

## **Indoor air quality in schools of a highly polluted South Mediterranean area**

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## **ABSTRACT**

This study aimed at surveying lower secondary schools in southern Italy, in a highly polluted area. A community close to an industrial area and three villages in rural areas were investigated. Indoor temperature, relative humidity (RH), gaseous pollutants (CO<sub>2</sub> and NO<sub>2</sub>), selected biological pollutants in indoor dust, and the indoor/outdoor mass concentration and elemental composition of PM<sub>2.5</sub> were ascertained.

Temperature and RH were within, or close to, the comfort range, while CO<sub>2</sub> frequently exceeded the threshold of 1,000 ppm, indicating inadequate air exchange rate. In all the classrooms, median NO<sub>2</sub> levels were above the WHO threshold value. *Dermatophagoides p.* allergen concentration was below the sensitizing threshold, while high endotoxin levels were detected in the classrooms, suggesting schools may produce significant risks for endotoxin exposure.

Concentration and solubility of PM<sub>2.5</sub> elements were used to identify the sources of indoor particles. Indoor concentration of most elements was higher than outdoors. Re-suspension was responsible for the indoor increase of soil components. For elements from industrial emission (Cd, Co, Ni, Pb, Sb, Tl, V) the indoor concentration depended on penetration from the outside. For these elements, differences in rural vs industrial concentrations were found, suggesting industrial sources may influence indoor air quality nearby schools.

**Key words:** PM<sub>2.5</sub>; heavy metals; indoor comfort parameters; air pollution; endotoxin; *Der p 1*

## **Practical implications**

- In the studied area, poor ventilation and high concentration levels of CO<sub>2</sub> and NO<sub>2</sub> characterized most of the considered classrooms. This may indirectly affect the productivity of occupants also causing non-specific symptoms. The concentration of elements in indoor PM<sub>2.5</sub> was sustained by soil particle re-suspension and penetration of outdoor particles. In the evaluated context, industrial sources may have a significant influence on the indoor air quality in schools.

## 1 INTRODUCTION

In Europe and all over the world, there have been increasing concerns regarding the effects of indoor environments on human health. Indoor environments are characterised by typical sources and peculiar chemical and physical features that require extensive specific studies. The World Health Organization (WHO) has published specific guidelines for IAQ<sup>1,2</sup>, producing a comprehensive review of the scientific evidence on health problems associated with building moisture and biological and chemical agents in indoor sites. A strategy for the prevention and control of diseases related to indoor environments has also been developed in the framework of the Fifth Ministerial Conference on Environment and Health organized by the WHO - European Region (Parma, March 2010). Recent reports highlighted the potential health-related concerns associated to dust particles exposure<sup>3</sup>, in particular in areas close to industrial sites where higher heavy metal concentration in indoor dust has been reported<sup>4</sup>. Multidisciplinary reports about indoor measurements in heavily polluted areas on health-relevant chemical and physical properties are still scanty<sup>5</sup>.

In addition to the specific sources related to indoor activities, indoor air quality (IAQ) has been shown to have a direct association with the quality of outdoor air<sup>6</sup>; the contribution due to the infiltration of pollutants from outdoor sources has been analysed in some previous studies, some of which focused on particulate matter (PM)<sup>7-8</sup>. Particularly in very polluted areas, such as industrial sites or urban areas of developing countries, indoor air may reflect the poor quality of the outdoor atmosphere, and domestic and school environments, where urban populations – and children in particular – typically spend up to 90% of their time, thus requiring special attention<sup>9-10</sup>.

Recently, data related to IAQ in schools were collected in different European Countries<sup>11-14</sup> and several studies have shown that children who study and live in industrial areas have a tendency to present increased respiratory symptoms when compared to those living in other

areas<sup>15-16</sup>. IAQ problems in school environments are more serious than in other categories of buildings. Schools are places with a high population density, in which different types of pollutants may be introduced and remain for a long time due to insufficient outside air supply, and are often characterised by infrequent interventions for environmental remediation and building maintenance<sup>17</sup>. Many of the more common indoor sources, such as smoking and cooking, are usually not present in school buildings, but several studies have demonstrated that exposure to airborne particles in classrooms can be high anyway<sup>18-21</sup>, also including increased airborne bacterial concentration in respirable particulate matter<sup>22</sup>.

The presence of outdoor pollution sources – such as vehicles, industrial complexes, petrochemical plants, gas/oil stations, and commercial facilities – in the proximity of school buildings may represent an important health risk factor, in particular for vulnerable individuals such as children.

Furthermore, several factors such as poor buildings quality, lack of hygiene procedures and insufficient ventilation (natural and/or mechanical) may worsen schoolchildren's exposure to indoor pollutants<sup>23-25</sup>. School indoor environments frequently present poor IAQ due to high indoor CO<sub>2</sub> concentration: this is associated with decrease in annual average daily attendance<sup>26</sup> and students' performance<sup>27-28</sup>. In addition, biological agents, such as endotoxins and dust mite allergens (*Dermatophagoides pteronyssinus* – *Der p 1*), can significantly affect the air quality in school environments<sup>29-30</sup>. Moreover, presence of mold is linked to adverse health effects such as asthma symptoms, coughing, wheezing, and upper respiratory tract symptoms<sup>31</sup>.

Sicily, in the Mediterranean area of southern Italy, is characterised by the presence of three vast polluted sites, where large petrochemical industries and power plants are located not far from urban areas. The aim of the present work is to evaluate the IAQ and to assess the presence of specific indoor pollutants in schools located in one of these areas (Gela, on the southern Mediterranean coast of Sicily), considering both schools located inside the urban area,

close to the petrochemical plant, and schools located in a rural area surrounding the city and the plant. All the lower secondary school buildings of the Gela Health District were investigated by taking measurements of indoor comfort parameters (temperature – T – and relative humidity – RH), gaseous pollutants (carbon dioxide [CO<sub>2</sub>] and nitrogen dioxide [NO<sub>2</sub>]), biological pollutants in indoor dust (endotoxins and *Der p 1*), mass concentration and elemental composition of particles below 2.5 µm (PM<sub>2.5</sub>). The possible sources of PM<sub>2.5</sub> and the relationship with outdoor PM were investigated.

## **2 MATERIAL AND METHODS**

### **2.1 Study design**

Between March 2012 and February 2013, in the context of “RESPIRA” Project – *Indoor and Outdoor Air Quality and Respiratory Health in Malta and Sicily* – an environmental investigation was performed on the Health District of Gela, in southern Sicily (Italy), in the Mediterranean basin (Figure 1). A petrochemical industry, operating since 1965, is located close to the urban area of Gela (Figure 1, panel B).

The study involved all 12 lower secondary schools in the four communities of the Health District of Gela (Figure 1): Gela (six schools, 77,000 inhabitants) representing the industrial area, and Niscemi (three schools, 26,400 inhabitants), Mazzarino (two schools, 11,800 inhabitants), and Butera (one school, 4,900 inhabitants) in rural areas, which are located about 15, 27, and 16 km from Gela, respectively. School samplings were carried out during the spring, from March 21 to May 26, 2012, with the only exception of one school in Niscemi (NI03), which was sampled in November 2012. Moreover, to obtain a more robust dataset, 72 additional sites were selected for the evaluation of outdoor PM<sub>2.5</sub> concentration and elemental composition (36 in the residential area of Gela and 36 in the residential areas of Niscemi, Mazzarino, and

Butera). Seventy of the 72 samplings were carried out during the cold season, from September 24, 2012, to February 22, 2013; the last two were carried out in May 2013.

The study was approved by the Ethical Committee of the Provincial Health Authority of Caltanissetta (Italy) on December 15, 2011. All parents of the children signed an informed consent. The respect of individual privacy concerning clinical data was granted.

In each school (three classrooms at the same time) we measured CO<sub>2</sub> and NO<sub>2</sub> concentration, temperature, relative humidity, contamination with *Der p 1* allergen and endotoxin, fine fraction of airborne particulate matter (PM<sub>2.5</sub>) and its elemental content. Outdoor PM<sub>2.5</sub> was simultaneously monitored in the courtyard of each school. Table 1 describes the characteristics of the monitored classrooms. The schools were identified by means of the initials of the city and a progressive number: (GE1-6 – Gela, NI1-3 – Niscemi, MZ1-2 – Mazzarino, BU1 – Butera).

