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Air pollution impact assessment on agroecosystem and human health characterisation in the area surrounding the industrial settlement of Milazzo (Italy): a multidisciplinary approach

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Abstract In order to evaluate the impact of atmospheric pollutants emitted by the industrial settlement of Milazzo (Italy) on agriculture, sulphur dioxide and ozone levels in air were monitored and the data were used to estimate yield losses of the most widespread cultures. Trace element concentrations in crops and soils were also detected and metabolic profiles of soil microbial communities were considered. *Vibrio fischeri* test was used to appraise airborne pollutant ecotoxicity and epidemiological studies on causes of death distribution were carried out to characterize health state of people living in the area. All the sampling points were selected in farms on the basis of a theoretical meteo-diffusive model of industrial air pollutants. Experimental SO_2 and O_3 values mainly exceeded the threshold established by Italian and EU regulations to protect vegetation and they correspond to estimated significant crop losses. Conversely toxic element residues in soils and in agroalimentary products were generally lower than the fixed values. SO_2 and O_3 concentrations, toxic element contents and ecotoxicity levels of airborne pollutants were not related only to industrial site emissions, while the fluctuations on metabolic profiles of soil microbial communities seem to agree with the predicted deposition of xenobiotic compounds from the industrial plants. The epidemiological study evidenced a better health state of populations living in the investigated area than in the Messina province and the Sicily region but, inside the area, males living in the municipalities closest to the industrial settlement exhibited a worst health state than those in the very far ones.

Keywords Agriculture · Air pollution · Crop losses · Geographical epidemiology · Mortality · Oil refinery · Microbial communities · Thermoelectric plant · Toxic elements

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Introduction

During the past years air pollution impact on environment, agriculture and health in areas surrounding thermoelectric power plants and industrial sites has received an increasing attention in order to prevent or minimize adverse effects or restore already compromised ecosystems. For such purposes multi-disciplinary approaches, aimed to characterize the state of the different matrices involved along the pathway from the risk sources to the adverse effects induced, are required.

Air quality may be assessed by physico-chemical measures of pollutants, by biological monitoring and/or by mathematical models applied to emissions sources (Pless-Mulloli et al. 2000; Williams and Ogston 2002; Cetin et al. 2003). Chemical analysis by means of passive samplers and/or automative gauges measure the emissions of pollutants into the environment but provide little information on the toxicological activity of the contaminants. Biological monitoring assesses the effects of air mixtures on reactive organisms, highlighting the interactions (synergistic, additive and antagonistic effects) among individual compounds.

Exposure to air pollutants causes adverse effects both on environment, agriculture and human health. Impact assessment on crops generally means to evaluate the effects of air pollutants like gaseous sulphur and nitrogen compounds, photochemical oxidants and total suspended particulate matter (TSP). Many studies have shown that tropospheric O_3 is the most important phytotoxic air pollutant and its concentration could increase in the future (Collins et al. 2000). Actually, O_3 effects are included in the global change phenomena especially for its characteristic of long-range transboundary pollutant (Fuhrer and Booker 2003). The AOT40 index (Accumulated exposure Over a Threshold of 40 ppb) has been used to assess the yield reductions and the economic damage due to O_3 (Kärenlampi and Skarby 1996; Aunan et al. 1998; Nali et al. 2002). The SO_2 critical levels (threshold values above which chronic effects may occur) set by UNECE (2004) could be applied to evaluate the potential impact of SO_2 on agriculture (Sanders et al. 1995; Garcia-Huidobro et al. 2001). Furthermore, in recent years several researches have been carried out to relate concentrations of pollutants to plant exposure and many authors proposed and/or used dose-yield response relations to estimate SO_2 and O_3 effects on plants productivity (Triolo et al. 1996; Pleijel et al. 2004).

TSP depositions could influence soil chemical composition and subsequently the absorption and the accumulation of toxic elements in plant tissues. These phenomena could also disrupt biochemical pathways (Chen et al. 1997; Briat and Sebrun 1999; Kabata-Pendias 2000; Haughand et al. 2002). Moreover high levels of toxic elements could concentrate into edible tissues of fruits and vegetables and represent a health hazard to man and animals.

In addition, soil contents of toxic elements and other contaminants could induce alterations in diversity and metabolism of indigenous microbial populations (Fritze et al. 2000; Shi et al. 2002).

Geographical epidemiological investigations may be carried out through the use of the mortality data, which are considered indicators of public health. In Italy they represent the only sanitary data always available at municipal level. Even though mortality is influenced by several confounding factors including individual susceptibility, lifestyle, socio-economic characteristics and population mobility, data associated to some causes of death may be used to formulate hypotheses about the existence of some risk factors for people living in a particular area, according to previous epidemiological and toxicological studies (Organizzazione Mondiale della Sanità 1997; Wakefield and Elliot 1999; Elliot and Wartenberg 2004).

Many epidemiological investigations have been carried out to assess the health impact of different industrial sites on resident populations. The stronger associations detected were between lung cancer and petrochemical industries, smelters, steelworks and complex industrial areas (Suarez Varela et al. 1995; Bhopal et al. 1998; Pless-Mulloli et al. 1998; Yang et al. 1999; Benedetti et al. 2001); leukemia, multiple myeloma and lymphomas on one hand and oil refinery, motor car factories, manufactures of solvents and paints on the other hand (Knox and Gilman 1997; Benedetti et al. 2001; Speer et al. 2002); respiratory diseases or acute irritative symptoms on eyes and mucous membranes and petrochemical emissions, steels or other industries (Yang et al. 1997; Bhopal et al. 1998; Jedrychowski 1999; Fontana et al. 2000). Some other associations with solid tumours, liver cancer, gastric cancer, colorectal cancer and anaemia have been detected too (Suarez Varela et al. 1995; Knox and Gilman 1997; Fontana et al. 2000; Medrado-Faria et al. 2001; Martuzzi et al. 2002; Uccelli et al. 2002).

The aim of the present study was to assess air pollution impact on the area surrounding the industrial plants of Milazzo (Italy) using a multidisciplinary methodology.

The contribution of the industrial thermoelectric power plant and oil refinery to SO_2 and TSP concentrations at soil level was evaluated through a mathematical model that considers the pollutant emissions and the meteo-diffusive characteristics of the area.

The concentrations of SO_2 and O_3 were measured by passive sampling and standard bioassay was performed for assessing toxicity of airborne bioavailable chemical pollutants.

The effects of air pollution on agricultural ecosystem have been carried out both by chemical analysis of toxic element residues in soils, fruits and vegetables and by theoretical estimation of crop rate losses. The impact of contaminants on soil microbial communities was also evaluated.

Finally the distribution of death causes has been used for epidemiological studies to assess the health state of people living in the studied area: even if it results from many different factors, it reflects also the industrial settlement impact which represents the most important air pollution source in this area.

Study area

The monitored area is situated in the surrounding of the industrial pole of Milazzo, on the North coast of Sicily (Italy) and includes 21 towns. The land is characterized by plain on the coast and hills in the inner side. The rainfall regime is Mediterranean with a dry summer, a rainy winter and a sea breeze in the summer months. Agriculture is the main activity in this area and the most widespread products are from horticulture, olive and citrus orchards. Oil refinery, thermoelectric plant and small factories constitute the industrial settlement located in this area. Motorway and provincial road run across the north side, where is located Milazzo port.

Figure 1 shows the area selected for this study, the site of pollution sources and the SO_2 concentrations predicted by the diffusion model. Table 1 summarizes the location of the sampling sites pointed out in Fig. 1.

Materials and methods

Meteo-diffusive model

Among the different models developed by an ENEA (Italian National Agency for New Technologies, Energy and the Environment) research group, the so called CMPM98 model (Climatologic Model for Point Multi-source) was selected for our purposes, as it gives the possibility of evaluating the mean annual and 98° percentile air concentration levels of pollutants, as well as the wet and dry ground depositions. Moreover this model has the advantage to take into account the wind calm situations.

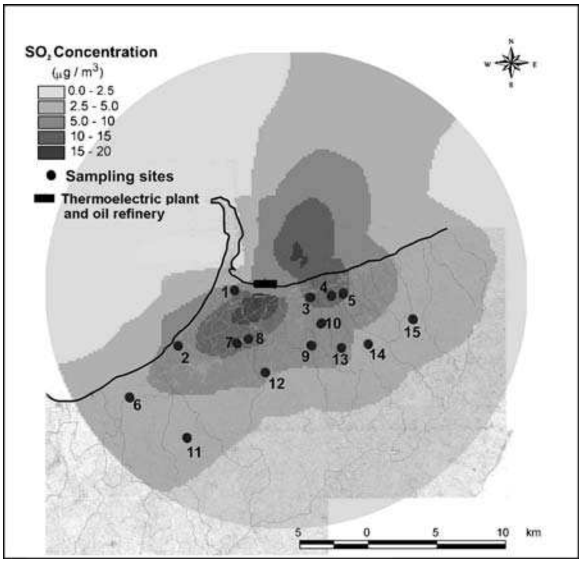

Fig. 1 Map of the study area and SO_2 concentrations at soil level evaluated by CMPM98 model

Table 1 Location of sampling sites

Sampling sites	Location
1	Milazzo
2	Barcellona Pozzo di Gotto
3	Pace del Mela
4	S. Pier Niceto
5	Torregrotta
6	Terme Vigliatore
7	Merì
8	S. Filippo del Mela
9	Gualtieri Sicaminò
10	Condrò
11	Castroreale
12	S. Lucia del Mela
13	S. Pier Niceto
14	Monforte S. Giorgio
15	Rometta

The CMPM model is based on the following assumptions:

- as concern the plume rise evaluations, the Briggs formulas (Briggs 1975) have been applied, assuming that the height of 1000 m cannot be exceeded, to take into account the frequent presence of stable zones aloft in the near shore site under investigation, consequent to subsidence of air masses during high pressure conditions or to the sea breeze air circulation;
- the climatologic diffusion deposition model considers also (Cagnetti et al. 1985) low wind speed situations. It has been assumed a wind speed value of 0.25 m/s (central value in the range 0–0.5 m/s, i.e., values below the instrument sensibility), and it has been assigned for each sector a frequency proportional to that of the first step of the wind velocity (0.5–1 m/s), for the same sector and stability category.

