

CHEMICAL COMPOSITION OF ATMOSPHERIC BULK DEPOSITION AT THE INDUSTRIAL AREA OF GELA (SICILY, ITALY)

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Abstract

Bulk deposition has been collected at six sampling sites in area of Gela plain (Italy) in the period from February 2008 to May 2009. Samples collected each two weeks were analysed for the major ion and trace elements content. Preliminary results allow identifying three different sources that control the abundance of the elements in atmospheric deposition: (1) sea spray, (2) geogenic dust, and (3) anthropogenic pollution. Due to the closeness of the coast, clear evidence of sea spray input is detectable for most of the samples. The high excess of non sea-salt sulphate (50 - 90% of the total) is prevalingly ascribable to the abundant SO₂ emissions of the refinery. The pH values of the collected samples range from 4.2 to 8.6, with 80% of them above pH 6.5, indicating an extensive neutralization. This is due to NH₃ coming from widespread agricultural activities in the plain of Gela, and geogenic CaCO₃ either from local or from regional (desert dust) sources. Elevated levels of trace metals (Zn, V, Sb, Ni, Cr, Ni and Cu) can be observed in the samples collected close to the industrial area. All these elements can be identified as “anthropogenic” and attributed to the human activities, mainly to the industrial emissions, but a contribution could also derive from the intensive vehicular traffic.

1. Introduction

The chemical composition of precipitation is influenced both by natural and anthropogenic sources, and is the result of the incorporation of particles and gases into the water droplets. Particularly, the composition of precipitation is influenced by (1) the strength of emission sources, (2) the chemical reactions in the atmosphere, and (3) the mechanisms of scavenging of the moving air masses. In the last decades, much attention has been devoted to acid rain, claimed to be responsible for soil and freshwater acidification and forest decline and damage to historical buildings (Avila and Alarcon 1999).

Furthermore, atmospheric concentrations of many trace elements have been significantly affected by man's activities. The quantification of these changes and their effect on terrestrial and aquatic ecosystems is important because of their potential adverse effects (Nriagu and Davidson 1986). In addition, the analysis of trace species in atmospheric particles and precipitation is very important because certain species are emitted from particular source types and they can be used as tracers for these sources (Rahn and Lowenthal 1985).

The study area (about 480 Km²) corresponds to the Gela plain on the southern coast of Sicily. The climate of the island can be considered the typical Mediterranean climate, characterized by long, hot and dry summer periods (from May to September) and a mild rainy winter season. Within such rainwater regime the study area belongs to most arid part of Sicily with average annual rainfall of about 400 mm.

The town of Gela (about 77,000 inhabitants) is the site of a major industrial area of Sicily. It hosts one of the largest petroleum refineries in Europe, which is one of the top-ten greenhouse gas emitter in Italy. The energy supply is given by a power plant that burns pet-coke, a very dirty fuel. The harmful effects on human health in this area are well documented with high mor-

tality in the cohort of the petrochemical plant workers and excesses mortality and morbidity of the local population (Musmeci *et al.* 2009).

The aim of the present study is to characterize the chemical composition of the bulk deposition in the area both for major ions and for trace elements.

