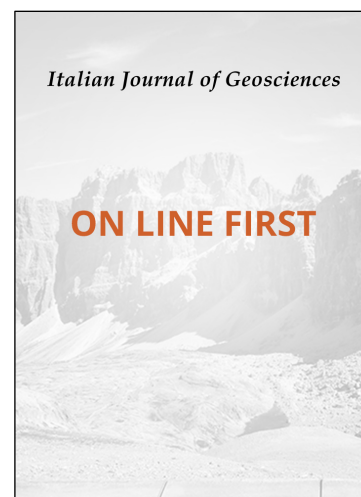




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A Christmas gift: Signature of the 24th December 2018 eruption of Mt. Etna on the chemical composition of bulk deposition in eastern Sicily

FILIPPO BRUGNONE (1), WALTER D'ALESSANDRO (2), SERGIO CALABRESE (1, 2), LORENZA LI VIGNI (1),
SERGIO BELLOMO (2), LORENZO BRUSCA (2), VINCENZO PRANO (2), FILIPPO SAIANO (3) & FRANCESCO PARELLO (1)

ABSTRACT

The eruption of Mt. Etna occurred on December 24th 2018 was characterized by strombolian activity and fire fountains, emitted by the New South-East Crater and along a fissure that propagated towards SE. The influence of volcanic emissions on atmospheric deposition was clearly detectable at several kilometres from the source. Wet and dry (bulk) deposition samples were collected each month, through a network of eleven collectors, in the areas of Milazzo, and Priolo from June 2018 and June 2019. They were analysed for major ions and trace elements concentrations. The pH values range from 3.9 to 8.3, while the EC values range from 7 to 396 $\mu\text{S cm}^{-1}$. An extensive neutralization of the acidity has been recognised mainly due to the suspended alkaline dust particles, which have a buffering role in rainwater. A high load of Na^+ and Cl^- was observed at all sites, related to the closeness of the study areas to the coast, showing a high positive correlation ($R^2 = 0.989$) along the line of Na^+/Cl^- ratio in seawater. During the eruption, the volcanic plume was carried by the winds for long distance (more than 300 km) affecting the area of Priolo but not that of Milazzo, which was upwind with respect to Mt. Etna. The impact of volcanic HF was clearly recognised in the samples collected after the eruption. Volcanic SO_2 and HCl had a lower impact due to the overwhelming input of anthropogenic sulfate and marine chloride. On the contrary, the signature of the Mt. Etna eruption can be well recognised in the high concentrations of certain trace elements in the samples collected immediately after the eruption. The strongest contrast between affected and non-affected samples was recognised in Al, Cd, and especially in the volatile elements Tl and Te, which are typically enriched in volcanic emissions. The results showed that volcanic eruptions might have a relevant effect on the atmospheric chemistry and on the composition of rainwater up to distances of 80 km from the emission vents.

KEY WORDS: *Rainwater, Fluoride, Trace elements, Volcanic emissions.*

INTRODUCTION

Volcanic emissions are an important source of gases and particles to the atmosphere (CADLE, 1980; NRIAGU, 1989; HINKLEY *et alii*, 1999; OPPENHEIMER, 2003; LIOTTA *et alii*, 2010; CALABRESE *et alii*, 2011; LIOTTA *et alii*, 2016). The main chemical species emitted by volcanoes are H_2O , CO_2 , and SO_2 , and great quantities of halogens and trace

volatiles elements, such as Cd, Cu, As, Pb, Zn, Te and Tl, are also emitted. (AIUPPA *et alii*, 2002; CALABRESE *et alii*, 2011; CALABRESE & D'ALESSANDRO, 2015; CALABRESE *et alii*, 2016). The lower part of the troposphere above the central Mediterranean is significantly and continuously influenced by the passive degassing from Etna and Stromboli (about 3320 and 924 meters a.s.l. respectively), and to a lesser extent by the fumarolic field of Vulcano Island (about 290 a.s.l.). The persistent plumes release in the atmosphere thousands of tons of acid gaseous compounds along with great quantities of micrometric and sub-micrometric particles, including minerals, hydrosoluble salts, lithics, volcanic glass shards (CALABRESE & D'ALESSANDRO, 2015). Moreover, frequent explosions and episodic paroxysmal events may occur, considerably increasing the fluxes of volcanogenic elements, and ejecting huge amounts of volcanic ash that reach long distances from the source. For example, during the imposing 2002-2003 eruption of Etna, its ashes reached the islands of Malta and Cephalonia (Greece), respectively about 200 km south and 500 km east of Etna (DELLINO & KYRIAKOPOULOS, 2003).