The following input data are necessary for the model to run: meteo-diffusive matrix; release conditions (chimney height, its diameter, efflux velocity, emission temperature); emission intensity for every pollutant. In this case we have used meteo-diffusive matrices based on 30-year meteorological data, from January 1961 to December 1991.

The output data are the mean annual and 98° percentile air concentration values, and the annual ground deposition levels up to a distance of 20 km from the source location.

Ground dry deposition is easily evaluated once the deposition rate and the air concentration values are known. It has been assumed the following values for dry deposition velocity (Vd) of the different pollutants investigated: 0.002 m/s for SO_2 (Altshuller 1984), 0.001 m/s for TSP. As a conclusion the values of mean annual air concentration must be multiplied by the following values of Kd to obtain the total annual dry deposition on ground for the same pollutant: 63.000 m for SO_2; 31.500 m for TSP.

Ground wet depositions are very important near the source, while dry depositions obviously present maximum values at the same distance where there are maximum values for air concentrations. Unfortunately rigorous evaluation of the wet deposition levels needs to elaborate hourly data of wind rate and direction together with rain fallen in the same hour, at least on 3 years climatologic statistic. In many cases such series of hourly data are not available; this was the case for the site under investigation. Therefore an estimation was made of the wet deposition adopting the following assumptions:

- the mean annual rainfall is 643 mm/year;
- the rain is present on the site for 10% of the time of the year;
- the distribution of the wind direction at rain presence is the same of the neutral at category D (weather windy and/or cloudy).

The washout coefficient L is expressed by $L=KR$, where R is the rain intensity (mm/h) and K is a coefficient which depends on the pollutant. The mean rainfall intensity is assumed to be 2 mm/h. Using such assumptions and assuming that the chemical transformation of SO_2 to SO_4^{2-} is very low in time (1% per hour after Eliassen and Saltbones 1983), a washout factor of 10^{-5} s^{-1} for SO_2 has been found.

For the TSP the washout factor has been evaluated to 10^{-4} s^{-1}.

O_3 and SO_2 monitoring

Passive O_3 and SO_2 samplers were located in farms at different distance from the industrial site from May to October 2001. This period was chosen because summer solar radiation enhances O_3 formation and economically relevant crops are cultivated.

Analyst® passive samplers (Marbaglass, Rome, Italy) were used in the field as receptor for O_3 and SO_2 (De Santis et al. 1997; Manes et al. 2003). The samplers were exposed for a period of 1 month each, at 2–3 m above the ground. Capped samplers were also installed as a field blanks. The extraction were performed using 5 ml of aqueous solution (2.7 mM Na_2CO_3 and 0.3 mM $NaHCO_3$ for the ozone samplers; 2.7 mM Na_2CO_3, 0.3 mM $NaHCO_3$ and 0.003% H_2O_2 for the sulphur dioxide samplers). Nitrate and sulphate produced were determined by ion chromatography (DIONEX DX 120, USA equipped with an IONPAC AS9 column).

Crop losses evaluation

The SO_2 and O_3 average concentrations detected in each site and the data of the most widespread species cultivated in the study area (ISTAT 2000) were used for the theoretical estimation of crop losses by dose–response functions (Camposano et al. 1986; Giorgielli et al. 1994; Vitagliano et al. 1999; Centre of Ecology and Hydrology 2002; Nali et al. 2002). Since some functions for evaluation of the O_3 damage are based on AOT40 (ppb.h) index (Fuhrer et al. 1997), a set of proper relationships (Centre of Ecology and Hydrology 2002) was used to convert the O_3 average concentration (provided by passive sampling and calculated in the 3 months that coincide with the crops-growing time) on AOT40.

Analysis of toxic elements in soils and vegetables

Samples of agricultural soils, vegetable and fruit were collected in different sites from June to October 2001 by means of a random method.

As pre-treatment, vegetable and fruit samples (only edible parts) were homogenized by BUCHI mixer equipped with ceramic blades and therefore lyophilized, while soil samples were sieved at 2 mm, homogeneized by roll drum and dried in air at room temperature.

Al, As, Cr, Mn, Ni and V were analyzed by Instrument Neutron Activation Analysis (INAA) directly on solid samples, while Cd and Pb were analyzed by ElectroThermal Atomic Absorption after sample dissolution.

To determine Al, Mn and V, dried samples (about 50 mg) were irradiated in RABBIT apparatus of the ENEA TRIGA reactor, while about 500 mg of dried samples were irradiated in rotary rack apparatus (LAZY SUSAN) of the ENEA TRIGA reactor to analyze As, Cr and Ni. After appropriate decaying times, gamma spectra were measured by HpGe detector employing CANBERRA GENIE 2000 data acquisition system. NIST certified reference materials were used for calibration.

Sample dissolution was obtained by acid attack in a Microwave High Pressure Digestion System MILESTONE 1200. Generally 0.75 g of vegetable samples were completely dissolved employing 5 ml of concentrated HNO_3 (65%); only for particular samples (olive fruits for example) a (5:2) mixture of concentrated HNO_3 (65%) and HF (40%) was used. Soil samples (0.2 g) have been digested by 3 ml concentrated HCl (37%) + 2 ml concentrated HF (40%) + 1 ml concentrated HNO_3 (65%). In any case the final volume was 25 ml. A double channel IL VIDEO 22 AA Spectrophotometer was used operating at 283.5 nm and 228.8 nm wavelengths with D_2 background correction. 10 μl of sample solution were analysed employing mixed standard calibration solutions in the range 0.5–2.0 μg/L for Cd and 10–40 μg/L for Pb. The ashing and atomisation temperatures were 225°C and 1,800°C respectively. The accuracy of results was evaluated by the following certified reference materials: BCR CRM 062 (Olive leaves), NIST SRM 1573 (Tomato leaves) and SRM 1570a (Spinach leaves).

Ecotoxicological evaluation of airborne pollutants

Organic contaminants were collected using Semipermeable Membrane Devices (SPMDs) (Hutckins et al. 1990; Petty et al. 1993; Lohmann et al. 2001; Soderstrom et al. 2005; Petty et al. 2000a,b; Isidori et al. 2003).

Standard SPMDs (Hutckins et al. 1990; Petty et al. 1993) produced by Environmental Sampling Technologies, St. Joseph, MO, USA, were provided by Ecotox, Milan (Italy). They were deployed, covered with protected devices, in 8 sampling points into different farms located at variable distances from the industrial plants of Milazzo, in two periods of the year 2001: 10 July–6 August and 11 September–11 October. After exposure the SPMDs were retrieved, placed in containers and stored at −20°C until they were processed.

In the laboratory, each SPMD was rinsed to remove surface fouled residues, according the procedure of Johnson et al. (2000) and then was solubilized with 20 ml of an acetone:dymethylsulphoxide (DMSO) mixture (1:1 v/v) for 24 h. The acetone was evaporated by a gentle stream of nitrogen and the recovered sample was used for toxicity test. Two control SPMDs were in parallel processed and they constituted the laboratory blanks.

The complex mixtures of chemicals sequestered by SPMD were examined by the Microtox test, which measures the ability of a sample to inhibit the bioluminescence of the bacterium *Vibrio fischeri*. Sample extracts were diluted to achieve a 1% DMSO concentration because of its low toxicity to the Microtox organism.

The bioluminescent bacteria test was conducted according to the Microtox® standard protocol with a Model 500 analyser and a lyophilised culture of

V. fischeri NRRL-B-1117, supplied by Environmental Azur (Carlsbad CA, USA). Acute toxicity was performed according to the basic test (Microtox Manual 1995), in eight dilutions starting from initial concentration of mg SPMD/ml for each sample and luminescence was recorded after 5, 15 and 30 min of incubation at 15°C. The concentrations that cause a 50% reduction of bioluminescence (EC50) were calculated using Microtox Software vs. 7.82 and the EC50 values after 15 min of incubation were reported. For use in further calculations, the toxicity data were converted to toxic units (TU) using the formula TU=100/EC50.

Soil bacterial metabolism

Soil samples were collected from the surface of uncultured land (1–5 cm deep) and stored 5 days at 5°C. All of them were characterized as eutric fluvisols with medium texture (from clayey loamy to sandy loamy) except sample 12 with fine texture. After sieving in order to remove particles >0.5 mm, 20 g (dry weight) of each sample were mixed with 20 ml of PBS pH 7.0, homogenized for 2 min, sonicated for 50 s and left at room temperature for 2 h to allow the soil to sediment. The solution above the soil was diluted 1:2 with PBS and used for evaluation of microbial metabolism by single carbon source utilization pattern (Campbell et al. 1997) using Biolog Ecoplates™ (BIOLOG, Hayward, CA) containing 31 substrates. The plates inoculated with 125 µl/well were incubated 4 days at 28°C. Cluster analysis of the results was performed using Euclidean Distances (Ward's method) with STATISTICA 6. The total number of bacteria was estimated by evaluation of colony forming unit (CFU) of soil dilutions on 1/10 TSA plates (Difco) incubated 7 days at 28°C.