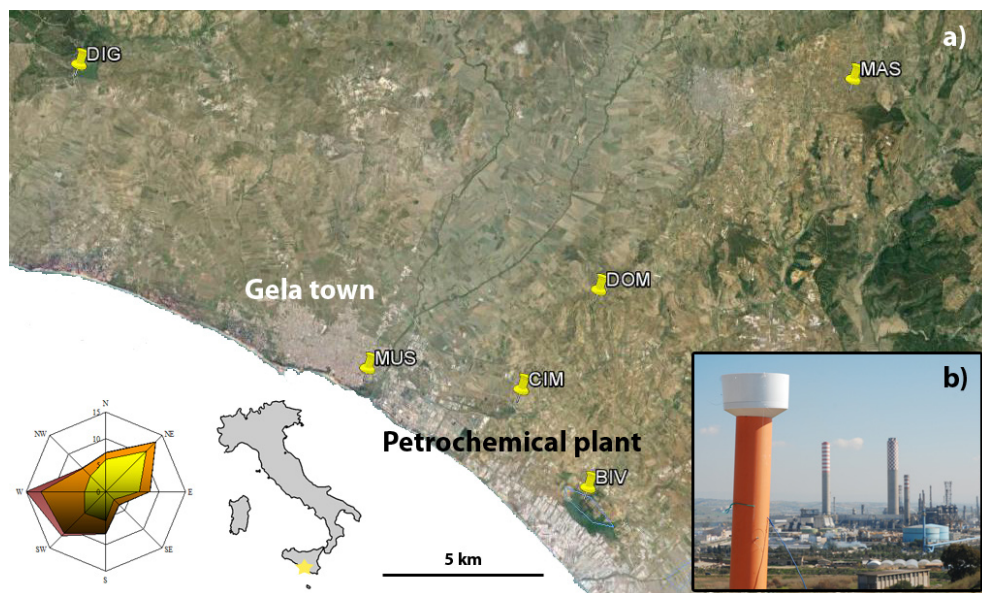


Figure 1. (a) Study area and raingauge position; (b) Picture of a raingauge.

2. Materials and Methods

Atmospheric deposition was monitored at the study area from February 2008 to May 2009. The adopted sampling and analytical protocols were chosen following guidelines published by the main international agency involved in the monitoring of atmospheric precipitation (NILU 2001; Ulrich *et al.* 2006). Samples were collected approximately twice a month at six rain gauges at various distances (1.4-17.9 Km) around the industrial area of Gela (Figure 1).

The design and installation of the collectors conformed to EMEP (European Monitoring and Evaluation Programme) site requirements for precipitation gauges. The rain gauges used were bulk collectors which remained open during the whole sampling period, thus receiving both wet and dry deposition (Figure 1). They were composed of a funnel and a polypropylene (PP) bottle. The funnel (Büchner type, Ø 240mm) can be separated in two pieces for easy and total cleaning. A sheet of filter paper (DP-400-240 - basis weight: $80 \pm 3 \text{ g m}^{-2}$; thickness: 0.180-0.190 mm; retention of particles: 35-40 μm) was put inside the funnel, and a HDPE disc was inserted between the filter paper and the perforated Büchner plate to avoid clogging of the holes. The filter-system (perforated plate, HDPE disc and filter paper) excluded a prolonged interaction between sampled rainwater and coarse particulate, and minimized evaporation. All the equipments were washed with a 2% nitric acid (Merck Suprapur) solution, and then rinsed several times with de-ionized (MilliQ) water, dried under laminar hood, packed in double clean plastic bags, and zipped until exposure in the field. Disposable plastic gloves were used whenever working with samples and sampling equipment. At the end of the sampling period, the sampling bottle was capped and transported in the laboratory for analysis.

All water samples were analyzed for 44 elements at the laboratories of DiSTeM and INGV-Pa. Ion chromatography was used for the determination of both major anions (F^- , Cl^- , SO_4^{2-} , NO_3^- , and Br^-) and major cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}), using a Dionex 120 ion chromatograph

and Dionex columns AS14A and CS12 respectively. The detection limits (mg l^{-1}) were 0.005 for F, 0.01 for Cl and Na, 0.05 for SO_4 and K, 0.05 for NO_3 , Mg and Ca, with precision $\leq 3\%$. Silica concentrations were as measured by using a UV-visible spectrophotometer (detection limits 0.03 mg l^{-1}). Trace elements were analysed by ICP-MS, with two different instruments (Perkin Elmer ELAN 6100 DRC-e and Agilent 7500ce). For the applied quality assurance and quality control (QA/QC) procedures see Calabrese *et al.* (2011).