## **2.2 Comfort parameters and gaseous pollutants**

Indoor continuous monitoring of gaseous pollutants was carried out for 48 hours in the three classrooms of each school at the same time. The sampling was performed by Aeroqual IQM 60 (Aeroqual Ltd, New Zealand) an instrumentation capable of monitoring common air quality parameters such as NO<sub>2</sub>, CO<sub>2</sub>, T and RH; data logging intervals were fixed at two minutes. The device was equipped with sensors for T (range: -20°C / +40°C, accuracy ±0.3°C, resolution 0.1°C), RH (range: 0-100%, accuracy ±2% RH, resolution 0.1% RH), CO<sub>2</sub> (Non-Dispersive Infra-Red technology, range: 0-2,485 ppm, detection limit: 5 ppm, resolution: 1 ppm), NO<sub>2</sub> (Gas Sensitive Electrochemical technology, range: 0-1 ppm, detection limit: 2 ppb; resolution: 1 ppb). For the purposes of the present study, the median values of CO<sub>2</sub> concentrations were calculated using only the data collected when the classrooms were occupied by students.



### 2.3 Biological pollutants in indoor dust

Sampling of biological indoor contaminants was performed in all the schools involved in the study. In each classroom, dust was sampled twice a day: the first sampling was carried out in the morning before the start of the lessons (T<sub>1</sub>), and the second in the early afternoon, immediately after the end of the lessons (T<sub>2</sub>).

A standardized procedure for collecting dust samples was followed, using a 2000 W Free-Space Evo vacuum-cleaner (Hoover Inc., New York) equipped with a dust collector device (Dustream™ collector and filters, Indoor Biotechnologies, Cardiff, UK). In each classroom, six areas (one square meter each) on the floor and six areas above the floor (desks, chairs, windowsills) were vacuumed in the same dust collector. Immediately after collection, the dust samples were sealed in pre-labelled and sterile zip-lock bags and stored at -20°C. Only samples containing > 20 mg of dust were analyzed.

The samples were extracted according to the Manufacturer's protocol (Indoor Biotechnologies, Cardiff, UK) and centrifuged for 20 minutes at 2,500 rpm at 4°C. The supernatant was divided into aliquots (200 µl each) and stored at -20°C until analysis.

Several extract dilutions (1:2, 1:3, 1:4, and 1:5) were analysed for *Der p 1* allergen with monoclonal antibody-based ELISAs, using quantitative ELISA kits from Indoor Biotechnologies, Inc.. The samples were read at 405 nm; allergen concentrations were obtained in ng of allergen/ml and then converted into µg of allergen/g of dust.

Endotoxin (~~or LPS~~) concentration was determined using the QCL-1000 kinetic chromogenic LAL assay (Lonza, Switzerland). Serial dilutions of extracts were prepared, and 50 µl of each were analysed by the microplate method according to QCL-1000 kit protocol. LAL-sample reactions were incubated at 37°C for 10 minutes; afterward, a substrate solution was mixed with the LAL-sample and incubated for additional six minutes at 37°C. The

absorbance of the samples, in direct proportion with the endotoxin amount, was determined by spectrophotometry at 405-410 nm. The endotoxin concentration was calculated from a standard curve (from 0.1 to 1.0 EU/ml of endotoxin). To standardize the different values and simplify the statistical analyses, endotoxin concentration was expressed in  $\log_{10}$ EU/mg dust. For each classroom, results relevant to T<sub>1</sub> and T<sub>2</sub> samples were averaged. Separate T<sub>1</sub> and T<sub>2</sub> measures are shown in Supplementary Material S1.

## **2.4 PM<sub>2.5</sub> sampling and elemental analysis**

Fine particulate matter was collected for 48 consecutive hours during working days (Monday to Friday) in 12 schools, following a standardised operating protocol. This sampling duration was necessary to collect a PM mass amount suitable for a reliable analytical determination of PM and trace element concentrations. In each school, identical samplings were simultaneously carried out in three selected classrooms and outdoors in the school yard. The 72 additional outdoor samplings at residential sites were carried out by following the same protocol.

All the indoor and outdoor PM<sub>2.5</sub> measurements were performed using quiet samplers (noise level < 35 dB), specifically developed for indoor environments and able to avoid any interference with school activities (Silent Sampler, FAI Instruments, Fonte Nuova, Rome, Italy). The instruments, operating at a flow rate of 10 l/min, were equipped with inertial impactors having a cut-point diameter of 2.5  $\mu$ m and with 47 mm polytetrafluoroethylene (PTFE) filters (2.0  $\mu$ m pore size, PALL Co.). The sampling head was kept at about 1 m above the ground. Simultaneous indoor and outdoor samplings were carried out in each school. At the end of the sampling and until the analytical phase, the filters were stored in the dark at 4°C.

The first step of the analytical procedure was the determination of the mass concentration of the collected particles. PTFE filters were conditioned at 50% RH and 20°C for 48 hours and

then weighed by using a 1 µg sensitivity automated microbalance (mod. ME5, Sartorius AG, Goettingen, Germany). The same protocol was followed to weigh the filters before and after the sampling phase.

The elemental analysis was carried out according to a procedure that allows the chemical fractionation of the total elemental content into a water-soluble fraction and a residual fraction. This approach provides insight into the chemical form in which the element is released into the atmosphere, allowing a more reliable identification of PM sources and enhancing the estimation of its bio-accessibility<sup>32,33</sup>. The filters were extracted under ultrasound (20 min) in a solution of acetate buffer (CH<sub>3</sub>COOH/CH<sub>3</sub>COOK 0.01 M; pH 4.3). The resulting solution was then filtered on cellulose nitrate membranes (0.45 µm pore size). The obtained fraction (*extracted fraction*) was then analyzed by plasma atomic spectroscopy inductively coupled with plasma mass detection (ICP-MS; 820 MS, Bruker Inc.) for the following elements: arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), rubidium (Rb), antimony (Sb), tin (Sn), thallium (Tl), vanadium (V). The samples were then subjected to microwave-assisted acid digestion, using HNO<sub>3</sub>:H<sub>2</sub>O<sub>2</sub> (2:1), filtered again at 0.45 µm and analyzed by ICP-MS for the *residual fraction* of the same elements. The detection limits of the method are reported in the Supplementary Material S2.

## 2.5 Data Analysis

For CO<sub>2</sub>, NO<sub>2</sub>, RH, T, endotoxin, and Der p 1, the results were reported as medians and interquartile ranges (IQR).

For the analysis of PM results, the statistical significance of the differences between the industrial site (Gela) and the rural areas (Butera, Mazzarino and Niscemi) were evaluated by Mann-Whitney U-test for non-normally distributed data. Indoor-outdoor differences were

evaluated by means of Wilcoxon signed rank test. A p-Value lower than 0.05 was assumed to be statistically significant. All analyses were performed in IBM SPSS statistics v20.

Mean concentration values in the three classrooms per each school were considered for calculating indoor/outdoor ratio and for the statistical evaluation of indoor vs. outdoor and industrial vs. rural differences.

### 3 RESULTS

#### 3.1 Indoor gaseous pollutants and PM<sub>2.5</sub>

Table 2 shows medians and IQR of the indoor values of RH, T, and CO<sub>2</sub> and NO<sub>2</sub> concentrations for each school (sampling frequency: two minutes), separately for occupied and unoccupied periods. Table 2 also reports the indoor concentration (mean, minimum and maximum values in the three classrooms), outdoor concentration and indoor/outdoor (I/O) ratio of PM<sub>2.5</sub>. In Supplementary Material S3 representative tracings relevant to continuous recording are reported for gaseous pollutants CO<sub>2</sub> and NO<sub>2</sub> along with RH and T during 24 hours timeframe in one classroom of schools GE05 and MZ01.

During the occupied periods, the median and IQR values of RH during the monitoring period ranged from 29% – 34% to 58% – 67% for NI01 and NI03, respectively; temperature values ranged from 19.6°C – 20.8°C to 26.7°C – 30.1°C for MZ01 and GE05, respectively.

The carbon dioxide median (and IQR) concentration during the lessons ranged from 343 – 530 ppm in MZ02 to 857 – 1,941 ppm in MZ01. The minimum median range of NO<sub>2</sub> was 50.6 – 60.8 µg/m<sup>3</sup> and the maximum was 95.2 – 105.0 µg/m<sup>3</sup>, found respectively in GE02 and NI03.