Epidemiological study

The selected area includes 21 municipalities. They have been studied both as a single area and as three concentric zones of 5 km each around the industrial settlement. Total mortality and several tumoral and non-tumoral causes of death (28 in males and 29 in females) have been investigated by ENEA's mortality database (source: the Italian Institute of Statistics), for the period 1980–1997. Standardized mortality rates (TSD) (standard population: Italy 1991 census), both regional and provincial standardized mortality ratios (SMR) and different zones' TSD ratios (RR) have been calculated. Statistical significance of SMR and RR has been evaluated by CI 95% regarding their lower limit as the equivalent of one tail significance test (Breslow and Day 1987).

Results and discussion

O_3 and SO_2 monitoring

The mean values of SO_2 concentrations measured in each sampling site are shown in Fig. 2. In the sites 6, 7, 9, 10, 11, 12, 13, 14, 15 mean concentration values of SO_2 exceeded 20 µg/m^3, which represents the threshold level (annual mean) established by the Italian and EU laws to protect ecosystems (DM n.60 02/04/2002 and Directive 1999/30/EC, respectively).

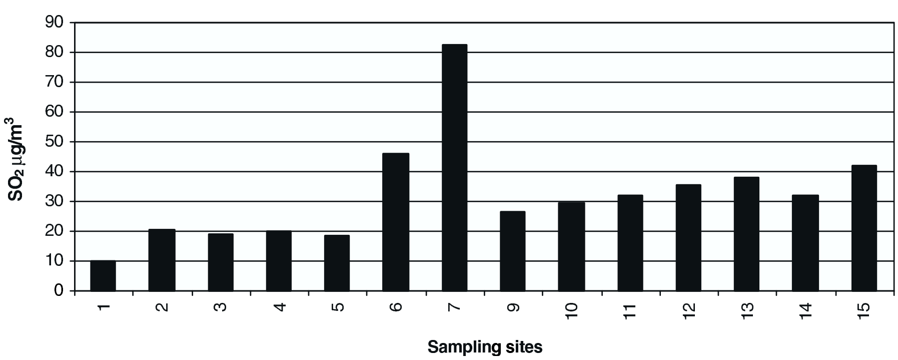

Fig. 2 SO_2 mean concentrations (µg/m^3) measured by passive samplers from May to October 2001

Figure 3 shows single values of the normalized SO_2 concentrations measured in the sampling sites. Normalization was obtained by the following mathematical relation:

$$C^*_{SO_2} = \frac{x_i - \bar{x}}{s}$$

where:

$C^*_{SO_2}$ normalized SO_2 concentration
x_i SO_2 concentration measured in the i-esime site
$\bar{x}$ mean SO_2 concentration values measured in the different sites at the same sampling period
s standard deviation of the SO_2 concentration values

Therefore the $C^*_{SO_2}$ distribution mean is 0 and the standard deviation (s) is 1.

In site 7, SO_2 concentrations result systematically higher than the other sites (>2.5 s). However in some sites (site 1, 3, 4, 5, 6 and 15), only one of the five sampling periods shows an SO_2 concentration value that exceeds (±) 1 s the mean value of the period. These occasional outfield values are probably due to local discontinuous pollutant emission sources.

SO_2 temporal and spatial distribution depends on wind speed and direction. In this case-study we have assessed a light wind direction prevalence from North-East towards South-West.

Experimental SO_2 concentrations were always higher than those evaluated by the diffusion model, which are illustrated in Fig. 1. Moreover, the observed gradient of pollutant concentrations is different respect to the theoretical model that predicted – only for thermoelectric power plant and oil refinery – the highest values in the area surrounding the industrial emission sources. Such differences between the model and the experimental monitoring could be explained by the presence of additional diffuse pollutant sources, not considered in the diffusion model. Among them, the intense road traffic in the season under study could be a significant source of pollutants.

O_3 mean concentrations measured in each sampling site ranged from 80 to 150 μg/m^3 (Fig. 4). Average O_3 concentrations in each site decrease during the different sampling periods and that confirms the pattern of O_3 concentration related to the solar radiation intensity. In Mediterranean regions summer O_3 concentrations are considerably higher than the natural one, which are generally in the range 10–20 ppb (Lorenzini 1999). In each monitoring site the experimental values were much higher than the natural background. In all the monitoring sites O_3 concentrations at surface level strongly overcame the AOT40 limit (6000 μg/m^3 h) established by the Italian law to protect vegetation (D.L. 21/05/2004, n. 183), which receipted the Directive 2002/3/EC.

Figure 5 shows single values of the normalized O_3 concentrations measured in the sampling sites; normalization was obtained by the same procedure applied for SO_2. As previously stated for SO_2, site 7 shows O_3 concentrations systematically higher than the other sites, excepted for one case (site 6 for 7/8–11/9/01 period). Instead site 3 ever shows values lower than the other sites.

Estimated AOT40 ranged from 18250 ppb h (in site 3) to 46666 ppb h (in site 7).

The relation between SO_2 and O_3 mean concentration values measured in the same site shows a fairly good linear regression coefficient (r=0.78). That

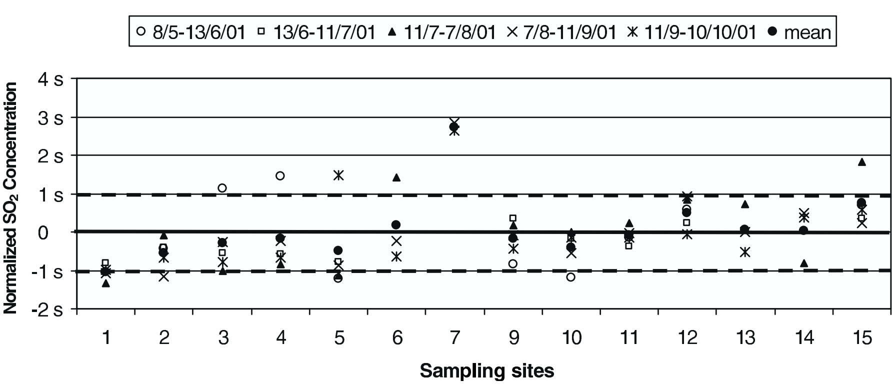

Fig. 3 Normalized SO_2 concentration in the different sampling sites. Comparison among SO_2 concentrations measured in various sampling periods and in different sampling sites

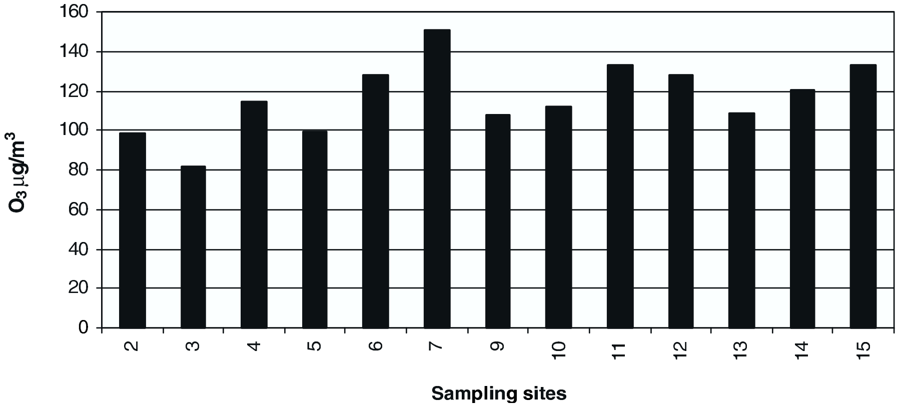

Fig. 4 O_3 mean concentrations (µg/m^3) measured by passive samplers from May to October 2001

confirms a correlated distribution of the pollutants in the study area.

Further, the highest gaseous pollutant concentrations were observed at site 7 (83 µg/m^3 for SO_2 and 161 µg/m^3 for O_3), where risks for human health and vegetation are predicted.

Crop losses evaluation

The assessment of SO_2 damage has shown crop losses of 4–6% for wheat, 4–7% for potato and 1–11% for citrus; olive net photosynthesis reduction was evaluated between 1 and 11%.

Estimated values for crop yield losses caused by O_3 were: 8–20% for tomato, 16–37% for potato, 8–19% for grape, 5–14% for alfalfa and 14–31% for citrus. Olive net photosynthesis reduction was evaluated between 25 and 47%.

The estimated yield losses are relevant for all the investigated species, but some overestimations could be argued because stomatal closure, which occurs in plant leaves in dry and hot environments, protects vegetation from pollutants damage.