3. Results and discussion

3.1 Major ions' concentrations

Minimum, maximum and volume-weighted-mean (VWM) concentrations ($\mu\text{eq/L}$) of the 6 sampling sites are shown in Table 1. The chemical composition of the six sites has a similar pattern with the prevailing ions being always Ca^{2+} , Cl and Na^+ , intermediate concentrations of SO_4^{2-} and Mg^{2+} and low (NH_4^+ , NO_3^- and K^+) to very low (F^- and Br^-) concentrations of the remaining ions. The sequence of the ionic composition can be summarised as follows: All sites display the same anionic sequence with $\text{Cl} > \text{SO}_4 > \text{NO}_3 \gg \text{F} > \text{Br}$ while the cationic sequence is generally $\text{Na} \approx \text{Ca} > \text{Mg} > \text{NH}_4 > \text{K}$. Exceptions are BIV, CIM and MUS where $\text{Na} > \text{Ca}$ and MAS where $\text{NH}_4 > \text{Mg}$.

Ion balance provides a useful tool to evaluate the completeness of the analysed ions. Even though most of the analysed samples falls within the acceptable range ($\pm 0.2 \text{ meq/L}$) for dilute waters (APHA, AWWA, WEF, 2005) all samples display cation excess. The sometimes strong deficiency in anions should be attributed to anionic species, such as HCO_3^- , CO_3^{2-} , CH_3COO^- , HCOO^- , $\text{C}_2\text{O}_4^{2-}$, NO_2^- , and PO_4^{3-} , which were not investigated in this study. All these ions except bicarbonate and carbonate have been sometimes identified, although not quantified, in the chromatograms. But through a rough estimation based on the specification of the producer of the used anionic column (Dionex) none of these anions were present in such concentrations to severely affect the ionic balance calculation. As we will show further on, the most probable missing anion is bicarbonate.

Table 1. Major ions' contents in bulk deposition of Gela plain

Site		pH	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	F^-	Cl ⁻	Br^-	NO_3^-	SO_4^{2-}
			$\mu\text{eq/L}$	$\mu\text{eq/L}$	$\mu\text{eq/L}$	$\mu\text{eq/L}$	$\mu\text{eq/L}$	$\mu\text{eq/L}$	$\mu\text{eq/L}$	$\mu\text{eq/L}$	$\mu\text{eq/L}$	$\mu\text{eq/L}$
MUS	min	6.37	81	3.7	51	99	0.8	0.4	130	0.2	4.1	69
	max	8.64	977	90	216	863	466	13.9	1170	1.4	91	403
	VWM	7.05	442	15.7	113	278	38	1.5	522	0.6	28	145
BIV	min	6.43	70	2.1	29	43	7.9	0.3	64	0.2	12	34
	max	8.64	769	170	200	644	503	5.4	796	1.4	140	480
	VWM	7.09	298	18.8	80	211	61	0.8	336	0.3	29	124
DIG	min	5.48	67	2.2	29	55	0.8	0.4	49	0.1	10	49
	max	8.03	495	43	127	827	279	4.5	580	0.9	163	340
	VWM	6.83	246	12.9	70	232	51	0.9	268	0.3	34	115
DOM	min	4.18	55	1.0	20	44	3.1	0.4	35	0.1	0.9	24
	max	8.38	544	28	157	904	138	5.4	660	1.3	274	422
	VWM	6.95	189	8.3	55	187	27	0.8	216	0.2	23	87
MAS	min	5.14	40	1.6	23	48	6.0	0.3	29	0.2	6.0	32
	max	8.86	537	126	274	1513	1017	17.2	647	0.9	231	979
	VWM	6.90	185	11.9	59	214	71	1.2	201	0.2	32	113
CIM	min	6.88	325	10	86	206	16	1.0	387	0.4	22	135
	max	7.07	596	35	151	535	36	5.2	690	0.8	164	272
	VWM	6.94	451	13.8	109	324	18	1.7	535	0.6	44	182

