourly data are measured.
In "remote site" of Monte Cimone, atmospheric particulate is sampled with a dichotomy impactor (PM1 and PM1-10): total and hydro-soluble carbon and ions are analysed. Primary aim also allows to fill the gap of information about chemical composition of both primary atmospheric aerosol, that is directly emitted by sources, and secondary aerosol, that derives from chemical reactions in atmosphere. Some ozone precursors measures is guaranteed in rural site of San Pietro Capofiume by means of an automatic gas chromatographer with flame ionization (GC FID) for determining some volatile organic compounds. About second aim, activities concern the management and the execution of measures of nanometric aerosol size distribution in real time with differential mobility analyzer. Those studies are executed in main and rural sites: in rural site measures are managed by Helsinki and Kuopio University and by the Finnish Meteorological Institute. Results give a view of conditions and modality of formation and growth of particles, both in urban and in rural area.

WorkPackage 2: Physical measurements; meteorological and chemistry-transport modeling. Routine measures program. Main goals of WP2 are the characterization of the planetary boundary layer (PBL) - the lower part of the atmosphere where aerosol dispersion, transport, coagulation and nucleation take place - and of the energy exchange between soil and atmosphere (surface energy balance, SEB), which is the main drivers for turbulence. Standard measurements collected by the meteorological networks are provided to the other WPs. Special measurements focusing on PBL and SEB are carried out by means of a lidar/ceilometer (mixing height retrieval), a sonic anemometer coupled with a fast infrared gas analyzer (surface turbulent fluxes) and a time domain reflectometer (soil water content and temperature). These meteorological data provide a powerful information basis in order to perform diagnostics and improvement of the non-hydrostatic meteorological model COSMO and of its post-processing algorithms. Similarly, the chemical data provided by the other WPs are used to perform diagnostics and improvement of NINFA, the implementation of the chemistry-transport model CHIMERE over Northern Italy, and of its post-processing algorithms.

WorkPackage 3: Campaigns of atmospheric intensive measures - Intensive observations program. The goal is the management, sampling activities in the main (Bologna) and in the rural sites (San Pietro Capofiume) and chemical-physical analysis of aerosol samples about the following parameters:
a) organic substance speciation (polar organic compounds, IPA, Nitro-IPA, Oxi-IPA and linear hydrocarbons) in the PM2.5. The aim is to increase the speciation provided by "routine measurement program", for specific pollutants in organic carbon compounds.
b) Concentration trend of major aerosol chemical compounds measured with high time resolution (some minutes) by an aerosol mass spectrometer (AMS). AMS measures allow to investigate formation process and aerosol accumulation in terms of meteorological, transport (wind), photochemical parameters and emission impact.
c) Size distribution of aerosol chemical compounds, obtained by multistadium impactor. The chemical species measured in the different size bins (0.05-10 μm) are inorganic ions, total and water-soluble organic carbon (WSOC), proxy secondary organic aerosol. Aerosol size is the most important parameter in order to determine the residential time in atmosphere; so the chemical measures, size segregated, allowed to discriminate the chemical compounds, locally emitted, from ones transported by remote sources.
d) Fine aerosol organic composition characterization obtained by nuclear magnetic resonance spectrometry (NMR) to identify and quantify the source apportionment from biological and combustion sources. NMR spectrometry uses the same AMS approaches, but with a lower time resolution and with higher detailed in the sources, in particular between natural and anthropic sources.
The aim is to provide further information, increasing the aerosol speciation to measures routinely in WP1, to epidemiology evaluations (WP6) and fill the gap about atmospheric aerosol chemical compounds both primary, emitted directly by sources, and secondary, produced by chemical reaction in atmosphere .

WorkPackage 4 – Predictive toxicology-Intensive observations program. Predictive toxicology is based on developing procedures that are able to predict toxic effects (the output) from chemical and biological information (the input). This offers the opportunity to validate toxicity data by comparing the predictions with realworld measurements. WP4 aims at obtaining several information from biological systems, including mutagenic properties on bacterial and human cells, toxic and transforming effects in established murine models as well as on human cells, ecotoxicology profiles, markers of exposure at a molecular level, starting from real environmental samples of PM 2.5 and PM 1, collected at sites that should be representative of different urban situations and exposures. For reaching this goal, a bunch of new, innovative testing approaches have been chosen, including implemented protocols for Ames test and Comet assay and the prevalidated micronucleus assay, prevalidated in vitro test for cancer prediction, new tools for

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studying in vitro transformation on human cells, an innovative use of the well-known microtox assay to highlight the ecotoxicological profiles of contaminants. and toxicogenomics approaches, based on high-throughput profiling techniques, aiming at obtaining insight in the fundamental mechanisms of the toxicological response to the exposure to PM 2.5 and PM 1 as well as at identifying biomarkers of exposure that could be used in biomonitoring studies. Knowing the mode or the mechanism of action of the entire environmental complex mixtures could allow a better risk evaluation of the human exposure to environmental toxicants and a better comprehension of the effects of combined exposures. Data from chemical characterization, as obtained in other WPs, together with the biological information are the base for predicting the risk (especially the cancer risk) for human health. All the biological information could support the epidemiological studies, possibly offering a mechanistic interpretation of the epidemiological observations. The use of the microtox assay, a well-known test for assessing aquatic acute toxicity, to highlight the toxicity of airborne samples could lead to the validation of a rapid, sensitive and specific test for monitoring the impact of airborne contaminants on the environment.

