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Precipitation input of inorganic chemicals in the S. Vitale pine stand of Ravenna (Italy)

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Abstract
This study reports the differences in the local precipitation input of inorganic chemicals at urban, industrial and woodland sites of a coastal area in northern Italy. The role of the local wind circulation was investigated to determine the contribution of the industrialised area to pollution above the woodland in terms of chemical (SO_4) and particle (Ca^{++}) depositions. Data collected via the monitoring network of greater Ravenna were compared with those collected at an Apennine station (Brisighella, 80 km SW from Ravenna) taken as a "clean reference". Findings show the influence of wind direction in contributing to the local dispersal of chemicals at the different sites.

1. Introduction

The solution for environmental problems related to anthropogenic emissions is often connected to the quantification of the airborne chemical input to the terrestrial ecosystem, as well to the definition of the atmospheric patterns which act as "carriers" in returning the pollutants to the earth's surface. The main pathway of this pollutant-return to the ground must be attributed to pollutant deposition in both wet and dry processes (1).
Wet deposition can be roughly defined as the process by which hydrometeors deliver to the ground the primary pollutants or the chemicals produced *via* several reactions in the presence of water (2-3). This takes place by means of wash-out (impaction and interception) and rain-out (in-cloud nucleation, molecular diffusion, phoretic forces and condensation) mechanisms.
It is clear that the ground concentrations produced by wash-out can be considered indicative of the local atmospheric pollutant contents. On the other hand, the depositions produced by the rain-out mechanism are indicators of the chemical composition of the clouds, which can travel long distances after their formation, picking up varying chemical "contributions". While wash-out gives specific information on the local atmospheric load of pollutants, wash-out and rain-out are often difficult to separate.
This study was designed to elucidate the importance of wet deposition in determining the environmental profile of sites belonging to the same geographical area but characterised by varying topographic features. The possible role played by the local wind circulation in modulating the deposition of chemicals produced locally over the ancient woodland area of the S. Vitale pine stand was also investigated.

2. Site description and experimental

Located in northern Italy in the part of the Po valley facing the sea, greater Ravenna is marked by a flat terrain bordered on the north by marshland and on the east by the sea. The Apennine mountain range forms the boundaries, stretching across approximately 100 km westward and 60 km southward. A strip of sea pines along the shoreline reaches across the whole area. The city proper is located 8 km inland and an extensive industrial belt (petrochemical plants, an electric power station and other industrial sites) extends from the city to the coast. Pollutants were monitored at three sites (urban, industrial and a pine stand) to determine the differences in chemical composition, concentration (SO_4^{--} and Ca^{++}) and pH value for each meteorological condition. An additional station was set up at Brisighella (40 km SW of Ravenna in the Apennine range) to act as an indicator of clean atmosphere. The monitoring stations were equipped with wet and dry collectors (MTX, Italy); all samples were examined using ionic chromatography (Dionex 4000I, USA) and atomic absorption spectrophotometry (Perkin-Elmer 2280, USA); pH was measured with an Orion EA 940 (USA) analyser.

3. Results and discussion

Figure 1 shows the average precipitation intensity for the prevailing wind directions (NNE, WNW, ESE and SSW) at the four sites considered (1: city, 2: industrial zone, 3: pine stand and 4: Brisighella) over the period 1992-1993. Measurements were taken for each wind direction classification. For each class, the first three stations of the Ravenna area showed no significant differences in the precipitation amount, while station 4 recorded a larger amount of precipitation in each class due to its mountain position. If the different wind direction classes are compared, those having a westerly orientation (normally associated with the lows originating over the Tirrenian Sea) representing a prevail, common climatic pattern of Italy.
Figure 2 indicates the pH maxima and minima along with the upper and lower quartiles, and the median value. Despite the maximum pH value of 8.2, the woodland area exhibits more pronounced acidification in 25 % and 75 % of the data. By contrast, the lowest acidification is recorded at the industrial sites where chemicals are emitted.
The analysis of SO_4^{--} and Ca^{++} concentrations (Figures 3 and 4) indicates a possible explanation of the pH patterns.
The industrial area appears much more vulnerable to the presence of SO_4^{--}, reaching twice the concentration of the Apennine station, although the pH median value is about 5.8, the least acid. Particles may be posited as having a role (where Ca^{++} is their indicator) in neutralising the acidity of the atmospheric wash-out. The more marked concentration of Ca^{++} in the city and industrial areas can lead to a neutralisation of the acid compound emitted by the industrial plants through a "buffer effect".
The mean deposition levels of SO_4^{--} and Ca^{++} in the pine stand appear influenced by the wind direction (Table 1). The SO_4^{--} concentration values increase for westerly winds when the pine stand is downwind from the city and the industrial belt. Analogous to this is the pattern in the Ca^{++} deposition, along with an increase for ESE winds ascribable to the transport of sand from the nearby shoreline.