3.2 Origins of the major ions

Marine and non-marine contributions (terrestrial and/or anthropogenic sources) can be apportioned considering reference species representative of the marine source. Chloride or sodium are generally used as tracers of marine origin. On a Na vs. Cl plot (Figure 2) most of the samples plot along a straight line with a slope of 0.86, representing the bulk ocean water ratio (Keene *et al.* 1986). The high correlation (0.99) indicates a negligible influence of human activity or geogenic dust. The seawater origin of Na⁺ and Cl⁻ in the rainwaters of the Louros basin can be further evidenced by the inverse correlation between their VWM concentration of Cl and the distance of the pluviometers from the coast (Figure 2).

Assuming that all the chloride in the rainwater comes from the sea, and that no chemical fractionation occurs between chloride and the other ions after sea salt injection into the atmosphere, the proportion of sea salts in the rainwater can be determined using the ion to chloride ratios in sea water:

$$F_i = (X_i/Cl)_m \times (Cl/X_i)_r \quad (1)$$

Where F_i represents the marine fraction of element i and X_i represents the measured anions and cations. The subscript “m” and “r” designate marine and rainwater, respectively.

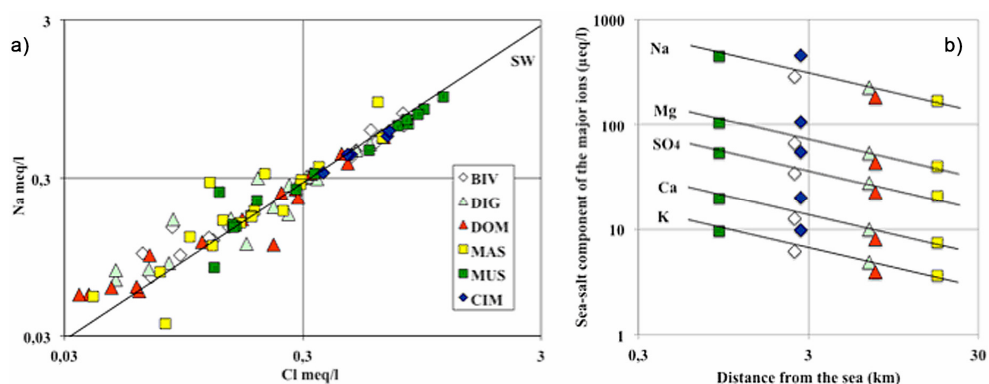


Figure 2. (a) Na vs. Cl binary plot. The black line represents the seawater Na/Cl ratio; (b) Major ions' volume weighted mean sea-salt fraction vs. distance from the coast.

As for the absolute concentrations of chloride also the obtained marine fractions calculated from the VWM decrease from the coast to the inner of the study area. The elements which are most influenced by sea salt contribution are Na⁺ (> 93%) and Mg²⁺ (from 68% to 98%) while K⁺ is less (from 30 to 70%). The non sea salt (nss) component of these to ions can be attributed to geogenic dust. Sulfate displays only limited contribution from sea salt (18-37%) while Ca²⁺ shows nearly no sea salt contribution (3-7%). The origin of the non marine sulfate can be attributed either to geogenic dust (evaporates outcropping in central Sicily) and to combustion related anthropogenic sources. The latter are probably prevailing and among them the local industry is the major contributor although a minor role could be played by automotive sources. Calcium is almost completely of non sea-salt origin derives from the weathering of the carbonate rocks which crop out extensively in the surrounding areas and are also widespread in the whole Mediterranean Sea area.

Due to the very low concentration of NO₃⁻ and NH₄⁺ in non-polluted sea water the contribution of sea salt to the concentration of these ions in the rainwater of the area has been considered nil. Most of the NH₄⁺ derives from agricultural sources probably from local origin, the lower part of the plain east of Gela being extensively cultivated. Nitrate can be attributed to the same combustion related anthropogenic sources as for non sea salt sulphate.