PM<sub>2.5</sub> ranged from 11.2 – 18.6 µg/m<sup>3</sup> to 32.7 – 68.0 µg/m<sup>3</sup> in NI03 and MZ02, respectively.

#### 3.2 Indoor endotoxins and Der p 1

A total of 72 samples (two for each classroom) were collected; endotoxin and *Der p 1* were evaluated in every sample (Supplementary Material S1).

To provide information relevant to indoor exposure to endotoxins and *Der p 1* allergen in each school, Table 3 shows the indoor values of endotoxin and *Der p 1*. The values were computed as the average of the samples collected at T<sub>1</sub> and T<sub>2</sub> in the three selected classrooms

of each school (N=36 [12 schools, three classrooms per each]). The median endotoxin (and range) values during the monitoring period ranged from 1.86 log<sub>10</sub>EU/mg (1.83 – 2.10) to 7.50 log<sub>10</sub>EU/mg (6.42 – 10.10), for NI03 and GE02, respectively. Overall, median LPS values at T<sub>2</sub> (3.49 log<sub>10</sub>EU/mg; 2.64 – 5.96) were significantly higher than at T<sub>1</sub> (3.28 log<sub>10</sub>EU/mg; 2.26 – 4.15), p=0.029, Wilcoxon Signed Rank Test).

Median *Der p* 1 values ranged between < 0.20 µg/g in BU01 and MZ02 and 0.84 µg/g in GE01. Due to technical problems, we did not include *Der p* 1 values in one school classroom, and median values of *Der p* 1 under the limit of detection were found in four school classrooms.

### **3.3 Elemental concentration in indoor and outdoor PM<sub>2.5</sub>**

Table 4 reports the concentration (mean, minimum and maximum) of PM<sub>2.5</sub> and elements measured indoors (N=36) and outdoors (N=12) in the twelve schools considered in the study, the p-value of the difference between indoor and outdoor values, their I/O ratio and the correlation coefficient R. The concentration of the 16 elements was calculated as the sum of the extract and residual fractions. For Tl and V, some concentration values were between the limit of detection (LOD) and limit of quantification (LOQ); these values were included in the calculation of the mean value, but they were not considered in the calculation of the I/O ratio (Supplementary Material S2).

Table 5 shows the concentration values (mean, minimum and maximum) of PM<sub>2.5</sub> and elements in the indoor atmosphere of the twelve schools, divided into six “industrial” schools and six “rural” schools. For each element, the p-value of the difference between industrial and rural areas is reported.

The same distinction between industrial and rural areas is made in Table 6, where the outdoor concentration of PM<sub>2.5</sub> and each element is reported (mean minimum and maximum). Here the database has been strengthened by including further measurements carried out in

residential sites, for a total of 84 data points: 42 in the industrial area (six school yards and 36 residential) and 42 in the rural areas (six schoolyards and 36 residential).

The solubility percentage of the considered elements both indoors (schools) and outdoors (divided into school yards and residential sites) is reported in Table 7 separately for industrial and rural sites.

## **4 DISCUSSION**

### **4.1 Indoor gaseous pollutants and PM<sub>2.5</sub>**

Specific guidelines have been developed for comfortable indoor environments, considering parameters such as RH, T<sup>34</sup>, CO<sub>2</sub> and NO<sub>2</sub> concentrations<sup>2</sup>, and differentiating between warm and cold seasons. In the present study, all the schools were examined during the warm season, between March and June, except for NI03, which was examined in November. Nevertheless, in the southern Mediterranean area, November is generally characterized by a mild climate, as evident from temperature reported in Table 2.

According to the definitions in the ANSI/ASHRAE report, during the winter period the indoor comfort temperature should be in the range 20 - 23°C, while in summer it should be between 23 and 26°C. The temperature values recorded in this study (Table 2) exceeded the comfort values in three of the twelve schools: an average temperature of 26.5°C was recorded at GE01 (25.5–28.5), 28.3°C at GE05 (26.7–30.1) and 28.0°C at NI01 (27.2–28.7). Concerning relative humidity, we found that during the monitoring period mean RH values ranged from 31% (29 – 34) to 60% (58 – 67). These values remained in most cases in the comfort range for indoor RH values, which are assumed to vary from 30% to 60%. In fact, maintaining RH below 50% inhibits mould growth, dust mite infestation and bacterial proliferation<sup>35,36</sup>. On the contrary, RH levels below 25% – never found in the present study – were associated with

irritation and possible dry mucous membranes,<sup>37</sup> while lower absenteeism rates in humidified relative to non-humidified schools were reported<sup>38</sup>.

Some variables interact to determine whether people are comfortable in the temperature and relative humidity of the indoor environment where they live. Factors such as the clothing, activity level, age, and physiology of people in schools vary widely; therefore, the thermal comfort requirements differ for each individual<sup>34</sup>. An increase in temperature was positively associated to the risk of daytime attacks of breathlessness (Odds ratio 1.26) by Mi et al<sup>39</sup>. Moreover, toxicology studies have demonstrated an alteration of the absorption patterns of certain toxicants due to increases in room temperature<sup>40</sup>. Nevertheless, the climate of Mediterranean area in the evaluated sites protects against extremes of hot and cold.

Indoor environment of a school, and in particular IAQ, may affect health, comfort and performance of schoolchildren<sup>41-43</sup>. Conversely, we found that CO<sub>2</sub> values, during occupied periods (Table 2), largely exceeded the threshold of 1,000 ppm, considered as acceptable<sup>44</sup>. Indoor CO<sub>2</sub> levels above 1,000 ppm may be considered as indicative of unacceptable ventilation rates with respect to body odors, even though lower CO<sub>2</sub> concentrations values do not necessarily guarantee that the ventilation rate is adequate for removing air pollutants from indoor sources. Our data indicate that the median concentration of CO<sub>2</sub> exceeded 1,000 ppm in four schools, recording 1,123 ppm in GE02 (760 – 1389), 1,182 ppm in GE03 (456 – 1,791), 1,199 ppm in GE04 (582 – 1,594) and 1,477 ppm in MZ01 (857 – 1,941). CO<sub>2</sub> concentrations are often used as a surrogate for the rate of outside air supply per occupant. Moreover, a multicenter European study showed that schoolchildren exposed to CO<sub>2</sub> levels higher than 1,000 ppm present significantly higher risk for dry cough and rhinitis<sup>12</sup>, and CO<sub>2</sub> levels were found to be negatively correlated to attention test with an apparent dose-response relation, and to performance indices<sup>45</sup>. Thus, the indoor concentrations of CO<sub>2</sub> recorded in the present study show that the classrooms of the investigated schools present an inadequate air exchange rate.



This result is likely associated with the lack of mechanical ventilation systems, which could help maintain correct room temperature during both warm and cold periods. It is interesting to note that, in our dataset, higher temperature values are associated with lower CO<sub>2</sub> concentrations (R=0.75), probably due to a more frequent opening of the windows during warmer days (for example, in MZ01: median indoor T = 19.7°C, outdoor T range 7-16°C, median CO<sub>2</sub> = 1,477 ppm, while in GE05: median indoor T = 28.3°C; outdoor T range 12-21°C [when a desert dust outbreak was occurring – see Supplementary Material S4], median CO<sub>2</sub> = 611 ppm) (Supplementary Material S3). Conversely this natural ventilation might have favored the infiltration of gaseous and particulate pollutants from outdoors<sup>46</sup>.

In all the measured classrooms, median NO<sub>2</sub> levels resulted above the threshold value of 40 µg/m<sup>3</sup> (as annual mean) indicated by the 2010 WHO guidelines. In schools, the usual indoor sources of NO<sub>2</sub> (e.g., cooking, smoking) are not present, thus NO<sub>2</sub> levels could be more influenced by factors such as season, proximity of fossil fuel burning and pollution sources. Moreover, the average NO<sub>2</sub> levels obtained in our samples are generally higher than in other indoor environment studies<sup>47</sup>, and this could increase the risk for respiratory diseases<sup>25</sup>.