WorkPackage 5 – Campaigns of indoor intensive measures - Intensive observations program. The main goal of the WP5 is to improve the understanding of population exposure to outdoor air pollution within indoor settings. Considering the general objectives of the project, we focus on physicochemical properties of particulate matter. The data help to address two important issues in epidemiological research and exposure science: 1) how different is the exposure for people living near busy urban streets compared to people living in residential/rural areas and 2) what are the seasonal differences in physicochemical characteristics of indoor particulate matter which could be responsible for the increased health risk found to be associated with particulate matter during the warm season. Indoor environments are selected with characteristics as similar as possible (e.g. volume, building materials, height from street level) to reduce the influence of the specific features of the indoor environments and to highlight the relative impact of direct emissions from traffic. Mass concentration and chemical composition measurements are carried out on $PM_{2.5}$ together with size distribution of particulate matter in the range of 5.6÷560 nm. Concentrations of some gaseous pollutants specifically associated to traffic (e.g., benzene, carbon monoxide, nitrogen dioxide) are measured as well. Outdoor and indoor measurements are simultaneously carried out in two sites.

WorkPackage 6 – Epidemiological analysis: long and short term. Main objective is to investigate possible associations between exposure to particulate (and its components) and health effects. Epidemiological analyses are made, specifically for short-term and long-term effects. Studies on short-term effects are related to hourly or daily variations in exposure levels to air pollutants, whereas analyses of long-term effects are mainly focused on spatial heterogeneity of mean concentrations of pollutants, as a proxy of population exposure on a long time

period. Health effects to short-term exposure to particulate and its components are investigated, using environmental data, from main and satellites site of the Supersite Project and fixed monitoring network, as information for exposure assessment. Time-series studies are the main epidemiological study design to investigates possible associations between daily variations of air pollutants and disease occurrences in each day. The analyses control for time-dependent variables, (trends and seasonality) and for meteorological data. Health data are gathered from mortality, morbidity and emergency access registries. Epidemiological analyses on long-term effects aim to evaluate possible associations between health effects and long-term exposure to particulate and its components. The enrolment of population under investigation follows the statement of cohort studies. The retrospective cohort is clearly defined and involves residents in study areas of the Project. The cohort follow-up is made by means of record-linkage procedures with mortality and morbidity registries. A special issue regards the retrospective exposure assessment of enrolled population. Different geographic approaches (proximity models, land use regression models, dispersion models) is adopted. A preliminary ongoing activity, to identify the main research needs and define the study protocol, is the state-of-the-art review of these kind of studies, particularly focused on which pollutants (and components) are related to cause-specific mortality and/or to disease onset, and the identification of more susceptible sub-groups of population.

WorkPackage 7 - Environmental data analysis. The main goal is to identify and quantify the contribution of fine PM primary and secondary sources (source apportionment) by receptor models using experimental database of PM2.5 chemical composition. WP7 uses as input data chemical composition results, obtained by daily sampling (WP1) in main site (MS) and satellites (US1/2), and by intensive campaigns (WP3) in the main site (MS) and rural site (RS3)). Furthermore WP7 uses aerosol size distribution and environmental parameter trends (WP1). Besides WP7 focuses on identification of the aerosol sources, causes of the accumulation of toxic substances (WP4 and WP6) in atmosphere. Outputs are estimations of emission sources, useful comparison with air quality models (WP2) and estimates the exposed population (WP5) and therefore for the risk assessment (WP4). The temporal series of the particulate chemical composition in the main site and satellites are analyzed to evaluate processes and sources that are responsible of seasonal trends of primary and secondary chemical compounds in different areas of the region. Moreover, events related to long range transport are identified and quantified. Data collected during the intensive observation program (IOP) are instead used to study variability of chemical compound concentrations in high time resolution, related to trends of sources contribution and to photochemical processes and chemical transformation of particulate. Particles size distribution is also studied during high pollution episodes, in order to determine sources and processes responsible of the observed trends. Data are supplied in high time resolution, so factors and contributions of sources, responsible for the daily cycles

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and trends of hourly concentrations, can be investigated. Furthermore organic composition speciation allows to assess the contribution of the primary and secondary sources of organic fine particulate, with an accuracy that can not be obtained just from temporal series analysis of organic carbon provided by the "Routine measurement program". Sources analysis of organic particulate needs specific methodologies and studies. Methods are receptor models, which have been widely used in analysis of experimental data obtained in "Supersite" projects. Among these methods, "positive matrix factorization" (PMF) is privileged because specifically designed for applications to the studies of the atmospheric particulate. PMF has also been widely developed to mass spectra analysis of aerosol organic substances measured with aerosol mass spectrometer (AMS), that allowed the quantification of the car exhaust emissions and the secondary sources contribution. A similar statistical analysis of nuclear magnetic resonance (NMR) spectra is integrated for the detailed study of the organic sources due to secondary origins and biofuels combustion. Finally, detailed estimate of the emission contributions to organic substance concentrations can be carried out with receptor models as "Chemical mass balance" (CMB) that uses a input database of organic compounds concentrations as emissions tracers .

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