3.3 Acid neutralization

The measured pH values in the rainwater samples collected in the Gela plain display a large range from 4.18 to 8.86, but the median values at the sites are comprised between 6.83 and 7.09 pointing to a low acidity of the rainwater in the study area. This is a common feature of most of the rainwaters of the Mediterranean Sea region (Avila and Alarcon 1999; Al-Momani *et al.* 1995b; Al-Momani 2003; Kita *et al.* 2004).

The neutralization factors (NFs) of Ca^{2+} , NH_4^+ and Mg^{2+} were computed for different alkaline constituents using the formulae suggested by Possanzini *et al.* (1988). It is known that NO_3^- and SO_4^{2-} are the major acidic anions in the atmosphere, whereas Ca^{2+} , NH_4^+ and Mg^{2+} are the major acid neutralizing cations. The neutralization factors were obtained by the formula below:

$$(\text{NF})_X = [X] / \{[\text{NO}_3^-] + [\text{nssSO}_4^{2-}]\} \quad (2)$$

where $X = \text{nssCa}^{2+}$, NH_4^+ or nssMg^{2+} .

Values obtained from the volume-weighted averages of the six sites range from 1.67 to 2.17 for Ca^{2+} , from 0.10 to 0.57 for NH_4^+ and from 0.01 to 0.15 for Mg^{2+} thus suggesting that the main neutralizing component in rainwater is Ca^{2+} with a minor contribution of NH_4^+ while that of Mg^{2+} is nearly negligible.

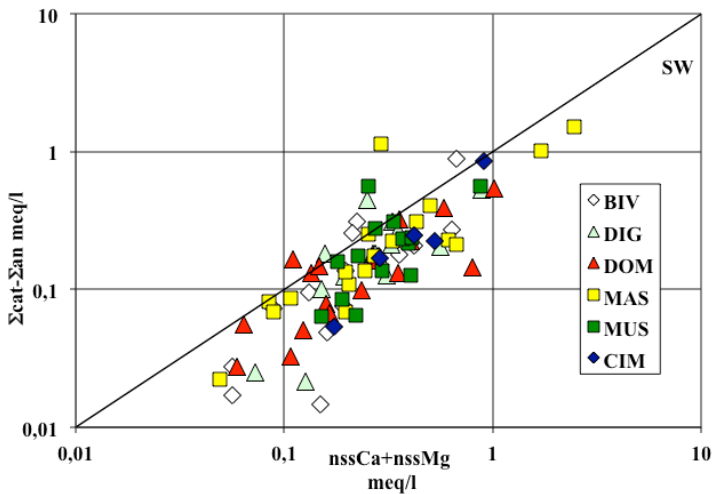
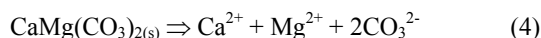
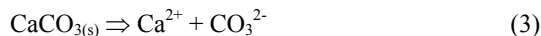


Figure 3. Binary diagram of $\text{nssCa} + \text{nssMg}$ vs. ionic imbalance. The black line represents the 1:1 ratio.

The main contribution of nssCa^{2+} to rainwater, at least in the Mediterranean area, comes from carbonate rocks. This contribution is particularly relevant in Sicily where these rocks represent a significant part of the outcrops. The dissolution of carbonate minerals like calcite, aragonite (both CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) will contribute to the rainwater nssCa^{2+} and nssMg^{2+} but also to CO_3^{2-} and HCO_3^- contents as follows:



In the presence of HCO_3^- , strong acids of anthropogenic origin can be titrated further releasing CO_2 to the atmosphere and increasing the pH of the rainwater:



As previously mentioned, both CO_3^{2-} and HCO_3^- have not been determined in the collected samples. In the graph of figure 3, $\text{nssCa}^{2+} + \text{nssMg}^{2+}$ vs. charge imbalance (the difference between total analysed cations and total analysed anions), the samples show a good alignment along the 1:1 ratio line supporting the hypothesis that CO_3^{2-} and HCO_3^- are the missing anions and confirming that carbonate minerals are the main neutralising agents of rainfall acidity in the area.