Toxic elements monitoring and effects evaluation

Aluminium (Al), arsenicum (As), cadmium (Cd), chromium (Cr), lead (Pb) manganese (Mn), nickel (Ni) and vanadium (V) contents were measured in agricultural soils, vegetables and fruits collected in different sites of the investigated area, near the refinery and the thermoelectric plant or in rural zones, which are inside the potential influence of industrial activities. In fact relevant levels of Pb, Ni and V are generally present in oil combustion emissions. Cd is produced in oil and coal combustion and contained in incinerator emissions, while its residues are present in phosphorous fertilizers. Moreover this toxic element is characterized by high propagation rate in food chains. As, Mn and V residues could arise from fertilizers and pesticides and determine risks for consumers of agroalimentary products. Cr in phos-

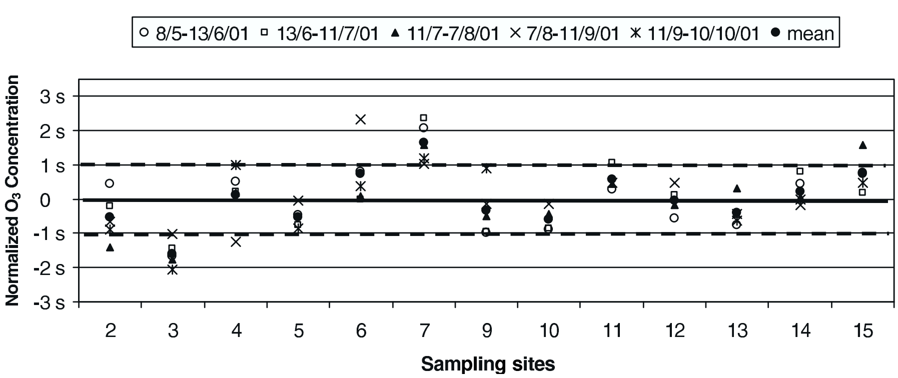

Fig. 5 Normalized O_3 concentration in the different sampling sites. Comparison among O_3 concentrations measured in various sampling periods and in different sampling sites

Table 2 Concentrations of toxic elements (mg/g or μg/g dry weight) in soil samples collected in the study area

Sampling sites	Al (mg/g)	As (μg/g)	Cd (μg/g)	Cr (μg/g)	Mn (mg/g)	Ni (μg/g)	Pb (μg/g)	V (μg/g)
1	84.3	16.4	0.44	87.8	8.8	32.4	33	116
1A	79.8	12.7	0.25	63.1	10.9	n.d.	28	118
1B	65.6	4.1	0.34	46.7	5.0	22.3	37	64
2	75.8	11.4	0.55	61.9	8.0	18.5	33	93
4	84.7	3.9	0.33	79.5	7.9	23.2	14	112
7	81.9	10.2	0.28	79.6	7.5	39.8	27	114
8	80.0	10.9	0.13	60.0	6.6	24.3	26	122

n.d., not detectable

phorous fertilizers and in waste sewage sludge could contaminate drinking water and food and large quantities of this micronutrient are dangerous for humans. Moreover Al may accumulate in food chains and produce toxic effects at high doses.

The concentrations of toxic elements in soil samples are reported in Table 2. Considering the contents of each element, no relevant differences among the data referred to all sampling site were observed. Furthermore, toxic element concentrations were lower than the values fixed by the Italian law for public and private green areas (DM n.471, October/25/1999). Otherwise V concentrations were found to exceed the established threshold of 90 $\mu g/m^3$ in six sites.

Moreover a comparison of Pb, Cd and Ni levels with the data reported for Italian unpolluted agricultural soils (Ferraresi and Corticelli 2002) showed low contents of these pollutants in examinated samples.

Table 3 Concentrations of toxic elements (μg/g fresh weight) in fruit and vegetables samples collected in the study area

Samples	Sampling sites	Al	As	Cd	Cr	Mn	Ni	Pb	V
Lattuce	2	7.2	n.d.	0.019	0.04	0.81	n.d.	0.012	0.02
	7	1.9	n.d.	0.029	0.005	1.99	0.012	<0.04	0.01
Pea	2	6.5	n.d.	0.013	0.12	2.77	0.23	0.06	n.d.
Potato	4	6.3	0.004	0.037	0.13	1.24	n.d.	0.06	0.02
Courgette	4	2.2	0.001	0.002	0.003	0.41	0.015	0.007	0.002
Aubergine	1	1.6	0.006	0.03	0.008	1.19	0.024	0.02	n.d.
	15	4.3	n.d.	0.055	0.013	1.19	0.019	0.05	0.003
Tomato	1	4.2	n.d.	0.011	0.012	1.55	0.034	<0.01	0.011
	2	1.7	n.d.	0.014	0.01	0.78	0.011	<0.01	n.d.
Lemon	8	1.2	n.d.	0.004	0.06	0.34	n.d.	0.029	n.d.
	10	1.8	0.002	0.005	0.08	0.34	n.d.	0.07	0.003
Medlar	8	1.3	0.002	0.009	0.14	0.42	n.d.	0.08	n.d.
Orange	4	1.2	0.001	0.006	0.08	0.27	n.d.	0.18	n.d.
	9	1.2	n.d.	0.016	0.06	0.21	n.d.	<0.04	n.d.
	14	1.2	0.001	0.001	0.09	0.28	n.d.	<0.02	n.d.
Olive	1	4.7	n.d.	0.018	0.15	1.54	0.38	<0.1	0.032
	6	2.9	n.d.	0.01	0.1	1.3	n.d.	<0.1	n.d.
	8	4.2	n.d.	0.022	0.16	1.15	0.36	<0.1	n.d.
	9	3.9	n.d.	0.005	0.07	1.32	0.14	<0.1	n.d.
	10	2.2	n.d.	0.008	0.14	1.75	n.d.	0.2	n.d.
	11	3.8	n.d.	0.013	0.16	1.97	n.d.	<0.2	n.d.
	12	3.7	0.015	0.048	n.d.	1.41	0.24	<0.1	n.d.
	13	4.7	n.d.	0.015	n.d.	1.39	n.d.	0.4	n.d.

n.d., not detectable

Table 4 Comparison between toxic elements daily intake of fruit and vegetables and WHO toxicity limits

	Al (mg/day)	As (μg/day)	Cd (μg/day)	Cr (μg/day)	Mn (mg/day)	Ni (μg/day)	Pb (μg/day)	V (μg/day)
a (estimated intake)	1.16	1.74	6.61	23.53	0.37	33.52	10.68	3.9
b (WHO limits)	60	128	60	250	–	600	214	200
% (a/b 100)	1.9	1.3	11	9.4	–	5.6	5	1.9

Source: World Health Organization (WHO) (1996) and INRAN (Turrini et al. 2001) data processing

Toxic element residues in fruit and vegetable samples are listed in Table 3. There were any correlations between these results and theoretical data of particulate depositions predicted by the mathematical model. It was probably due to the presence of pollutants emitted by diffusive sources.

Human health risks coming from toxic elements ingestion were evaluated with reference to EU laws on the basis of their contents in collected samples. EC regulation n° 466/2001 stated maximum level of some contaminants (Pb, Cd) in agroalimentary products: all experimental data of Cd and Pb concentrations were much lower than the maximum values admitted.

In order to assess risk for consumers by eating considered fruits and vegatables, daily intake of toxic elements was computed referring to Italian mean diet data (Turrini et al. 2001). Therefore, obtained values were related with human maximum intake limits set by World Health Organization (WHO) (1996) for each element. The percentage values found in this comparison have shown an acceptable risk for consumers (Table 4).

Ecotoxicity of airborne pollutants

The results of acute toxicity of SPMDs extracts are given in Table 5, that reports the toxic units (TU) obtained by milligram of the SPMD per millilitre of the bacterial suspension. All the samples inhibited the bioluminescence of *Vibrio fischeri*, except sample 10 in the second period (September–October) of membranes exposure. Laboratory blanks resulted not toxic for *Vibrio fischeri*.

The extract TU values range was considerable; in fact, considering the daily toxic load, values between 12 and 0.33 were found. However, TU values did not identify a particular trend of toxicity distribution. A presence of random toxicity peaks was observed for samples collected over the July–August and September–October periods; in the first case the most toxic sample (site 2) as well as the less toxic one (site 10) were included.

Toxicity comparison between the two sampling periods is shown in Fig. 6. It pointed out a random variability in toxicity levels of almost all samples

Table 5 Toxicity of SPMD extracts of airborne samples collected during two sampling periods (expressed as Toxic Unit and obtained with Microtox test)

Sampling sites	Toxic unit[a]	95% CI[b]	TU[a]	95% CI[b]
	10 July–6 August		11 September–11 October	
SPMD control	–	–	–	–
2	322	250–400	139	131–145
3	238	212–277	67	64–70
5	133	123–145	238	208–277
6	156	149–161	222	192–250
7	181	169–196	33	30–38
10	9	3–33	nt[c]	–
11	80	71–89	89	84–95
15	182	137–244	232	200–270

[a] Fifteen-min incubation

[b] Confidence Interval of Toxic Unit, $P<0.05$

[c] Not toxic

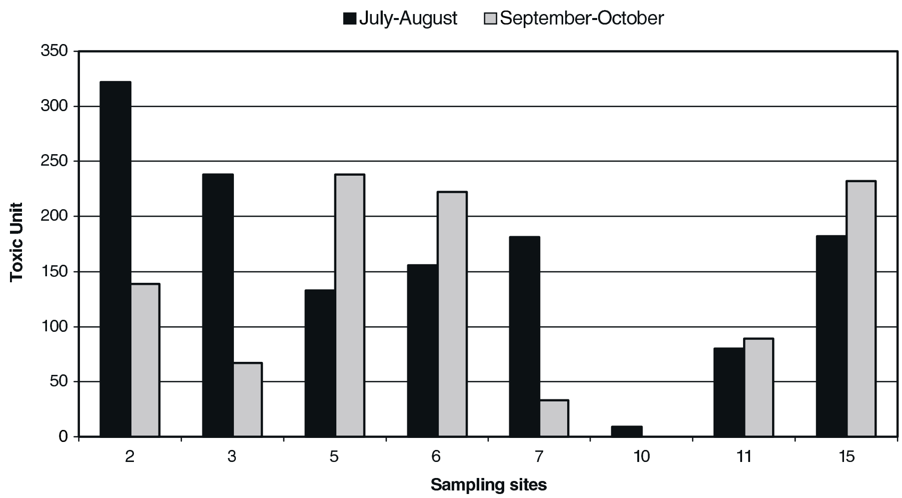

Fig. 6 Toxic Unit of SPMD extracts comparison between two sampling periods

except sample 11. The observed increases (sites 5, 6, 15) were generally of low intensity respect to the decreases (sites 2, 3, 7).

