Natural versus anthropogenic influences on the chemical composition of bulk precipitation in the southern Apennines, Italy: A case study of the town of Potenza

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ABSTRACT

This paper presents new data on the chemical composition of precipitation in a selected area of the southern Apennines of Italy; these data are used to assess natural and anthropogenic contributions to the precipitation. The town of Potenza was used as a representative urban site, and the major and minor element (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, and Li^+, NO_2^-, F^-, Br^-, PO_4^{3-}) and trace element (Zn, Fe, Al, Sr, Mn, Ba, Cu, Cr, V, As, Pb, Ni, and Cd) concentrations of bulk precipitation from three different sampling sites within the study area were determined between June 2011 and May 2012. The majority of the collected rainwater has pH values higher than 5.6. The composition of this rainwater was dominated by Ca^{2+} the element with the highest total volume-weighted mean concentration (TVWA), followed by Cl^-, SO_4^{2-}, Na^+, NO_3^-, K^+, Mg^{2+}, and NH_4^+. The TVWA of the trace metals decreased in the order Zn > Fe > Al > Ba > Sr > Mn > Pb > Cu > As. Neutralising factor (NF_{Xi}) values indicate that Ca^{2+} is the dominant neutralising cation within this rainwater, with lower contribution from NH_4^+ and Mg^{2+}. The precipitation analysed during this study has a negligible marine influence as determined using Cl^- concentrations as a proxy for the abundance of sea salts. Precipitation F_i values (marine fraction of element i) indicate that Na^+ is the element with the highest seawater component, and we found partial marine contributions for the SO_4^{2-} and Mg^{2+} concentrations within this rainwater. Enrichment factors (EF) of selected elements were calculated to identify the sources of non-crustal elements: K^+, Mg^{2+}, Fe, and Ca^{2+} are the only elements dominantly sourced from the crust, whereas Mn and Ba have highly variable EF values (10–100) suggesting that a small proportion of these elements was derived from anthropogenic sources in addition to a more significant crustal contribution. Sr, Cu, Pb, Zn, and As are highly enriched with respect to average crustal compositions, confirming that the concentrations of these elements within precipitation are significantly controlled by human activities.

1. Introduction

The assessment of the origin of chemical constituents dissolved in rainwater is difficult, primarily as the composition of rainwater is the result of complex interactions between cloud dynamics and microphysical processes. The initial research into precipitation chemistry was a response to the acid rain responsible for damage to vegetation (Emberson et al., 2001) and soil (Yagasaki et al., 2001), water acidification (Aggarwal et al., 2001), and the deterioration of buildings (Kanazu et al., 2001). The chemical composition of precipitation is usually related to local sources of pollution in urban areas (Conlan et al., 1995), whereas in remote areas rainfall compositions can be used to measure the extent of anthropogenic and natural sources of pollution (Hayashi et al., 2001). A recent research has also outlined the harmful effects of pollution on people's health, a subject that has grown in importance in recent times (Künzli et al., 2000). In general, the chemical composition of rainwater is indicative of the source of dissolved chemical constituents and the local and regional dispersion of pollutants; these data can also be used to evaluate the potential impact of these constituents on ecosystems.

The pH of precipitation depends on the neutralisation effect of certain rainwater components, such as NH_3, $CaCO_3$ and hydroxide (Flues et al., 2002). Large quantities of sulphur and nitrogen oxides are emitted to the atmosphere by human activity; these gases are subsequently converted into strong acids (sulphuric and nitric) that in turn cause acid rain. Metals in the atmosphere are generally derived from industrial

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sources, especially high-temperature processes such as non-ferrous metal smelting, fossil fuel combustion, and vehicle exhausts, and remain in the atmosphere as suspended particles until removed by a variety of natural cleansing processes, including dry deposition and washout by rain (Hamilton-Taylor and Willis, 1990). Heavy metals emitted by combustion are relatively soluble and reactive, primarily as the particles that carry these metals are small. This means that these metals dissolve readily in rain, especially under low-pH conditions, resulting in polluted rainwater (Migon et al., 1997). Road transport emissions are thought to be the principal source for the majority of atmospheric pollutants (MMA, 2000), and rain is thought to efficiently scavenge pollutants present as atmospheric aerosols (Obaidy and Joshi, 2006). These atmospheric aerosols are a complex mixture of suspended solid and liquid particles with different physical and chemical properties (e.g., size distribution, optical properties, and chemical compositions) that originate both from anthropogenic and natural sources (Caggiano et al., 2011).