The mean values of indoor PM<sub>2.5</sub> concentrations were higher than 25 µg/m<sup>3</sup>, the threshold value defined by the WHO for outdoor environments<sup>48</sup>, with the exception of GE03, where the concentration was 21.7 µg/m<sup>3</sup> (16.4 – 31.1), GE05, where it was 24.3 µg/m<sup>3</sup> (13.3 – 37.3) and NI03, where it was 14.7 µg/m<sup>3</sup> (11.2 – 18.6). Indoor PM<sub>2.5</sub> values exceeded the outdoor concentrations in all the schools, with the sole exception of GE05; as discussed below, the sampling period at GE05 was affected by a desert dust advection, which altered the regular composition and size distribution of PM.

Indeed, I/O ratios above one indicate the presence of indoor sources (Table 4). Most of the typical indoor sources of PM are negligible in schools (tobacco smoke, cooking, wood burning) but in rooms with high occupancy (number of person/m<sup>2</sup>) like classrooms, the specific

PM sources due to the presence of people cannot be neglected. These include the release of skin fragments and hairs from human bodies, the penetration of soil particles adhering to children's footwear and clothes, the release of fibers from clothes<sup>20</sup>. In addition, the constant process of re-suspending particles previously deposited on indoor surfaces (floor, furniture) due to the movements of the occupants plays an important role<sup>8,49-51</sup>. Moreover, indoor concentrations of PM, as well as of gaseous pollutants, may be negatively influenced by limited ventilation.

#### **4.2 Indoor Der p 1 and endotoxin**

Since *Dermatophagoides* is a dominant sensitization allergen for asthma, dust mite exposure has raised the attention of many investigations and the relationship between the level of environmental indoor allergens and the development of some allergic diseases has been investigated<sup>14</sup>. Moreover, recent evidence has shown that removing mite allergen from indoor environments may be of clinical benefit<sup>52</sup>. Thus, we analyzed the Der p 1 concentration in samples obtained at T<sub>1</sub> and T<sub>2</sub>. In each classroom, no significant difference in allergen level was observed (Table 3, Supplementary Information S1). The within- and between-classroom changes were calculated to evaluate the allergen concentration in the schools. Across study schools, *Der p 1* allergen concentration was below the sensitizing threshold (2 µg/g of dust) and thus also below the level usually considered to trigger symptoms (10 µg/g of dust)<sup>53</sup>. It is likely that the indoor temperature and humidity characteristics we found in the evaluated classrooms and the absence of carpets and drapes – where dust mites grow – in classrooms may limit the growth of dust mites. It is noteworthy that, in the same geographical area, markedly higher concentrations of Der p 1 (median 1.46 µg/g of dust, IQR 0.25-7.18) were found in house dust samples<sup>54</sup>. Conversely, in the same experimental setting, home endotoxin was found to be significantly lower in homes (median 2.20 [1.78-2.59] log<sub>10</sub>EU/mg dust, median and interquartile range) than in schools (median 3.41 [2.52-4.51] log<sub>10</sub>EU/mg dust, p<0.0001).

We identified high levels of endotoxins by chromogenic LAL test across study classrooms. To standardize the different values, the concentration was expressed in  $\log_{10}$ EU/mg dust: a higher LPS level was found in classrooms following the occupation of children ( $T_2$  samples), and LPS (expressed in  $\log_{10}$  units) resulted a thousand-fold higher with respect to the reference value for endotoxin (44-105 EU/mg dust)<sup>1</sup>. This suggests that, in our experimental setting, schools, and not homes, may represent the most significant risk for endotoxin exposure, as previously reported by Sheehan et al<sup>55</sup>. Moreover, Jacobs et al. demonstrated that school endotoxin levels were positively associated with non-atopic asthma, which suggested exposure at school can contribute considerably to the overall environmental exposure of children to endotoxin.<sup>56</sup> We hypothesize in this study school hygiene procedures were not adequate in effectively removing indoor endotoxin contamination.

#### **4.3 Elemental concentration in indoor and outdoor PM<sub>2.5</sub>**

Data reported in Table 4 show that the elemental concentrations measured indoors were always higher than outdoors, as was also observed for PM<sub>2.5</sub> mass concentration. However, for some elements, the mean I/O value was only slightly higher than one (As, Cd, Ni, Sb, Tl, V;  $1.0 < I/O < 1.4$ ), while for other elements it ranged from 1.5 to 3.5 (Ba, Be, Co, Fe, Mn, Pb, Rb, Sn). High I/O were recorded for Cu (6.6) and Mo (8.3). Moreover, the elements in the first group were characterized by a very high correlation between indoor and outdoor concentrations (R between 0.75 and 0.99) and low variability of the I/O ratio. The elements in the second group, instead, were characterised by a poor correlation of indoor and outdoor values ( $R < 0.55$ ) and a wider variability range of I/O values among the different schools. For Cu and Mo there was no correlation between indoor and outdoor concentrations and the I/O variability is very high.

The first group includes elements that have no internal sources: their indoor concentrations depend entirely on infiltration from outside. As an example, Figure 2 (upper panel) shows the concentrations recorded indoors (average of three classrooms and standard deviation) and outdoors at the examined schools for one of these elements (vanadium, a reliable tracer of heavy oil combustion). During the period considered, indoor concentrations of vanadium were similar to outdoor values across study schools. This suggested an efficient infiltration of particles due to natural ventilation (through windows or doors)<sup>57-58</sup> and to cracks and leaks in the building envelope, a mechanism that is particularly efficient for fine and ultra-fine particles such as those produced by combustion sources<sup>59</sup>.

The second group is well represented by beryllium, a tracer of local soil particles and of long-range transported dust (Figure 2, middle panel). For this element, the indoor concentrations were generally higher than outdoors (in some cases, much higher), due to the accumulation of deposited particles that were re-suspended by the children's movements. A different behaviour ( $I/O < 1$ ) was observed at GE05 and, to a lesser extent, NI01. During the period of the sampling at GE05 (April 2-4, 2012), an intense desert dust intrusion was recorded in the area of southern Sicily, (as shown by the simulation of the DREAM model (BSC-DREAM8b, operated by the Barcelona Supercomputing Center and available at <http://www.bsc.es/ess/bsc-dust-daily-forecast/>; Supplementary Material S4 upper panel). This event was responsible for an increased concentration of outdoor PM, an increased contribution of soil-related components and wind intensity and directions different from those recorded during the rest of the study period (see Supplementary Material S5). As desert particles are generally characterised by coarse size dimensions, their ability to penetrate into indoor environments is poor, resulting in indoor concentrations from this source being lower than outdoors. This consideration holds also for particles below 2.5  $\mu\text{m}$ , which generally includes the tail of size distribution of desert dust. Moreover, as soil-related components dominate the

mass concentration of PM during desert dust events, this behaviour affected not only the desert dust tracers but also the mass concentration of PM<sub>2.5</sub>. This explains the I/O ratio below one recorded for PM<sub>2.5</sub> at GE05 (Table 2). A weaker desert dust event was also recorded during the sampling at NI01, carried out on May 2-4, 2012 (see Supplementary Material S4 lower panel); also in this case, the outdoor concentration of beryllium was slightly higher than indoors. During all the other periods, soil-related components were dominated by local sources and indoor concentrations exceeded outdoor values.

The lower panel of Figure 2 shows the concentration of copper. In this case, all the indoor concentrations were higher than outdoors, with the exception of NI03. The same behaviour was observed for Mo. High Cu and Mo concentrations were due to the use of vacuum-cleaners for the collection of indoor dust samples to be analysed for biological pollutants. Most vacuum cleaners are equipped with copper brush motors; in some models, a copper-molybdenum alloy is used. During vacuuming, copper-molybdenum particles are released into the environment where they can persist for several hours<sup>60</sup>. School NI03 was vacuum-cleaned the day before the sampling of PM and, in this case, the indoor concentrations of the two tracers were lower than outdoors. The occurrence of high Mo and Cu concentrations in indoor environments where vacuum cleaners are used constitutes a possible health risk and merits further investigation.

The indoor-outdoor concentrations of the other elements in the 12 schools are reported in Supplementary Material S6.

Table 5 reports the concentrations of PM<sub>2.5</sub> and elements in the indoor school environments grouped as “industrial” and “rural”. In spite of the low volume of data, a significant difference between the industrial and rural sites was observed for some elements. These include elements mostly deriving from industrial emissions: Cd, Co, Ni, Pb, Sb, Tl, V. It is worth noting that, in previous studies, industrial/combustion sources have been shown to emit elements mainly in their soluble chemical form and in the fine fraction of PM<sup>33</sup>.