A comparison was performed with estimate concentrations of particulate airborne and the higher TU value of each analysed sample (Fig. 7). It showed that high toxicity samples (2, 3, 5, 7) were not only included in the areas with particulate high concentrations (0.7–1.2 μg/m^3) according to the theoretical model but also (sites 6, 15) in the areas with low pollutant concentrations (0.1–0.3 μg/m^3). In the same area was conversely included a low toxicity sample (site 11). Therefore, it is possible to suppose that some interfering factors were accumulated by SPMDs during exposition in the farms. We could hypothesize that these factors may essentially be referable to different classes of environmental pollutants: pesticides applied in agriculture and products from combustion engines, both contributing to the toxic effects on bacteria. To this point of view, samples of low and high pesticides impact were respectively located on Terme Vigliatore and Rometta (sites 6 and 15), Condrò and Castroreale (sites 10 and 11), while the considerable toxicity decrease showed by sample 1 could be ascribed to traffic reduction from the summer period to the September–October one. These hypotheses require more detailed investigations, but these preliminary results show that Microtox is a suitable bioassay that may be used in combination with SPMDs technique for an initial screening of air quality.

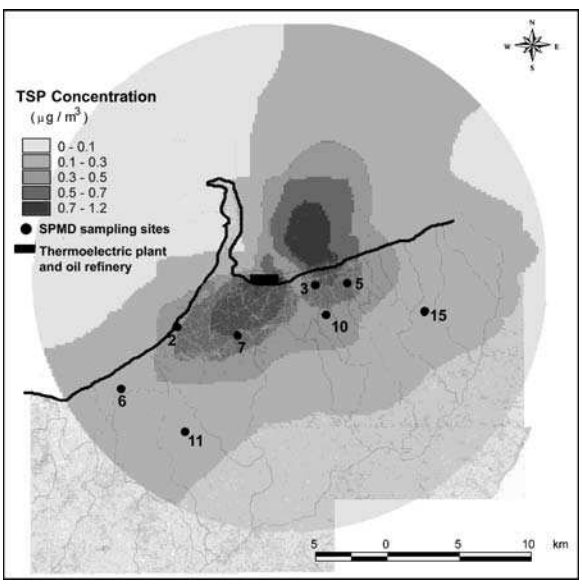

Fig. 7 Estimated concentrations of Total Suspended Particulate matter and distribution over the studied area with regard to the sites of SPMD$_S$ exposure

Soil bacterial metabolism

The evaluation of CFU/g soil is reported in Table 6. The total number of bacteria was constant in all the locations except for sites 6, 7, and 12 where the values were significantly higher. Figure 8 reported the cluster analysis of soils on the basis of microbial metabolism of 31 substrates used as single carbon source and shows two distinct groups separated by a linkage distance higher than 6%. Four samples grouped in one cluster reported the lower average

Table 6 Number of bacteria/g soil evaluated by colony forming units on 1/10 TSBA

Sampling sites	N° bacteria/g
1	4.7×10^4
2	6.0×10^4
4	3.1×10^4
5	9.6×10^4
6	8.23×10^5
7	1.9×10^6
8	4.63×10^4
9	3.43×10^4
12	3.4×10^5
13	7.53×10^4

values for each of the carbon sources tested and were collected respectively from site 1 (nearby the emission source) and sites 4, 8, 5 estimated at high and medium deposition from the theoretical model. The samples grouped in the second cluster presented the higher values and were collected in sites at a greater distance from the emission source, estimated at low or low-medium level of deposition. The only exception was sample 7 collected from a site at high level of deposition but grouping with samples of the second cluster and in this case, some unknown factors may have affected the values of microbial metabolism and growth.

Epidemiological study

Tables 7 and 8 show the causes of death configurations in the total area for males and females respectively. For each cause number of cases, TSDs with the relative standard error (SE) and both provincial and regional SMRs are reported. The statistically significant excesses of SMRs are evidenced in bold characters. The high number of statistically significant defects of SMRs suggest that the health status of people living in the area is better than that expected on the basis of the provincial and even more of the regional mortality. The only mortality excess is related to violent and poisoning death causes in males. Similar pictures with high numbers of statistically significant mortality defects have been detected also for each of the 5 km zones (data not shown).

In Tables 9 and in 10 the statistical significant RRs of zone 1 in respect of zone 2 and 3 respectively are reported. The males of the zone closer to the industrial settlement show a higher mortality for leukemia, cardiovascular disease, respiratory disease and asthma than the males of zone 2. A higher mortality for cardiovascular and respiratory diseases in males was evident also in respect of zone 3, in

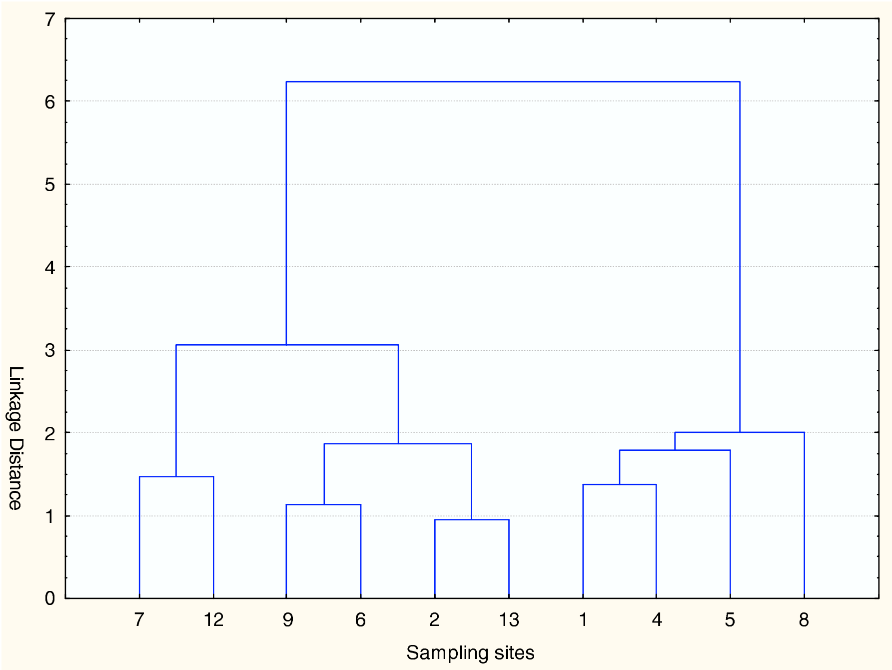

Fig. 8 Cluster analysis of soils from 10 sites based on substrate metabolism of 31 different single carbon sources evaluated with Biolog EcoPlates™. Euclidean Distances (Ward's Method) were calculated by STATISTICA 6

Table 7 Number of death, standardized mortality rates (TSD) (standard population: Italy 1991 census), standard errors (SE) and provincial and regional statistically significant standardized mortality ratio (SMR) in the males of the investigated area during 1980–1997

Total area (Zones 1+2+3)

Males

Causes of death	Number	TSD	SE	Provincial SMR	Regional SMR
All causes	11880	977,32	9,06	96,26**	92,72**
All causes (0–64)	2959	290,24	5,41	95,07**	91,89**
All tumors	2610	215,42	4,25	92,99**	91,51**
All tumors (0–64)	853	86,14	2,97		92,73*
Stomach cancer	256	21,33	1,35		
Colorectal cancer	236	19,58	1,28		
Liver cancer	187	15,29	1,13	85,8*	72,57**
Pancreas cancer	81	6,79	0,76		78,22*
Larynx cancer	73	6,04	0,71		
Lung cancer	707	58,55	2,22		91,85*
Lung cancer (0–64)	272	27,70	1,69		
Pleural cancer	16	1,32	0,33		
Bladder cancer	157	12,91	1,04	83,89*	
Prostate cancer	214	17,48	1,20		
Brain cancer	51	4,29	0,60		68,59**
Brain cancer (0–14)	1	0,37	0,37		
Non-Hodgkin's lymphomas	39	3,24	0,52		67,93*
Hodgkin's disease	15	1,25	0,33		
Multiple myeloma	28	2,27	0,43		
Leukemia	112	9,22	0,88		
Leukemia (0–14)	1	0,37	0,38		16,1*
Cardiovascular diseases	5386	445,84	6,14		95,16**
Cardiovascolar diseas (0–64)	781	80,65	2,92	90,85**	88,76**
Respiratory diseases	1001	82,64	2,64		84,81**
Respiratory diseases (0–64)	145	14,34	1,21		
Cronic resp. Diseases (0–64)	89	9,30	1,00		
Asthma	38	3,11	0,51	68,06*	56**
Genitourinary sistem diseases	250	20,63	1,32		
Liver cyrrosis	291	24,48	1,45		66,66**
Diabetes	352	28,18	1,51		81,19**
Infectious diseases	44	3,57	0,54		
Congenital malformations (0–14)	45	15,92	2,38		
Injury and poisoning	707	58,34	2,21	**111,81****	
Car accidents	209	17,03	1,19		

The SMR values in "excess" are evidenced in bold characters.

*$p<0.05$

**$p<0.01$

addition to all causes, all tumours and lung tumours mortality. Ionizing radiations represent the main aetiological factor for leukemia. Moreover exposure to benzene, solvents, electromagnetic fields and pesticides may also be important (Zanetti and Crosignani 1992; Simonato 1996; Waterhouse et al. 1996).