Atmospheric deposition processes (wet and dry), provide the pathways through which volcanic volatiles emitted into the atmosphere return to the Earth's surface. Scavenging mechanisms by rainfall plays an important role in removing particles and dissolved gaseous pollutants from the atmosphere involving two main processes (KAJINO & AIKAWA, 2015). The first one is called rainout, which takes place within the clouds and mainly involves gas condensation and fine particles absorption in cloud droplets. This process is related to the activation of cloud condensation nuclei (CCN), which play a fundamental role in the condensation of the droplets on aerosol particles (i.e., heterogeneous nucleation), since water droplets form, by homogeneous nucleation, only in air supersaturated by 300-400%, while supersaturation is usually lower than 1%, (HOUBE, 2003, LIOTTA *et alii*, 2017). A second process is called washout (below-cloud scavenging), which efficiently removes the coarse particles. The washout process occurs during the raindrop fall, from the base of the clouds down to the ground, changing the chemical composition of the rainwater.

The main sources of chemical elements in rainwater are atmospheric aerosol particles, such as sea salts (usually, the largest fraction of CCN), geogenic dust, biogenic material and anthropogenic emissions. The dissolution of gases and particulate matter emitted by different sources,

(1) Università degli Studi di Palermo, Dipartimento Scienze della Terra e del Mare, via Archirafi, 36, 90123, Palermo, Italy.

(2) Istituto Nazionale di Geofisica e Vulcanologia, via Ugo la Malfa 153, 90146, Palermo, Italy.

(3) Università degli Studi di Palermo, Dipartimento di Scienze Agrarie, Alimentari e Forestali, viale delle Scienze ed.4, 90128, Palermo, Italy.

Corresponding authors e-mail: sergio.calabrese@gmail.com

the chemical and physical reactions that occur during local and regional scale transport, the removal processes discussed before, have a strong impact on the chemical composition of rainwater (ARSENE *et al.*, 2007; GALY-LACAUX *et alii*, 2009). Water-soluble chemical species, such as Na, Cl, Mg and sea salt SO_4 (ss- SO_4) are enriched in sea-salt aerosol (KEENE *et alii*, 1986), and they are the main part of the total ions content of rainfall in coastal areas (ARIMOTO *et alii*, 1987; BERNER & BERNER, 1987; HALSTEAD *et alii*, 2000). Non sea salt Ca and Mg, Si, and Al are often originated from soil dust and terrigenous component (XU & HAN, 2009). Non sea salt SO_4 (nss- SO_4^{2-}) and NO_3 are mainly formed by conversion of anthropogenic emitted gaseous precursors (e.g., SO_2 and NO_x - SEINFELD & PANDIS, 1998), which come from anthropogenic sources such as energy production, urban transport, industry and agriculture (CONRADIE *et alii*, 2016).

Mount Etna is one of the most active and most monitored volcanoes of the Earth (BONACCORSO *et alii*, 2004). It is a composite stratovolcano rising over 3320 m above eastern Sicily (BONFORTE *et alii*, 2019), built upon tensional faults cutting a thick continental crust (CHESTER *et alii*, 1985). The present-day Etna's activity consists of persistent passive degassing at the summit craters (ALLARD, 1997; AIUPPA *et alii*, 2006; CALABRESE *et alii*, 2011), interrupted by lava emissions and occasionally paroxysmal eruptions (BONACCORSO *et alii*, 2004). Mount Etna is widely regarded as a big source of volcanic gases into the troposphere in the Mediterranean basin, and its gas emissions account for a significant percentage respect to the worldwide average volcanic budget. The SO_2 flux from Mt. Etna's plume has been routinely measured by the INGV since 1987. SO_2 flux ranges between 600 to 25,000 Mg d⁻¹; fluxes greater than 10,000 Mg d⁻¹ were prevalently measured during eruptive events. During eruptive periods, Etna's emissions can be dispersed over long distances and cover wide areas of the Mediterranean region.