According to the data in Table 4, most of the above elements (Cd, Ni, Sb, Tl, V) are included in the group of species that have no indoor sources and that can easily penetrate classrooms (I/O close to 1, very good indoor-outdoor correlation). All these observations are in agreement with an industrial/combustion origin of the indoor particles containing these elements.

To confirm this hypothesis, we considered the outdoor elemental concentration in the rural and industrial sites. Given the low number of schoolyard samples, the statistical significance of the differences rural vs. industrial sites was poor (data reported in Supplementary Materials S7). In order to strengthen the statistical significance level we included 72 additional outdoor samples collected at residential sites in the same geographical areas (36 industrial and 36 rural sites) and analysed by using the same method. The data in Table 6 show significant differences between outdoor industrial and rural sites for most elements assessed. These include both elements released by non-exhaust traffic sources (brake and tyre abrasion, road-dust re-suspension)<sup>33,61</sup> and the above elements from industrial/combustion sources. Industrial sources, releasing particles mainly in the fine size fraction, may thus have a significant influence on the indoor air quality of schools.

It is worth noting, in any case, that the concentration levels of As, Cd, Ni and Pb measured in the industrial sites were one-two orders of magnitude lower than the target values (As: 6 ng/m<sup>3</sup>; Cd: 5 ng/m<sup>3</sup>; Ni: 20 ng/m<sup>3</sup>) and limit value (Pb: 500 ng/m<sup>3</sup>) stated by the European Community (Directive 2008/50/EC) and adopted by Italian legislation. These limits apply to the annual average concentration in PM<sub>10</sub>, while the data of this study refer to PM<sub>2.5</sub> and to a shorter observation period (on the whole, about six month). However, the above elements are almost entirely included in the fine fraction of atmospheric particles, and their concentration in PM<sub>2.5</sub> is generally similar to that in PM<sub>10</sub><sup>32,33,61</sup>.

Further information about the sources of atmospheric PM and about their strength can be obtained by studying the solubility of elements<sup>32,33,61</sup>. It is well known, in fact, that each emission source releases elements as chemical species having a characteristic solubility. Moreover, the solubility of elements in atmospheric PM influences their bioavailability.

The solubility percentages of all the considered elements are shown in Table 7, where outdoor results in schoolyards and in residential sites have been disaggregated. The results show, for most elements, that the solubility in schools was quite similar indoors and outdoors, suggesting the prevalence of common main sources and confirming the main role played by outdoor particles in determining indoor concentration. It is worth noting that also industrial and rural sites generally showed similar solubility values, suggesting that the same sources, although with different strengths, had an effect on the PM composition in the whole area. Conversely, as expected, Ba and Mo show relevant solubility differences between indoor and outdoor environments (Ba is more soluble indoors, Mo is more soluble outdoors), indicating different source contributions to indoor and to outdoor PM. Possible indoor sources for these elements are the use of chalk, for Ba, and vacuum cleaner brush motors for Mo<sup>60, 62</sup>.

In most cases, we observed a similar elemental solubility in schoolyards and at residential sites, although the samples were collected during the warm and cold season, respectively. This indicates that the same emission sources predominated not only over the entire territory but also all over the year.

A peculiar behaviour was shown by Rb, which showed much higher solubility in the outdoor samples collected during the cold period, and by As, which showed, instead, lower solubility. This finding indicates a different strength of the main emission sources of these two elements during the two periods of the year. A reasonable explanation is the contribution of biomass burning for domestic heating, a PM source that increases during the winter, from which Rb and As are emitted as soluble and insoluble species, respectively<sup>63</sup>. Biomass burning

products are contained in the fine fraction of PM, which has been shown to easily infiltrate indoors. It is thus conceivable that during the wintertime these elements and other biomass burning toxic products, such as polycyclic aromatic hydrocarbons, easily infiltrate into indoor school environments. The concentration values for the two solubility fractions of Rb and As are shown in Figure 3, separately for indoor (classrooms) and outdoor (school yards and residential sites) along with those of Be and V (Supplementary Material S8 reports the same graphs for the other elements).

For beryllium, the solubility percentage showed small variations, indicating that the same main source (i.e., soil) is responsible for Be emission in all the considered environments and periods. However, indoor concentrations increased during the warm period (school yards samples were higher than residential site samples), due to the easier re-suspension of soil during the drier period. For vanadium, the total concentration was generally due to two main sources: combustion of fossil fuels (mainly soluble species) and soil re-suspension (mainly insoluble species)<sup>58</sup>. The data in Figure 3 show that the V species in the soluble fraction were mainly responsible for the increase in concentrations at the industrial sites.

## 5 CONCLUSION

The results of this study show that most of the examined classrooms were characterized by poor ventilation and high concentration levels of CO<sub>2</sub> and NO<sub>2</sub> under occupancy conditions, which may indirectly affect the productivity of occupants and cause non-specific symptoms.

High levels of endotoxin were identified in all the classrooms, suggesting that schools may represent a significant risk for endotoxin exposure. Conversely, in all the schools, *Der p 1* allergen concentration was below the sensitizing threshold.

The concentration of elements in indoor PM<sub>2.5</sub> was generally higher than outdoors. The main sources are soil particle re-suspension due to the presence of occupants and penetration



of outdoor particles. For elements produced by industrial emissions, a significant difference between industrial and rural sites was observed, showing that industrial sources may have a significant influence not only on the quality of outdoor atmosphere but also on indoor school environments. Particles of industrial origin contains toxic elements mainly in the form of soluble chemical species, which are more bio-accessible and may thus constitute a risk to children's health. The regular monitoring of IAQ is desirable for keeping buildings and occupants under compliant and safe conditions.

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**TABLES**

**Table 1** - Characteristics of the monitored classrooms.

School Code	Sampling period (2012)	Type of site	Classroom grade	Floor	Room Area (m <sup>2</sup> )	Room volume (m <sup>3</sup> )	N° of Students	Occupancy (N° person/m <sup>2</sup> )
GE01	26-28/4	Industrial	2	0	36	108	26	0.72
			2	0	35	105	25	0.71
			3	1	35	105	24	0.68
GE02	10-12/5		1	1	17	51	16	0.94
			2	1	17	51	13	0.76
			3	1	25	75	27	1.08
GE03	27-29/3		1	0	20	50	25	1.25
			2	1	25	100	27	1.08
			1	3	20	80	27	1.35
GE04	21-23/3		1	1	16	51	25	1.56
			2	1	33	100	26	0.79
			3	0	20	60	24	1.20
GE05	2-4/4		1	2	45	180	26	0.57
			2	0	54	162	23	0.43
			3	1	38	152	26	0.68
GE06	19-21/4		1	0	30	90	24	0.80
			3	2	30	90	17	0.57
			2	0	47	141	22	0.47
BU01	17-19/4	3	1	30	90	20	0.67	
		1	2	30	90	24	0.80	
		2	0	30	90	23	0.77	
MZ01	29-31/3	1	0	30	90	20	0.67	
		3	1	30	90	23	0.77	
		2	2	30	90	26	0.86	
MZ02	8-10/5	1	0	25	75	24	0.96	
		3	0	20	60	18	0.90	
		3	1	20	60	18	0.90	
NI01	2-4/5	1	0	35	105	23	0.65	
		2	0	35	105	25	0.71	
		3	1	60	180	17	0.28	
NI02	24-26/5	1	0	35	105	26	0.74	
		1	1	35	105	26	0.74	
		3	0	35	105	26	0.74	
NI03	22-24/11	2	0	30	90	16	0.53	
		3	0	30	90	30	1.00	
		3	1	30	90	26	0.86	

**Table 2** - Relative humidity, temperature, CO<sub>2</sub> and NO<sub>2</sub> concentration (median and interquartile range); indoor concentration (mean, minimum and maximum), outdoor concentration and indoor/outdoor (I/O) ratio of PM<sub>2.5</sub>. Except for PM<sub>2.5</sub>, data are presented separately for occupied and unoccupied hours.