Cardiovascular diseases, the first cause of death in Italy, are related to many different factors such as hypertension, stress, obesity, cholesterol levels and some pollutants like carbon monoxide and lead that are present mainly in cigarette smoke but also in ambient air (Forastiere et al. 1994; Organizzazione

Table 8 Number of death, standardized mortality rates (TSD) (standard population: Italy 1991 census), standard errors (SE) and provincial and regional statistically significant standardized mortality ratio (SMR) in the females of the investigated area during 1980–1997

Total area (Zones 1+2+3)					
Females					
Causes of death	Number	TSD	SE	Provincial SMR	Regional SMR
All causes	11036	1015,68	9,83	97,03**	92,85**
All causes (0–64)	1694	162,88	4,01	94,01*	90,94**
All tumors	1869	161,14	3,77	91,75**	90**
All tumors (0–64)	682	68,07	2,62		
Stomach cancer	159	14,29	1,15		
Colorectal cancer	224	19,61	1,33		
Liver cancer	175	15,46	1,18	84,04*	72,56**
Pancreas cancer	58	4,94	0,65	75,95*	66,98**
Larynx cancer	5	0,45	0,21		
Lung cancer	98	8,28	0,84	81,17*	81,12*
Lung cancer (0–64)	35	3,49	0,59		
Pleural cancer	10	0,93	0,30		
Bladder cancer	27	2,37	0,46		
Uterus cancer	169	14,50	1,13		
Breast cancer	395	33,66	1,71		
Breast cancer (0–64)	193	19,39	1,40		
Brain cancer	57	4,62	0,62		
Brain cancer (0–14)	2	0,80	0,57		
Non-Hodgkin's lymphomas	23	1,91	0,40	61,38*	60,29*
Hodgkin's disease	9	0,74	0,25		
Multiple myeloma	12	1,00	0,29	55,17*	53,86*
Leukemia	84	7,04	0,78		
Leukemia (0–14)	2	0,73	0,52		
Cardiovascular diseases	5908	560,33	7,40		95,47**
Cardiovascolar disease (0–64)	370	37,31	1,95	87,84*	81,36**
Respiratory diseases	578	54,60	2,32		89,94*
Respiratory diseases (0–64)	76	7,04	0,82		
Cronic resp. diseases (0–64)	34	3,40	0,59		
Asthma	34	2,87	0,50		
Genitourinary sistem diseases	168	15,15	1,18		
Liver cyrrosis	174	14,99	1,15		61,98**
Diabetes	606	54,11	2,23		81,96**
Infectious diseases	40	3,43	0,56		
Congenital malformations (0–14)	51	19,48	2,74		
Injury and poisoning	312	27,90	1,61		86,5**
Car accidents	46	3,80	0,58		

The SMR values in "excess" are evidenced in bold characters.

$^*p<0.05$

$^{**}p<0.01$

Mondiale della Sanità 1997). Due to the inhalatory modality of exposure, respiratory diseases are the main causes related to non-carcinogenic effects of air pollutants like sulphur oxides, suspended particulate matter, photochemical pollutants, some metals and organic volatile compounds (Lebowitz 1996; Katsouyanni et al. 1997; Organizzazione Mondiale della Sanità 1997). Air pollutants may play an important role in asthma attach induction in susceptible people, whose predisposition is genetically determined.

Table 9 Statistically significant mortality rates (standard population: Italy 1991 census) between zone 1 (0–5 km from the industrial site) and zone 2 (5–10 km from the industrial site) in the period 1980–1997

Cause of death	Males	Females
All causes		
All causes (0–64)	0,91*	
All tumors		
Liver cancer	0,71*	
Lung cancer		
Lung cancer (0–64)		
Brain cancer		
Hodgkin's disease		
Leukemia	**1,58***	
Cardiovascular diseases	**1,07***	
Respiratory diseases	**1,17***	
Respiratory diseases (0–64)		
Asthma	**2,24***	
Liver cyrrosis		
Congenital malformations (0–14)		
Injury and poisoning		
Car accidents		**2,09***

The "excesses" are evidenced in bold characters.

*p<0.05

**p<0.01

Table 10 Statistically significant mortality rates (standard population: Italy 1991 census) between zone 1 (0–5 km from the industrial site) and zone 3 (10–15 km from the industrial site) in the period 1980–1997

Cause of death	Males	Females
All causes	**1,12****	
All causes (0–64)		
All tumors	**1,14***	
Liver cancer		
Lung cancer	**1,34***	
Lung cancer (0–64)		
Brain cancer		
Hodgkin's disease		
Leukemia		
Cardiovascular diseases	**1,11****	
Respiratory diseases		
Respiratory diseases (0–64)		
Asthma	**2,00***	
Liver cyrrosis		
Congenital malformations (0–14)		
Injury and poisoning		
Car accidents		

The "excesses" are evidenced in bold characters.

*p<0.05

**p<0.01

Table 11 Statistically significant mortality rates (standard population: Italy 1991 census) between zone 2 (5–10 km from the industrial site) and zone 3 (10–15 km from the industrial site) in the period 1980–1997

Cause of death	Males	Females
All causes	**1,08****	
All causes (0–64)	**1,12***	
All tumors		
Liver cancer	**1,67***	
Lung cancer	**1,29***	
Lung cancer (0–64)	**1,54***	
Brain cancer	0,51*	
Brain cancer (0–14)		
Hodgkin's disease	0,19*	
Leukemia		
Cardiovascular diseases		
Respiratory diseases		
Respiratory diseases (0–64)	**2,09****	
Asthma	0,34**	
Liver cyrrosis	**1,43***	
Congenital malformations (0–14)		0,47*
Injury and poisoning		0,70*
Car accidents		

The "excesses" are evidenced in bold characters.

*p<0.05

**p<0.01

Lung tumour, whose incidence has drastically raised during the last decades, is the first tumoral cause of death in males in Italy and in the most of industrial countries. Cigarette smoking is the main risk factor but also professional exposure to toxic compounds like asbestos, chromate, inorganic arsenic, polycyclic aromatic hydrocarbons and radon are involved. Environmental exposure to air pollutants plays a role too as evidenced by the higher incidence of lung tumours in urban than in rural areas in industrial countries. It has been estimated that from 2.5 to 10% of lung tumours in urban areas are due to air pollution (Zanetti and Crosignani 1992; Hemminki and Pershagen 1994; Kafdar et al. 1996; Organizzazione Mondiale della Sanità 1997; Uccelli et al. 2000).

In Table 11 the statistical significant RRs of zone 2 in respect of zone 3 are shown. In this case male population of zone 2 exhibits a higher mortality for all causes and for lung tumours (in both cases also in people less than 65 years old), liver cancer, respiratory diseases (in people less than 65 years old) and cirrhosis. Liver cancer and cirrhosis have been usually

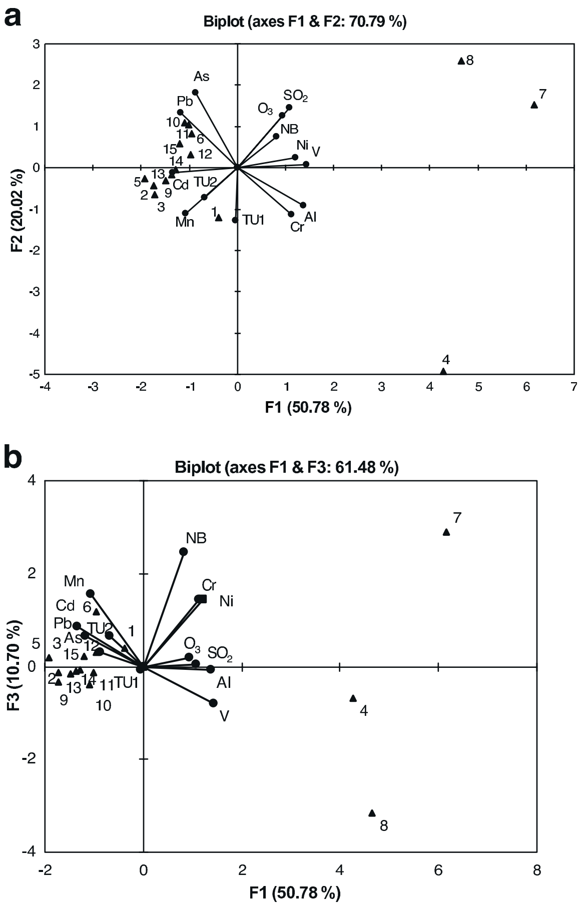

Fig. 9 Biplots of (**a**) F1 and F2 axes (70.79%) and (**b**) F1 and F3 axes (61.48%) obtained by Principal Components Analysis (PCA) carried out using as data input: O_3 and SO_2 concentrations in air, airborne pollutant ecotoxicity (TU1=Toxic Units 10 Jul/6 Aug, TU2=Toxic Units 11 Sept/11 Oct), toxic element (Al, As, Cd, Cr, Mn, Ni, Pb, V) concentrations and bacterial growth (Number of bacteria/g soil – NB) in soils

associated to *virus* hepatitis B infection, to elevated alcohol consumption and, probably, to cigarette smoking. Also professional exposure to some pollutants like polychlorinated biphenyls (PCBs) in petroleum refinery could be involved (Zanetti and Crosignani 1992; ISPESL 1995; Simonato 1996). In all cases but the one for car accident of zone 1 in respect of zone 2, females show no significant RR excess.

On the other hand, municipalities of zone 3 are characterized in respect of zone 2 by a higher mortality for brain tumors, Hodgkin's disease and asthma in males and for congenital malformations, injuries and poisoning in females. Even if etiology of brain cancer is still not well known, it has been associated to farmers' exposure to pesticides and to professional exposure in petroleum industry or to electromagnetic fields. Hodgkin's disease is usually connected to occupational exposure to solvents, phenoxy acids and chlorophenols (Zanetti and Crosignani 1992; Simonato 1996). Male population of zone 2 has a higher mortality for all causes in people less than 65 years old and for liver cancer than males of zone 1.

Multivariate analysis

Principal Component Analysis (PCA) has been carried out by *XL-STAT* (Addinsoft), employing as data input: O_3 and SO_2 concentrations in air, airborne pollutant ecotoxicity (TU), toxic element (Al, As, Cd, Cr, Mn, Ni, Pb, V) concentrations and bacterial growth (CFU) in soils.