In the morning of December 24th 2018, strombolian activity and fire fountains started from the New South-East Crater, along an eruptive fissure that propagated towards SE along the fracture formed during the 1989 eruption (BONFORTE *et alii*, 2019). The present study reports on the chemical composition of bulk depositions in the areas of Priolo and Milazzo, Eastern Sicily (Italy). The concentrations of major and trace ionic species, their temporal variation and possible sources are presented and discussed, with the aim to highlight the signature of the volcanic eruption of Mount Etna in the chemical composition of atmospheric deposition in areas located at great distances from the emission source of volcanogenic elements.

SAMPLING SITES AND METHODS

STUDY AREA

The research program was carried out from June 2018 to June 2019 at two polluted sites located in Eastern Sicily and classified by the Italian Ministry of the Environment as Site of National Interest (SIN) (Fig. 1). These sites are defined as large, contaminated areas where strong environmental pollution may cause an important impact

in terms of health and ecological risks, as well as damage to cultural and environmental heritage.

The two areas have a millennial history, proven by many important archaeological evidences, and have seen an important industrial development during the last century.

Milazzo is a city of about 30,000 inhabitants sited on the northern coast of Sicily. The industrial development sharply increased since the 1950s, with a steel industry, energy production plants and, above all, the widest oil refinery in Europe, which is still active. The area is strongly polluted and recent impact assessment of industrial activities showed that emissions to the atmosphere (NO_x , SO_2 , particulate matter) are by far the most important releases (MEY, 2013).

The SIN of Priolo, includes the municipalities of Priolo (12,000 inhabitants), Augusta (36,000 inhabitants), Melilli (13,000 inhabitants), Siracusa (122,000 inhabitants), Floridia (23,000 inhabitants), and Solarino (8000 inhabitants), covers an area of 550 km². It includes the huge Siracusa petrochemical district (the widest in Europe, about 27 km²) that extends from the north of Siracusa to Augusta, and where the main industrial activities include oil refinery, processing of oil-related products and energy production. Born in the 1950s and increasing in the two following decades, many of the industrial plants reduced or ceased their activity from the 1980s, creating serious remediation problems.

GEOLOGICAL DESCRIPTION

The Milazzo area belongs to the Alpine Peloritani Chain in the Southern Sector of the Calabrian Peloritani Arc (GALADINI & MESSINA, 2004; CARBONE *et alii*, 2011; LENTINI *et alii*, 2011). It is made up of the Aspromonte Unit (AsU) Variscan high-medium grade basement, which consists of Variscan gneissic bodies including metric amphibolite lenses. Locally, Variscan two-mica marbles, augen gneissic bodies, and Late-Variscan peraluminous leucomonzogranites are also present. The basement is locally covered by Late Miocene deposits consisting of gray-whitish limestone containing corals, algae and molluscs, and by quaternary deposits (CARBONE *et alii*, 2011; LENTINI *et alii*, 2011; MACAIONE *et alii*, 2012; MESSINA *et alii*, 2013). The Holocene alluvial deposits characterizing the Barcellona-Milazzo Plain, which includes the south of Milazzo City and the refinery, mainly consist of crystalline clastic elements of the metamorphic units.

The Priolo area lies at the border between the north-eastern edge of the Hyblean Plateau (max. altitude 987 m) and the adjacent Catania-Gela trough, bordered to the east by the faults system of the Ibleo-Maltese escarpment. The Hyblean foreland consists of thick Mesozoic limestones (>5000 m) partially covered by Quaternary volcanic deposits (FINETTI *et alii*, 2005).

CLIMATE SETTING

Data of four weather stations located at Torregrotta (SIN Milazzo), Augusta (SIN Priolo), Siracusa (SIN Priolo), Palazzolo Acreide (local background) (Fig. 1) and belonging to the SIAS monitoring network (<http://www.sias.regione.sicilia.it/>) have been acquired.