School	Relative Humidity (%) <sup>a</sup>		Temperature (°C) <sup>a</sup>		CO <sub>2</sub> (ppm) <sup>a</sup>		NO <sub>2</sub> (µg/m <sup>3</sup> ) <sup>a</sup>		PM <sub>2.5</sub> <sup>b</sup> (µg/m <sup>3</sup> )		
	Occupied	Unoccupied	Occupied	Unoccupied	Occupied	Unoccupied	Occupied	Unoccupied	Indoor	Outdoor	I/O ratio
GE01	48 (46-51)	47 (46-51)	26.5 (25.5-28.5)	26.1 (25.3-28.9)	831 (420-1,328)	332 (269-380)	79.0 (70.9-87.1)	79.0 (66.9-87.1)	30.3 (28.1-32.8)	16.9	1.8
GE02	52 (51-54)	52 (52-53)	21.9 (20.9-22.6)	22.1 (21.5-22.6)	1123 (760-1,389)	381 (363-400)	54.7 (50.6-60.8)	54.7 (50.6-58.8)	29.8 (20.7-43.0)	18.0	1.7
GE03	53 (50-56)	53 (50-56)	22.6 (22.1-23.7)	22.5 (22.0-23.3)	1182 (456-1,791)	369 (340-440)	62.8 (58.8-66.9)	64.8 (58.8-66.9)	21.7 (16.4-31.1)	11.1	2.0
GE04	50 (47-53)	49 (47-52)	22.2 (21.2-23.0)	21.8 (21.0-22.5)	1198 (582-1,594)	373 (364-400)	68.9 (56.7-77.0)	70.9 (62.8-77.0)	30.9 (28.0-33.9)	21.1	1.5
GE05	40 (36-44)	41 (37-45)	28.3 (26.7-30.1)	28.0 (26.3-29.8)	611 (379-825)	351 (340-361)	81.0 (72.9-89.1)	81.0 (72.9-91.2)	24.3 (13.3-37.3)	32.1	0.8
GE06	51 (49-53)	51 (49-53)	24.2 (23.3-24.7)	24.2 (23.2-24.6)	545 (387-945)	363 (332-443)	81.0 (75.0-91.2)	79.0 (75.0-89.1)	29.8 (17.8-47.8)	13.5	2.2
BU01	55 (52-58)	55 (52-57)	20.1 (19.3-21.1)	19.8 (19.2-20.5)	878 (327-1,562)	320 (315-332)	62.8 (54.7-72.9)	66.9 (58.8-77.0)	28.6 (26.0-32.5)	10.8	2.6
MZ01	52 (50-55)	51 (49-55)	19.7 (19.6-20.8)	19.5 (19.1-20.2)	1477 (857-1,941)	310 (296-330)	68.9 (60.8-75.0)	70.9 (64.8-77.0)	29.6 (18.2-44.3)	15.0	2.0
MZ02	34 (32-38)	35 (32-39)	25.8 (25.3-26.9)	25.6 (25.0-26.6)	391 (343-530)	316 (310-330)	70.9 (60.8-89.1)	68.9 (58.8-85.1)	50.4 (32.7-68.0)	8.5	5.9
NI01	31 (29-34)	31 (30-34)	28.0 (27.1-28.7)	27.9 (27.1-28.7)	538 (356-994)	331 (305-345)	87.1 (64.8-105.0)	87.1 (68.9-101.0)	48.7 (35.1-63.6)	26.3	1.9
NI02	47 (45-48)	47 (45-49)	25.8 (24.9-26.9)	25.7 (24.8-26.5)	565 (352-902)	323 (299-345)	70.9 (54.7-91.2)	70.9 (54.7-91.2)	45.9 (24.0-63.7)	19.1	2.4
NI03	60 (58-67)	60 (58-67)	22.2 (20.6-23.2)	22.1 (20.6-22.9)	797 (464-1316)	364 (263-500)	99.3 (95.2-105.0)	99.3 (95.2-105.0)	14.7 (11.2-18.6)	12.3	1.2

a Median (and interquartile range) of values continuously recorded during 48-h monitoring.

b Mean (minimum and maximum range) of indoor PM<sub>2.5</sub> values from cumulative 48-h samplings carried out at three classrooms in each school.

**Table 3** - Median and interquartile range of indoor endotoxin and *Dermatophagoides pteronissinus* 1 (*Der p 1*) values.

School	Endotoxin (log <sub>10</sub> EU/mg)	<i>Der p 1</i> (µg/g)
GE01	3.00 (2.50-4.27)	0.84 (0.43-1.46)
GE02	7.50 (6.42-10.10)	0.78 (0.68-1.14)
GE03	3.61 (2.94-3.95)	< 0.20 (< 0.20-0.70)
GE04	2.67 (1.93-2.87)	0.26 (0.20-0.41)
GE05	3.41 (3.26-6.53)	0.25 (< 0.20-0.38)
GE06	2.83 (1.67-10.01)	< 0.20 (< 0.20-0.29)
BU01	3.42 (3.22-3.47)	< 0.20 (< 0.20-< 0.20)
MZ01	4.66 (4.18-7.52)	-
MZ02	5.04 (3.52-8.65)	< 0.20 (< 0.20-< 0.20)
NI01	3.03 (2.04-3.83)	0.28 (0.21-0.36)
NI02	2.06 (2.35-3.40)	0.59 (0.25-1.06)
NI03	1.86 (1.83-2.10)	0.21 (< 0.20-0.34)

**Table 4** - Indoor and outdoor (I/O) concentration of PM<sub>2.5</sub> (µg/m<sup>3</sup>) and elements (sum of the extracted and residual fraction; ng/m<sup>3</sup>): mean value (min-max), p-value, I/O ratio, correlation coefficient (R).

	Indoor	Outdoor	p-value	I/O ratio	R
PM <sub>2.5</sub>	31.5 (11.2 - 68.0)	17.1 (8.5 - 32.1)	<0.0001	2.1 (0.4 - 8.0)	0.35
As	0.48 (0.25 - 0.86)	0.37 (0.21 - 0.64)	0.06	1.4 (0.7 - 3.0)	0.75
Ba	4.7 (1.0 - 10)	3.1 (0.6 - 13)	0.002	2.8 (0.5 - 8.6)	0.46
Be	0.007 (0.001 - 0.032)	0.005 (0.001 - 0.012)	0.05	2.1 (0.3 - 7.8)	0.47
Cd	0.39 (0.18 - 1.3)	0.34 (0.17 - 0.83)	0.45	1.3 (0.5 - 2.4)	0.85
Co	0.026 (0.008 - 0.053)	0.020 (0.008 - 0.036)	0.013	1.6 (0.4 - 4.7)	0.02
Cu	22 (6.0 - 56)	5.8 (1.5 - 16)	<0.0001	6.6 (0.4 - 21)	0.01
Fe	170 (29 - 410)	130 (23 - 310)	0.038	2.0 (0.5 - 5.9)	0.27
Mn	4.6 (1.3 - 11)	3.5 (1.3 - 7.5)	<0.0001	1.6 (0.6 - 3.2)	0.30
Mo	0.52 (0.07 - 1.3)	0.064 (0.004 - 0.12)	<0.0001	8.3 (0.1 - 20)	0.10
Ni	3.5 (1.4 - 7.6)	2.8 (1.3 - 7.2)	0.09	1.4 (0.8 - 2.8)	0.79
Pb	5.5 (1.4 - 12)	3.9 (1.2 - 7.3)	0.002	1.5 (0.7 - 3.7)	0.10
Rb	0.13 (0.05 - 0.19)	0.09 (0.03 - 0.16)	0.010	1.5 (0.6 - 2.9)	0.55
Sb	1.6 (0.24 - 6.6)	1.7 (0.20 - 6.2)	0.34	1.2 (0.5 - 2.5)	0.93
Sn	0.20 (0.02 - 0.34)	0.16 (0.07 - 0.28)	0.035	1.5 (0.7 - 2.3)	0.27
Tl	0.034 (0.004 - 0.11)	0.026 (0.002 - 0.079)	0.29	1.2 (0.4 - 2.1)	0.88
V	4.6 (1.4 - 15)	4.6 (1.3 - 17)	0.51	1.0 (0.7 - 1.5)	0.99

**Table 5** - Indoor concentration of PM<sub>2.5</sub> (µg/m<sup>3</sup>) and elements (sum of the extracted and residual fraction; ng/m<sup>3</sup>) in the classrooms (18 in Gela and 18 in the rural sites). Concentrations are reported as mean values (min-max).