The biplots reported in Fig. 9 show that the sites 4, 7 and 8 have different characteristics (for the considered variables), in respect to the other sites and that exist some correlations between the variables. Other than the above mentioned (§ 4.1) correlation between SO_2 and O_3 concentration, we can observe other correlations between toxic elements in soils, as: Pb and As, Al and Cr, Al and V.

Conclusions

On the basis of this work, SO_2 and O_3 seem to be the main environmental pollutants in the area surrounding the industrial settlement of Milazzo. During the monitoring period their concentrations overcame the limits established to protect vegetation and the assessment of the pollutant damage on agriculture has shown much higher crop losses due to O_3 than to SO_2.

Most of experimental data have shown that industrial emissions are not the only pollution sources in the study area. In fact SO_2 mean levels and the concentration gradient did not agree with the expected from the theoretical model that is based on the dispersion of the contaminants emitted from the industrial site. Moreover the Semipermeable Membrane Devices toxicological data associated with organic airborne pollutants seldom correspond to particulate concentrations evaluated in the same sites by the mathematical model.

Conversely, the evaluation of soil microbial metabolism seems to be in accord with the theoretical model of contaminant dispersion, showing a grouping of the sites corresponding to the estimated particulate deposition. This is in agreement with published data reporting a correlation between the presence of toxic elements or organic contaminants and a disturbance of soil microbial community (Westergaard et al. 2001; Shi et al. 2002).

Considering elemental concentrations in agricultural soils, no relevant differences were found among the investigated sites. Moreover high levels of toxic elements were not measured in crop samples collected in those farms where more important particulate fallout from thermoelectric power plant and oil refinery was assessed.

The epidemiological study has evidenced a good health state of people living in the examined area in respect both to the Messina province either to the Sicily region. But the risks of people residing in the municipalities inside the area seem to be not equally distributed. Health state of male population of the two zones closest to the industrial settlement was worst than that of the males of the very far zone. Behind a higher mortality for all causes, a statistical significant higher mortality for lung cancer and respiratory diseases in people less than 65 years old has been detected. Anyway mortality for all causes and respiratory diseases has shown a decrease from 1980 to 1997, while lung cancer mortality has shown an increase even if it remained at a lower level than the Italian mean. Such increased risks in industrial sites have been detected by other investigations (Suarez Varela et al. 1995; Yang et al. 1997; Bhopal et al. 1998; Pless-Mulloli et al. 1998; Yang et al. 1999; Jedrychowski 1999; Benedetti et al. 2001). Male residents in the zone closest to the industrial settlement have exhibited a higher mortality also for all tumors and cardiovascular diseases in respect of the very far zone. Males of the intermediated zone have shown a higher mortality also for liver tumors and cirrhosis. Both mortality for all tumors and liver tumors increased during the considered period. The higher male mortality for leukemia of the zone closest to the industrial settlement in respect of the intermediate one must also be considered, as some evidences associate this kind of tumors with living in the neighborhood of industrial sites (Knox and Gilman 1997; Benedetti et al. 2001; Speer et al. 2002). In female populations no indicative difference has been detected between the three zones. Because of the relevant numerical differences between males and females employed in factories, this different health state of the two sexes in relation with the distance from the industrial settlement lead us to hypothesize a greater influence of professional rather than environmental exposure.

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References

Altshuller, A. P. (1984). Atmospheric particle sulfur and sulfur dioxide relationship at urban and non urban locations. *Atmospheric Environment, 18*(7), 1421–1431.

Aunan, K., Pàtzay, G., Asbjørn Aaheim, H., & Martin Seip, H. (1998). Health and environmental benefits from air pollution reductions in Hungary. *Science of the Total Environment, 212*, 245–268.

Benedetti, M., Iavarone, & Comba, P. (2001). Cancer risk associated with residential proximity to industrial sites: A review. *Archives of Environmental Health, 56*, 342–349.

Bhopal, R. S., Moffatt, S., Pless-Mulloli, T., Phillimore, P. R., Foy, C., Dunn, C. E., et al. (1998). Does living near a constellation of petrochemical, steel and other industries impair health? *Occupational & Environmental Medicine, 55*, 812–822.

Breslow, N. E., & Day, N. E. (1987). *Statistical methods in cancer research I: The design and analysis of chort studies*. IARC Scientific Publication N. 82. Lyon: IARC.

Briat, J. F., & Sebrun, M. (1999). Plant responses to metal toxicity. *C.R. Acad. Sci. Paris. Sciences de la vie/Life Sciences, 332*, 43–54.

Briggs, G. A. (1975). *Plume rise predictions, lectures on air pollution and environmental impact analysis III* (pp. 59–111). Boston: Haugen.

Cagnetti, P., Brofferio, C., & Ferrara, V. (1985). Metodologie per la valutazione delle concentrazioni in aria e delle contaminazioni del suolo da rilasci aeriformi radioattivi. ENEA *Technical Report*, RT/PAS/85/26, Rome.

Campbell, C. D., Grayson, S. J., & Hist, D. J. (1997). Use of rhizosphere carbon sources tests to discriminate soil microbial communities. *Journal of Microbiological Methods, 30*, 33–41.

Camposano, F., Cirillo, M., & Triolo, L. (1986). Elaborazione di funzioni dose risposta degli effetti di SO_2 sulle rese di specie agricole. ENEA *Technical Report*/Studi Vasa (8), Rome.

Centre of Ecology and Hydrology (Natural Environment Research Council) (2002). Economic assessment of crop yield losses from ozone exposure. Contract EPG 1/3/170-The UNECE International Cooperative Programme on Vegetation.

Cetin, E., Odabasi, M., & Seyfioglu, R. (2003). Ambient volatile organic compound (VOC) concentrations around a petrochemical complex and a petroleum refinery. *Science of the Total Environment, 312*, 103–112.

Chen, T. B., Wong, J. W. C., Zhon, H., & Wong, M. H. (1997). Assessment of trace metal distribution and contamination in surface soils of Hong Kong. *Environmental Pollution, 96*, 6–68.

Collins, W. J., Stevenson, D. S., Jonson, C. E., & Dervent, R. G. (2000). The European regional ozone distribution and its links with the global scale for the years 1992 and 2015. *Atmospheric Environment, 34*, 2555–267.

De Santis, F., Allegrini, I., Fazio, M. C., Pasella, D., & Piredda, R. (1997). Development of a passive sampling technique for determination of nitrogen dioxide and sulphur dioxide in ambient air. *Analytica Chimica Acta, 346*, 127–134.

Eliassen, A., & Saltbones, J. (1983). Modelling of long-range transport of sulphur over Europe: A two year model run and some model experiments. *Atmospheric Environment, 17*(8), 1457–1473.

Elliot, P., & Wartenberg, D. (2004). Spatial epidemiology: Current approaches and future challenges. *Environmental Health Perspectives, 9*, 998–1006.

Ferraresi, A., & Corticelli, C. (2002). Cosa sono i metalli pesanti che si "nascondono" nel cibo. *Agricoltura, 6*, 17–19.

Fontana, V., Baldi, R., Franchini, M., Gridelli, P., Ceppi, M., Magnoni, U., et al. (2000). Epidemiologic study of the residents of southeastern area of the Municipality of La Spezia. *Epidemiologia e Prevenzione, 24*, 172–179.

Forastiere, F., Peducci, C. A., Di Pietro, A., Miceli, M., Rapiti, E., & Bargagli, A. (1994). Mortality among urban policemen in Rome. *American Journal of Industrial Medicine, 26*, 785–798.

Fritze, H., Perkiömäki, J., Saarela, U., Katainen, R., Tikka, P., Yrjälä, K., et al. (2000). Effect of Cd-containing wood ash on the microflora of coniferous forest humus. *FEMS Microbiology, Ecology, 32*, 43–51.

Fuhrer, J., & Booker, F. (2003). Ecological issues related to ozone: Agricultural issues. *Environment International, 29*, 141–154.

Fuhrer, J., Skarby, L., & Ashmore, M. R. (1997). Critical levels for ozone effects on vegetation in Europe. *Environmental Pollution, 97*, 91–106.

Garcia-Huidobro, T., Marshall, F. M., & Bell, J. N. B. (2001). A risk assessment of potential agricultural losses due to ambient SO_2 in the central regions of Chile. *Atmospheric Environment, 35*, 4903–4915.

Giorgielli, F., Minnocci, A., Panicucci, A., & Vitagliano, C. (1994). Effects of long-term SO_2 on olive tree gas exchange and leaf morphology. *ISHS Acta Horticulturae, 356*, 185–188 (II International Symposium On Olive Growing).

Haughand, T., Steinnes, E., & Frontasjeva, M. V. (2002). Trace metals in soil and plant subjected to strong chemical pollution. *Water, Air and Soil Pollution, 137*, 343–353.

Hemminki, K., & Pershagen, G. (1994). Cancer risk of air pollution: Epidemiological evidence. *Environmental Health Perspectives, 102*, 187–192.

Hutckins, J. N., Tubergen, M. W., & Manuweera, G. K. (1990). Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere, 20*(5), 533–552.

Isidori, M., Ferrara, M., Lavorgna, M., Nardelli, A., & Parrella, A. (2003). In situ monitoring of urban air in Southern Italy with the *Tradescantia* micronucleus bioassay and semipermeable membrane devices (SPMDs). *Chemosphere, 52*(1), 121–126.

ISPESL (1995). Mortalità per professioni in Italia negli anni '80. Progetto ReSò. *Collana Quaderni Istituto Superiore per la Prevenzione e la Sicurezza del Lavoro N.2*.

ISTAT (2000). V Censimento Generale dell'Agricoltura.

Jedrychowski, W. (1999). Ambient air pollution and respiratory health in the East Baltic region. *Scandinavian Journal of Work, Environment & Health, 25*(Suppl 3), 5–16.