This paper provides a baseline for the rainwater chemistry of the southern Apennines, and uses the town of Potenza as a case study. The chemistry of rainwater in this area has not been previously studied and the various environments in this area provide an excellent opportunity to study the effects of different phenomena on the composition of rainwater. Exposed crustal rocks within an area with a radius of a few tens of kilometres include a wide variety of lithologies, including volcanics, few metamorphics and fragments of oceanic crust, large carbonate platforms, and siliciclastic sediments. The area also has a significant amount of anthropogenic chemical input from large neighbouring urban sites (Naples, Bari, and Taranto) and industrial sites, including steel and automobile factories and an oil treatment centre. In addition, the fact that the overlap of natural and anthropogenic inputs to rainwater in the area around Potenza is a common feature worldwide meant that this case study can also be used as a more general model for assessing the composition of rainwater in other worldwide areas.

2. Materials and methods

2.1. Sampling sites

Potenza is located in the Basilicata region (southern Italy) and it is within the Apennine Mountains, less than 100 km from the coast (Fig. 1). The southern Apennines are featured by a wide variety of outcropping lithologies, primarily as a result of a complex geodynamic evolution of this area. The southern Apennines are a roughly NW–SE oriented segment of a fold-and-thrust belt and they contain siliciclastic and carbonate sedimentary, volcanic, and metamorphic lithologies. Siliciclastic sediments are widespread along the Bradanic foredeep and are dominated by terrigenous conglomeratic, sandy, and clayey sediments deposited during the emplacement of the southern Apennine accretionary wedge. The latter consists mainly of Middle Triassic to Miocene sedimentary successions, occasionally incorporating ophiolitic suites and both metamorphic and non-metamorphic rocks of the Liguride and Sicilide Complexes (Cello and Mazzoli, 1999). The western and eastern areas of the Apennine front are dominated by carbonate rocks belonging to the Campanian and Apulian platforms, respectively. A significant part of southern Italy is also covered by volcanic rocks

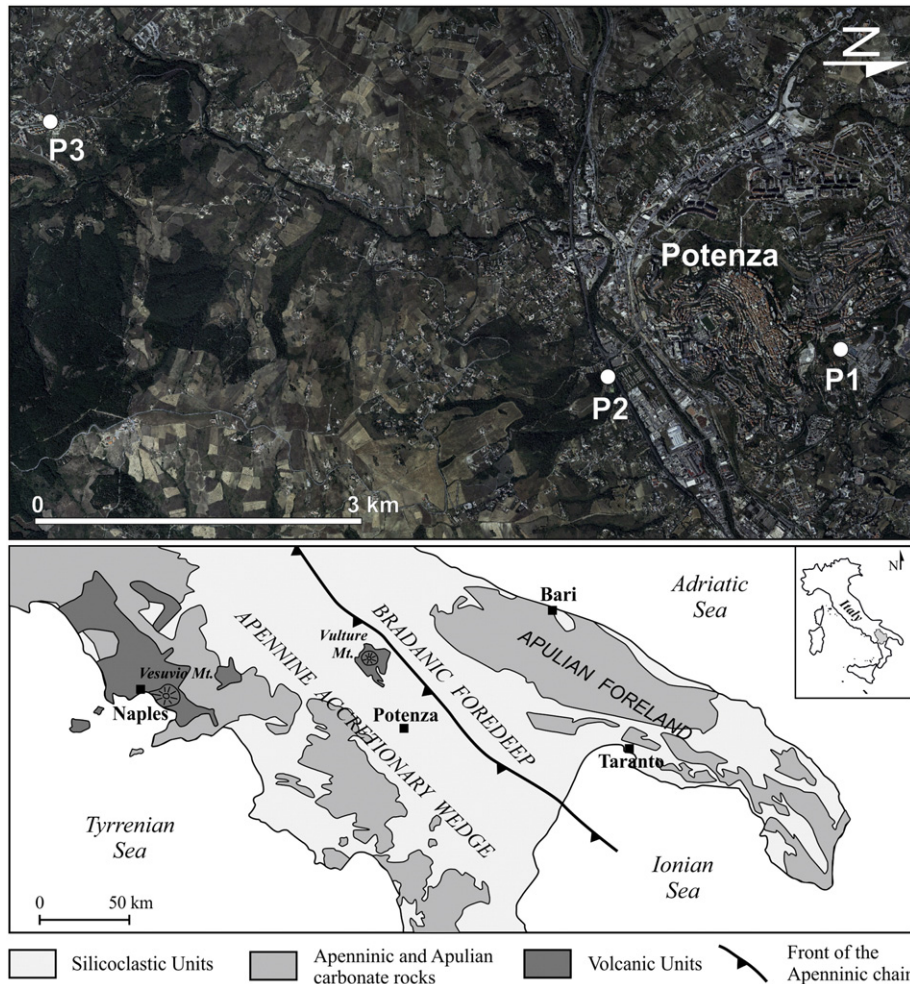**Fig. 1.** Location of the investigated area (P1, P2, and P3 are the sampling sites) and lithological sketch map of southern Apennines.