	Industrial	Rural	p-value
PM <sub>2.5</sub>	27.6 (13.3 - 47.8 )	35.5 (11.2 -68.0)	0.24
As	0.42 (0.25 - 0.73)	0.54 (0.25 - 0.86)	0.08
Ba	4.9 (2.4 – 10)	4.5 (1.0 - 9.3)	0.52
Be	0.005 (0.001-0.013)	0.007 (0.002 - 0.012)	0.12
Cd	0.43 (0.21 - 0.73)	0.32 (0.05 - 1.3)	0.02
Co	0.029 (0.012 - 0.047)	0.021 (0.008 - 0.053)	0.02
Cu	20 (7.2 - 38)	24 (6.0 – 56)	0.40
Fe	160 (83 - 350)	180 (29 - 410)	0.69
Mn	4.3 (2.5 - 8.3)	4.9 (1.4 - 11)	0.27
Mo	0.51 (0.16 - 1.3)	0.53 (0.071 - 1.0)	0.62
Ni	4.0 (1.6 - 7.5)	3.0 (1.4 - 7.6)	0.03
Pb	6.4 (3.6 – 12)	4.5 (1.4 – 11)	0.02
Rb	0.12 (0.052 - 0.18)	0.14 (0.089 - 0.19)	0.16
Sb	1.7 (0.27 - 6.6)	0.80 (0.24 - 2.4)	0.02
Sn	0.23 (0.13 - 0.34)	0.17 (0.02 - 0.39)	0.14
Tl	0.051 (0.009 - 0.11)	0.015 (0.004 - 0.038)	0.005
V	6.0 (2.8 - 15)	3.1 (1.4 - 4.8)	0.01

**Table 6** - Outdoor concentration of PM<sub>2.5</sub> (µg/m<sup>3</sup>) and elements (sum of the extracted and residual fractions; ng/m<sup>3</sup>) in school yards and residential sites: 42 in the industrial area (6 school yards and 36 residential) and 42 in rural areas (6 school yards and 36 residential). Concentrations are reported as mean values (min-max).

	Industrial	Rural	p-value
PM <sub>2.5</sub>	16.1 (9.4 - 26.1)	12.1 (4.7 - 34.3)	0.0003
As	0.61 (0.19 - 1.1)	0.64 (0.14 - 1.1)	0.97
Ba	3.2 (0.87 - 13)	1.5 (0.25 - 5.2)	< 0.0001
Be	0.0020 (0.0005 - 0.0088)	0.0017 (0.0004 - 0.016)	0.62
Cd	0.23 (0.050 - 1.1)	0.11 (0.047 - 0.83)	0.0002
Co	0.019 (0.010 - 0.038)	0.013 (0.008 - 0.033)	0.03
Cu	5.5 (1.2 - 22)	3.6 (0.76 - 21)	< 0.0001
Fe	110 (19 - 320)	67 (18 - 310)	< 0.0001
Mn	3.4 (0.45 - 10)	1.7 (0.40 - 7.5)	< 0.0001
Mo	0.22 (0.046 - 0.81)	0.10 (0.014 - 0.54)	0.0002
Ni	2.8 (0.76 - 7.3)	1.3 (0.65 - 3.2)	< 0.0001
Pb	5.2 (1.6 - 16)	2.0 (0.16 - 6.2)	< 0.0001
Rb	0.63 (0.043 - 1.4)	0.68 (0.034 - 1.8)	0.60
Sb	1.8 (0.24 - 9.7)	0.54 (0.84 - 4.7)	< 0.0001
Sn	0.47 (0.13 - 1.3)	0.19 (0.048 - 0.80)	< 0.0001
Tl	0.12 (0.005 - 0.87)	0.035 (0.002 - 0.12)	< 0.0001
V	4.7 (0.62 - 17)	1.7 (0.28 - 5.9)	< 0.0001

**Table 7 - Solubility percentage of elements.**

	Warm period				Cold period	
	Indoor (classrooms)		Outdoor (schoolyards)		Outdoor (residential sites)	
	Industrial (%)	Rural (%)	Industrial (%)	Rural (%)	Industrial (%)	Rural (%)
As	69	41	68	55	28	26
Ba	30	24	5.6	7.8	8.7	12
Be	19	22	19	21	24	25
Cd	72	48	62	56	40	60
Co	50	41	38	52	25	15
Cu	37	27	39	27	24	21
Fe	3.5	2.8	4.1	4.1	2.9	3.0
Mn	52	45	42	52	61	67
Mo	14	14	30	29	27	21
Ni	50	34	44	43	33	29
Pb	23	13	24	25	16	19
Rb	44	33	37	37	71	81
Sb	51	49	51	62	39	36
Sn	18	17	16	15	7.7	6.6
Tl	>80	>80	>80	>80	>80	>80
V	71	51	64	54	45	30



## **FIGURE LEGENDS**

**Figure 1** - The “RESPIRA” Project involved the 4 communities of the Health District of Gela (Red circles in panel A) in the south Mediterranean area (small box in panel B). It consists of the city of Gela (B: the red dotted line depicts the area of the petrochemical plant) and the rural areas of Niscemi, Mazzarino and Butera (C, D and E, respectively). The red flags highlight the investigated schools and the white flags indicate the 72 additional outdoor monitoring sites.

**Figure 2** - Indoor (three classrooms; mean value and standard deviation as error bars) and outdoor (school yards) concentration of V, Be and Cu. At each site, indoor and outdoor samplings were carried out side-by-side

**Figure 3** - Indoor (classrooms) and outdoor (separately for school yards and residential sites) concentrations of the soluble and insoluble fractions of Rb, As, Be and V. Indoor classroom samplings and outdoor monitoring at school yards were carried out simultaneously.