These observations confirm those of previous authors which pointed to a generalized acid-rain neutralization by atmospheric carbonate dust over the entire Mediterranean basin due both to Saharan dust (Loye-Pilot *et al.* 1986) and to the widespread outcrop of limestone formations (Al-Momani *et al.* 1995). The wash out of below-cloud alkaline aerosols neutralizes rain acidity caused by anthropogenic sources explaining why acid rain is not a major problem in this area and generally in the whole Mediterranean area (Al-Momani *et al.* 1995; Al-Momani 2003; Avila and Alarcon 1999; Kita *et al.* 2004).

3.4 Trace elements

The results of minor and trace elements concentration measured in bulk depositions are shown in table 2 and figure 4a. The most abundant elements (Sr, Al, Zn, B, Ba, Fe and Mn) show a range of median value between 1 and 100 $\mu\text{g/L}$. Elements such as V, Cu, Ni, Ni, Li, Se, Rb, Cr and As have median values ranging from 0.1 to 1 $\mu\text{g/L}$, while the least abundant elements are Mo, Sb, Pb, Co and Cd (median < 0.1 $\mu\text{g/L}$).

Coefficient Variation (CV%) reported in table 2 is the ratio of the standard deviation and the mean, it represent the data variability of the sample population considered. A constant metal deposition rate produce the lowest CV% in concentration, because it means that through the time of sampling the considered metal have almost the same concentration (depending essentially from direction of winds). A natural constant source of elements, for instance seawater aerosol, produces a constant daily deposition rate, in fact, elements such as B (average 5.5 $\mu\text{g/L}$ and CV% 58) and Se (0.33 $\mu\text{g/L}$, CV% 77) shown the lowest CV% derived from a seawater spray background. Geogenic elements derived from local (soils re-suspension) or regional (desert dust) sources have similar behaviour. For example Sr (average 49.6 $\mu\text{g/L}$ and CV 78%) and Li (average 0.37 $\mu\text{g/L}$ and CV 57%). By contrast, elements which shown the highest CV variability are connected to peculiar source which are not constant through the time, such as for example the anthropogenic metals (industrial or vehicular traffic). Among these metals there are As (average concentration 0.4 $\mu\text{g/L}$ and CV% 471), Ni (0.7 $\mu\text{g/L}$, CV% 305), Cd (0.02 $\mu\text{g/L}$, CV% 301), Zn (13.8 $\mu\text{g/L}$, CV% 155) and Cu (1.3 $\mu\text{g/L}$, CV% 152) that shown the highest CV% and are considered anthropogenic.

In figure 4b the enrichment factors calculated for each metal (Me) are showed:

$$EF_{\text{Al-crust}} = (C_{\text{Me}}/C_{\text{Al}})_{\text{rain}} / (C_{\text{Me}}/C_{\text{Al}})_{\text{crust}} \quad (7)$$

where C is the concentration in bulk depositions and in crust. According to the degree of enrichment the elements could be grouped as follows: highly enriched with $EF > 100$ (Se, Sb, B, Zn, Sr, Cd As, Mo and Cu; intermediately enriched elements with EF from 10-100 (Ni, V, Li, Mn, Ba, Pb, Co and Cr); not enriched with $EF < 10$ (Fe).

The fact that there are enriched elements respect to the crust highlight how others sources are present in the investigated area and affect the atmospheric precipitation. Evidence suggests that besides geogenic input these sources have seawater and anthropogenic origin.