Table 1
Mean deposition (mg/m2)

	SO_4^{--}				Ca^{++}			
	NNE	WNW	ESE	SSW	NNE	WNW	ESE	SSW
site 1	64.9	95.5	54.3	88.1	13.9	20.1	17.8	28.9
site 2	81.9	104.3	82.8	101.9	14.9	19.0	18.9	28.2
site 3	56.5	67.0	51.4	63.8	11.8	14.8	18.4	22.9
site 4	51.4	66.2	51.7	50.5	21.4	18.1	41.7	54.5

4. Conclusions

The findings support the hypothesis that the local acidification of the woodland area should be ascribed to the urban and industrial emissions of greater Ravenna. The deposition levels recorded for the two chemicals considered are related to the prevailing wind direction during the precipitation events.

5. References

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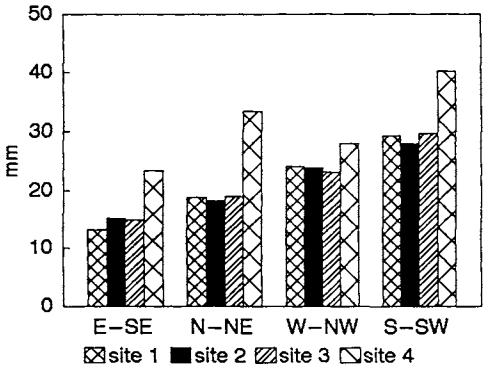

Figure 1. Average precipitation.

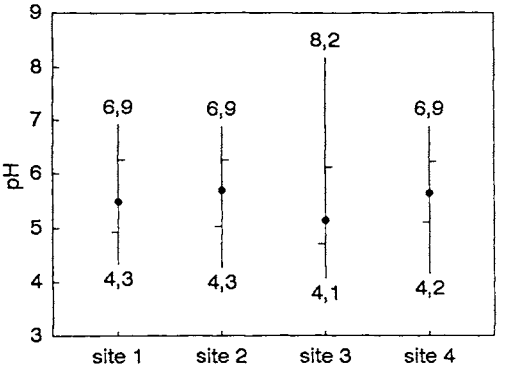

Figure 2. pH values recorded at the four measurement sites.

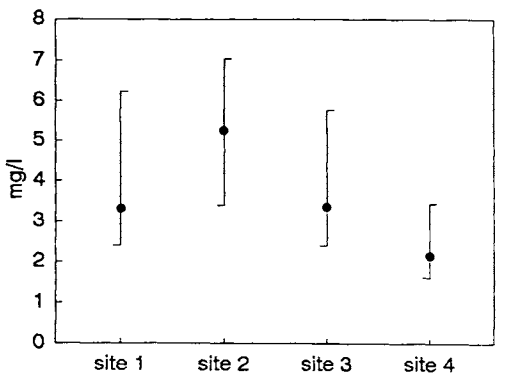

Figure 3. SO_4^{--} concentration values.

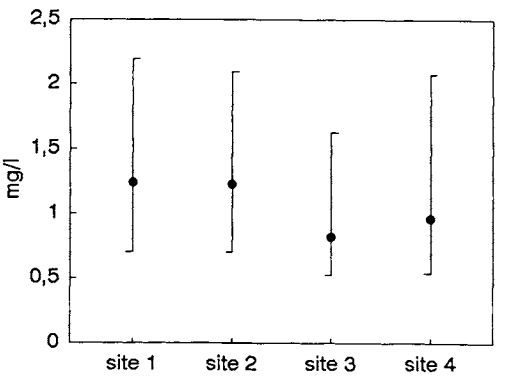

Figure 4. Ca^{++} concentration values.