Johnson, B. T., Petty, J. D., & Huckins, J. N. (2000). Collection and detection of lipophilic chemical contaminants in water, sediment, soil and air SPMD-TOX. *Environmental Toxicology, 15*(3), 248–252.

Kabata-Pendias, A. (2000). *Trace elements in soils and plants* (3rd ed.). Boca Raton, FL: Lewis, CRC.

Kafdar, K., Freedman, L. S., Goodall, C. R., & Tukey, J. W. (1996). Urban city-related trends in lung cancer mortality in US counties: White females and white males, 1970–1987. *International Journal of Epidemiology, 25*, 918–932.

Kärenlampi, L., & Skarby, L. (1996). Critical levels for ozone in Europe: Testing and finalizing the concepts. UNECE Workshop Report. University of Kuopio, Dept. Ecology and Environmental Science, Finland, 363 pp.

Katsouyanni, K., Touloumi, G., Spix, C., Schwartz, J., Balducci, F., Medina, S., et al. (1997). Short term effects of ambient sulphur dioxide and particulate matter on mortality in 12 European cities: Results from time series data from the APHEA Project. *British Medical Journal, 314*, 1658–1663.

Knox, E. G., & Gilman, E. A. (1997). Hazard proximities of childhood cancer in Great Britain from 1953–80. *Journal of Epidemiology and Community Health, 51*, 151–159.

Lebowitz, M. D. (1996). Noncarcinogenic respiratory disease. In R. Bertollini, M. D. Lebowitz, R. Saracci, & A. Savitz (Eds.), *Environmental epidemiology: Exposure and disease*. New York: World Health Organization, Lewis.

Lohmann, R., Corrigan, B. P., Howsam, M., Jones, K. C., & Ockenden, W. A. (2001). Further development in the use of semipermeable membrane devices (SPMDs) as passive samplers for persistent organic pollutants: Field application in a spatial survey of PCDD/Fs and PAHs. *Environmental Science & Technology, 35*, 2576–2582.

Lorenzini, G. (1999). *'Ozono' in Le piante e l'inquinamento dell'aria* (p. 116). Bologna: Edagricole–Edizioni Agricole.

Manes, F., De Santis, F., Giannini, M. A., Bazzana, C., Carogna, F., & Allegrini, I. (2003). Integrated ambient ozone evaluation by passive samplers and lower biomonitoring mini-stations. *Science of the Total Environment, 308*, 133–141.

Martuzzi, M., Mitis, M., Buggeri, A., Terracini, B., & Bertollini, R. (2002). Ambiente e stato di salute nella popolazione delle aree ad alto rischio di crisi ambientale in Italia. *Epidemiologia e Prevenzione, 26*, 1–56.

Medrado-Faria, M. A., Rodrigues de Almeida, J. W., & Zanetta, D. M. (2001). Gastric and colorectal cancer mortality in an urban and industrialized area of Brazil. *Revista do hospital* *das clinicas. Faculdade de medicina da Universidade de Sao Paulo, 56*, 47–52.

Microtox Manual (1995). *Acute toxicity basic test procedures*. Carlsbad, CA, USA: Microbics.

Nali, C., Pucciariello, C., & Lorenzini, G. (2002). Ozone distribution in Central Italy and its effect on crop productivity. *Agriculture, Ecosystems & Environment, 90*, 277–289.

Organizzazione Mondiale della Sanità (1997). *Ambiente e Salute in Italia*. R. Bertollini, M. Fabbri, & N. Di Tanno (Eds.), OMS Centro Europeo Ambiente e Salute, Divisione di Roma. Il Pensiero Scientifico Editore, Roma.

Petty, J. D., Jones, S. B., Huckins, J. N., Cranor, W. L., Parris, J. T., McTague, T. B., et al. (2000a). An approach for assessment of water quality using semipermeable membrane devices (SPMDs) and bioindicators tests. *Chemosphere, 41*, 311–321.

Petty, J. D., Orazio, C. E., Huckins, J. N., Gale, R. W., Lebo, J. A., Meadows, J. C., et al. (2000b). Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants. *Journal of Chromatography, 879*, 83–95.

Petty, J. D., Orazio, C. E., Huckins, J. N., & Zajicek, J. L. (1993). Application of semipermeable membrane devices (SPMDs) as passive air samplers. *Chemosphere, 27*(9), 1609–1624.

Pleijel, H., Danielsson, H., Ojanperä, K., De Temmerman, L., Högy, P., Badiani, M., et al. (2004). Relationships between ozone exposure and yield loss in European wheat and potato-a comparison of concentration and flux-based exposure indices. *Atmospheric Environment, 38*, 2259–2269.

Pless-Mulloli, T., Dunn, C. E., Bhopal, R., Phillimore, P., Moffatt, S., & Edward, S. J. (2000). Is it fasible to construct a community profile of exposure to industrial air pollution? *Occupational & Environmental Medicine, 57*, 542–549.

Pless-Mulloli, T., Phillimore, P., Moffat, S., Bhopal, R., Foy, C., Dunn, C., et al. (1998). Lung cancer, proximity to industry, and poverty in northeast England. *Environmental Health Perspectives, 106*, 189–196.

Sanders, G. E., Skarby, L., Ashmore, M. R., & Fuhrer, J. (1995). Establishing critical levels for the effects of air pollution on vegetation. *Water, Air and Soil Pollution, 85*, 189–200.

Shi, W., Becker, J., Bishoff, M., Turco, R. F., & Konopka, A. E. (2002). Association of microbial community composition and activity with lead, chromium and hydrocarbon contamination. *Applied and Environmental Microbiology, 68*, 3859–3866.

Simonato, L. (1996). Neoplastic diseases (lung cancer excluded). In R. Bertollini, M. D. Lebowitz, R. Saracci, & D. A. Savitz (Eds.), *Environmental epidemiology: Exposure and disease*. New York: World Health Organization, Lewis.

Soderstrom, H., Hajslova, J., Kocourek, V., Siegmund, B., Kocan, A., Obiedzinski, W., et al. (2005). PAHs and nitrate PAHs in air of five European countries determined using SPMDs as passive samplers. *Atmospheric Environment, 39*, 1627–1640.

Speer, S., Semenza, J., Kurosaki, T., & Anton-Culver, H. (2002). Risk factors for acute myeloid leukemia and multiple myeloma: A combination of GIS and case-control studies. *Journal of Environmental Health, 64*, 9–16.

Suarez Varela, M. M., Dominguez Lillo, C., & Llopis Gonzalez, A. (1995). A comparative study of mortality in agricultural and industrial areas in Spain. *European Journal of Epidemiology, 11*, 633–641.

Triolo, L., Barlattani, M., Ferrandi, L., Letardi, A., Testa, V., Zappa, G., et al. (1996). Valutazione degli effetti degli inquinanti sui sistemi vegetali per lo studio del sito di localizzazione di un inceneritore nel territorio della Provincia di Udine. In ENEA & Province of Udine (Eds.), *L'inceneritore nella provincia di Udine* (pp. 187–225). Rome: ENEA.

Turrini, A., Saba, A., Perrone, D., Cialda, E., & D'Amicis, A. (2001). Food consumption patterns in Italy: The INN-CA study 1994–1996. *European Journal of Clinical Nutrition, 55*, 571–588.

Uccelli, R., Binazzi, A., & Mastrantonio, M. (2002). Descrizione dello stato di salute delle popolazioni residenti in tre siti della Toscana (Livorno, Orbetello e Piombino) mediante il quadro della mortalità per causa. *Igiene e Sanità Pubblica, 23*(3), 101–118.

Uccelli, R., Mastrantonio, M., & Di Paola, M. (2000). Distribuzione delle cause di morte in comuni a diverso grado di urbanizzazione. *Epidemiologia e Prevenzione, 24*(1), 28–37.

UNECE (2004). Convention on long-range transboundary air pollution. International cooperative programme on effects of air pollution on natural vegetation and crops. Chapter III-mapping critical levels for vegetation, 13 pp.

Vitagliano, C., Minnocci, A., & Sebastiani, L. (1999). Physiological response of two olive genotypes to gaseous pollutants. *ISHS Acta Horticulturae, 474*, 431–434 (III International Symposium On Olive Growing).

Wakefield, J., & Elliot, P. (1999). Issues in the statistical analysis of small area health data. *Statistics in Medicine, 18*, 2377–2399.

Waterhouse, D., Carman, W. J., Schottenfeld, D., Gridley, G., & McLean, S. (1996). Cancer incidence in the rural community of Tecumseh, Michigan: A pattern of increased lymphopoietic neoplasm. *Cancer, 77*, 763–770.

Westergaard, K., Müller, A. K., Christensen, S., Bloem, J., & Sørensen, S. J. (2001). Effects of tylosin as a disturbance on the soil microbial community. *Soil Biology & Biochemistry, 33*, 2061–2071.

Williams, F. L., & Ogston, S. A. (2002). Identifying population at risk from environmental contamination from point sources. *Occupational & Environmental Medicine, 59*, 2–8.

World Health Organization (WHO) (1996). *Trace elements in human nutrition and health*. Geneva.

Yang, C. Y., Cheng, M. F., Chiu, J. F., & Tsai, S. S. (1999). Female lung cancer and petrochemical air pollution in Taiwan. *Archives of Environmental Health, 54*, 180–185.

Yang, C. Y., Wang, J. D., Chan, C. C., Chen, C. C., Huang, J. S., & Cheng, M. F. (1997). Respiratory and irritant health effects of a population living in a petrochemical-polluted area in Taiwan. *Environmental Research, 74*, 145–149.

Zanetti, R., & Crosignani, P. (1992). *Il Cancro in Italia. I dati di incidenza dei Registri Tumori 1983–1987* (p 425). Torino: Tipolitografia Silvestrelli e Cappelletto s.r.l.