For example, Sr shown a high EF despite being generally considered a geogenic source element (Al-Momani 2003), and this could be explained because the plane of Gela is mainly composed from clay, carbonate and evaporitic rocks which have higher content of Sr. Se is strongly enriched because according with literature (White 2003) it is a chalcophile elements and its behaviour being linked to sulfates (both from seawater and evaporitic). Li is a lithophile element and since it is linked with carbonates probably derives from the weathering of limestones. Intermediate enriched elements (V, Ni and As) are emitted from combustion of fossil fuels (Berg *et al.*

1994). Elements which shows the less EF in general have a low vapour pressure and are mainly associated with large particles with shorter ranges (e.g. Fe), most of these elements perhaps have also anthropogenic source (Berg *et al.* 1994).

Table 2. Trace elements contents in bulk deposition of Gela plain. CV% is the coefficient of variation expressed as percent

Elements ($\mu\text{g/L}$)	Min	Average	Median	Max	CV%
Li	0.06	0.37	0.31	0.91	57
B	0.06	6.1	5.5	23.7	58
Al	1.41	15.9	10.0	83.4	95
V	0.21	1.20	1.04	5.11	76
Cr	0.02	0.24	0.22	1.27	78
Mn	0.09	3.6	2.2	27.9	137
Fe	0.73	5.4	3.4	36.1	109
Co	0.01	0.05	0.03	0.37	135
Ni	0.06	0.7	0.3	17.6	305
Cu	0.11	1.3	0.8	14.7	152
Zn	1.59	13.8	5.7	109.0	155
As	0.03	0.4	0.1	14.8	471
Se	0.01	0.33	0.28	1.17	77
Rb	0.03	0.32	0.25	1.48	86
Sr	8.15	49.6	38.0	202.5	78
Mo	0.01	0.11	0.07	0.50	88
Cd	0.01	0.02	0.01	0.48	301
Sb	0.01	0.11	0.06	0.62	113
Ba	0.58	5.27	4.38	22.04	63

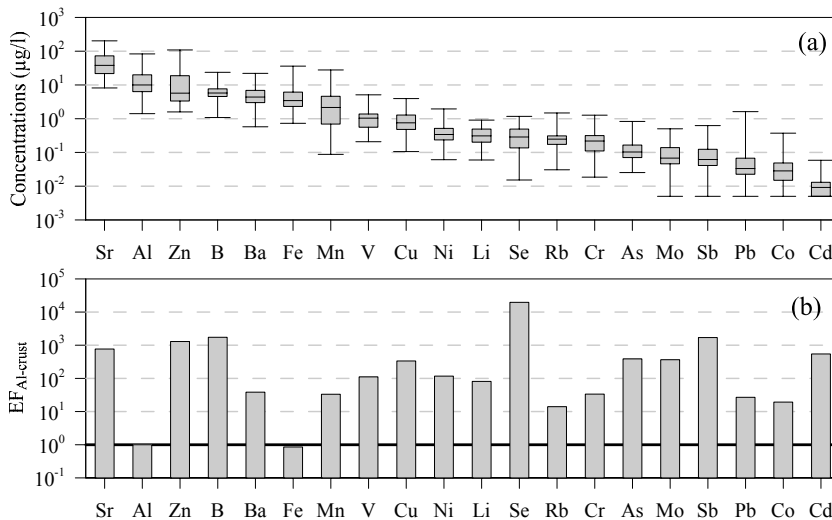


Figure 4. (a) Trace element concentrations in bulk deposition ($\mu\text{g/L}$).
 (b) Enrichment factors were calculated using Al as reference element.

4. Conclusion

In conclusion, preliminary results shows that the monitoring of bulk deposition at the Gela plain gives useful information on the levels of pollutants, and the degree of anthropogenic contamination, improving our understanding of the sources and cycling of elements in the studied area. The chemistry of atmospheric deposition reveals that major elements in bulk deposition are strongly influenced by the input from sea-salt aerosols (Na, Cl, B) and from geogenic dust (Ca, Li and Sr). The effects of human activities are mainly identified by high concentrations of sulphates and nitrates and in the high enrichment factors of many trace metals (Sb, Ni, Cr, Ni and Cu).

5. Acknowledgments

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6. References

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