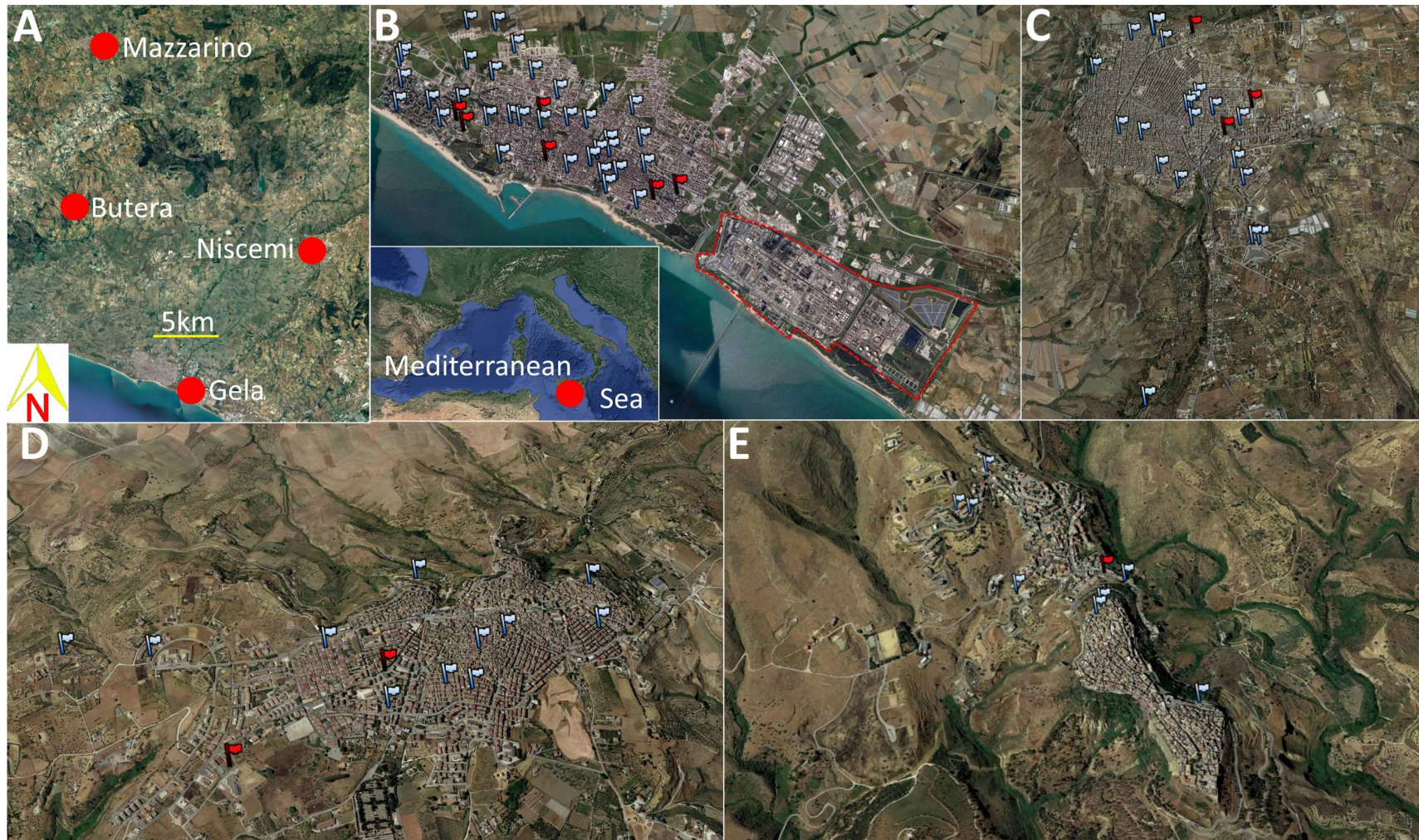


Figure 1

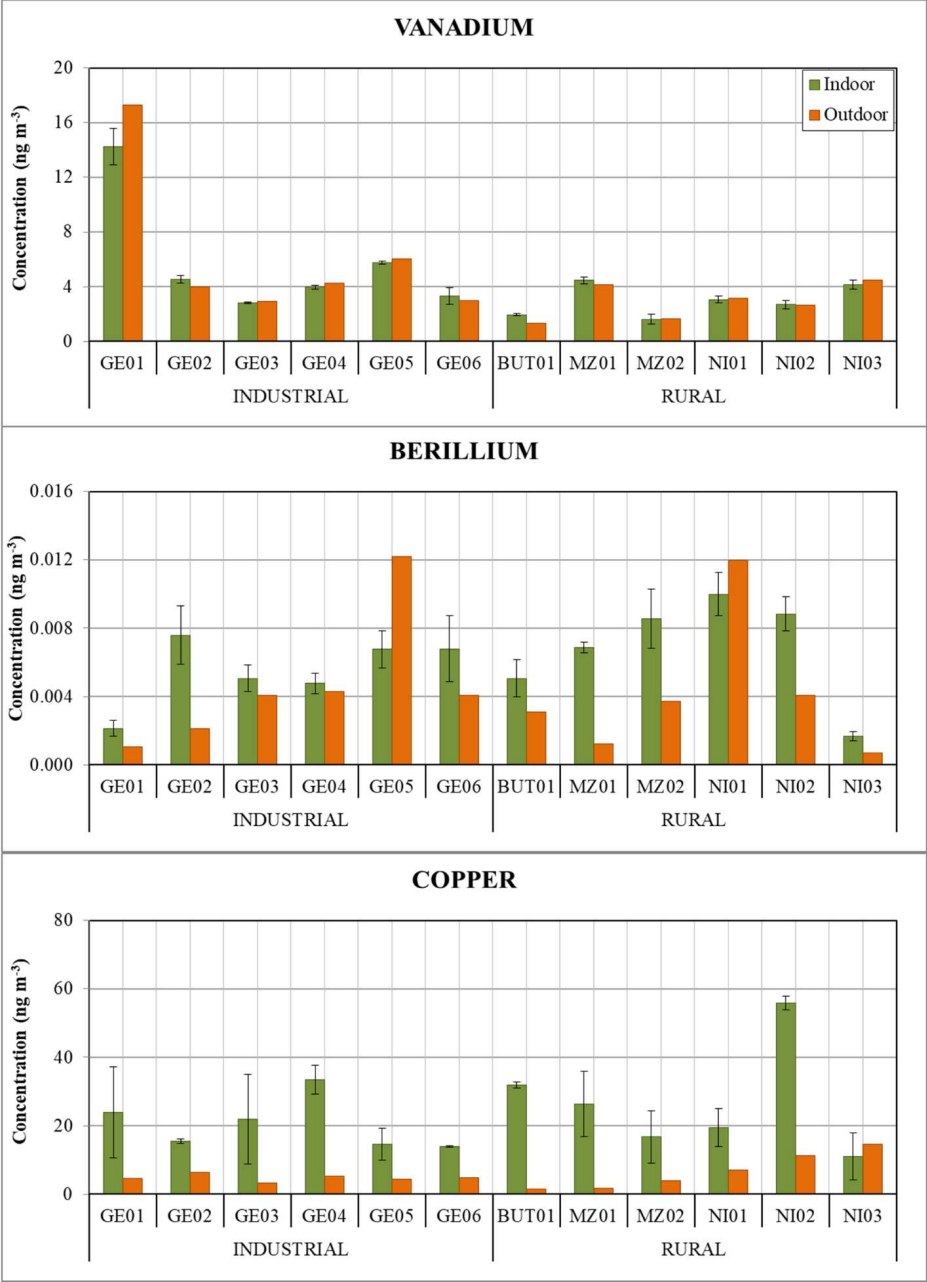
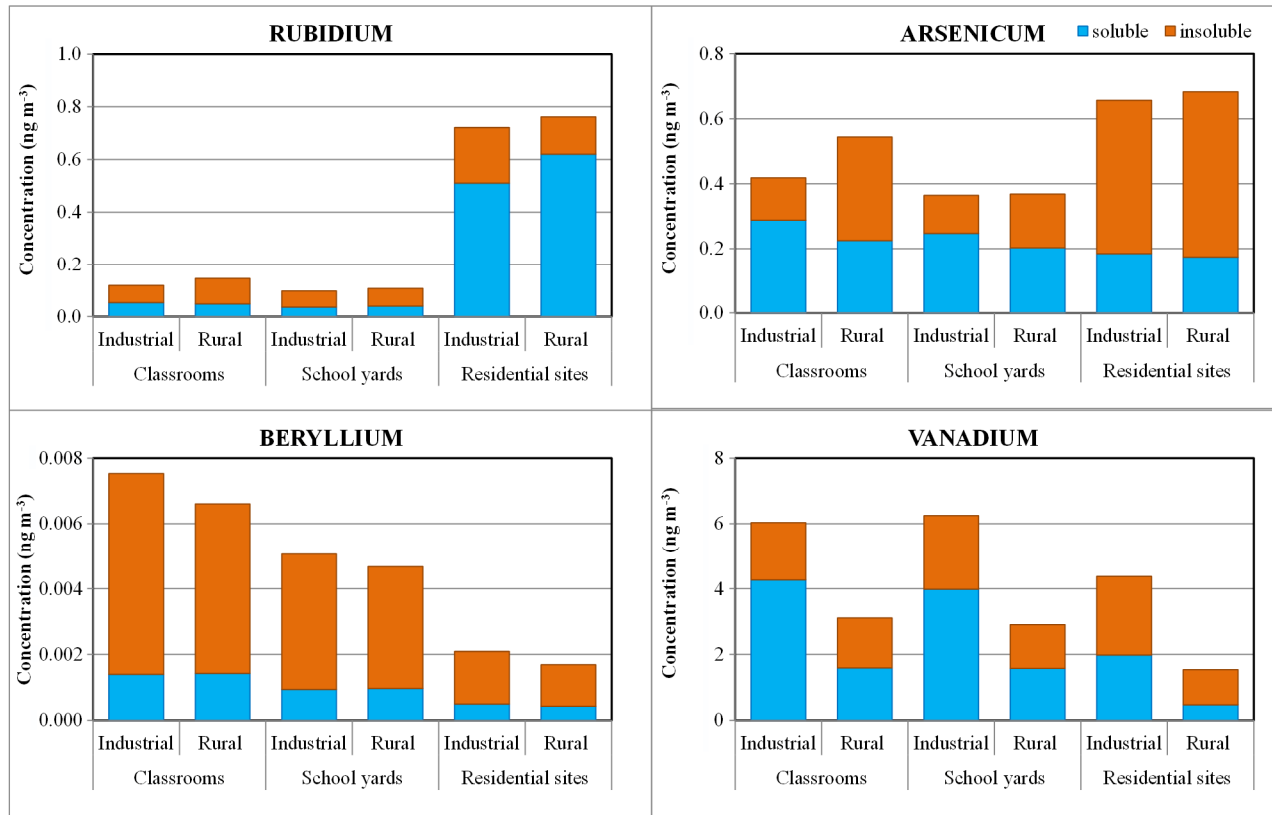


Figure 2



**Figure 3**