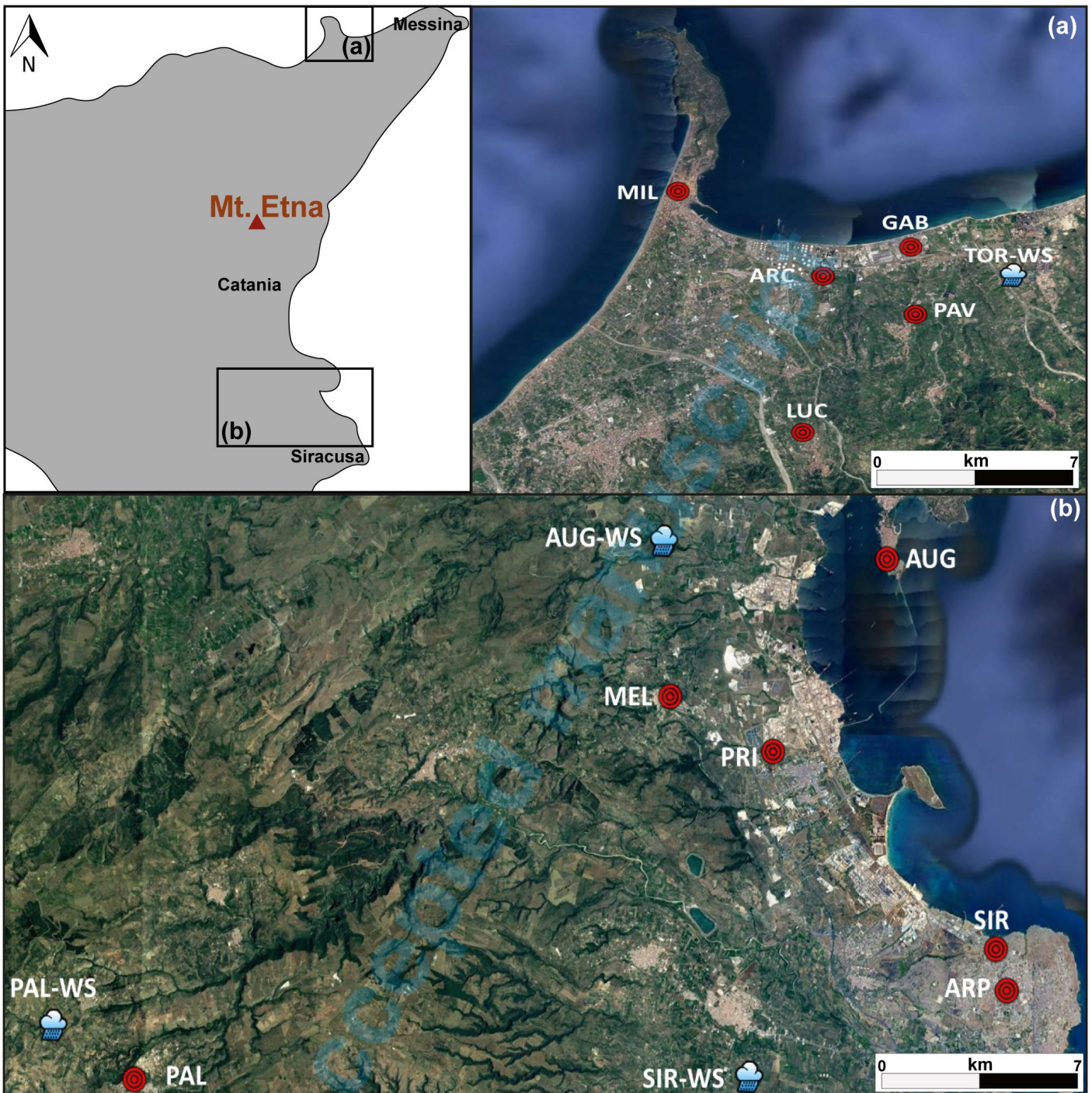


Fig. 1 - Location of monitoring sites (red circles) and SIAS's weather stations (rain clouds), in the area of Milazzo (a) and Priolo (b).

Figure 2 shows the rainfall values measured in the period June 2018 - June 2019. The highest rainfall value was recorded, in the period 15/09/2018 – 16/10/2018, at Siracusa's weather station (332.8 mm). In the Priolo area the rainfall events were concentrated in the autumn period (September – November). Considering the entire period of the study, the highest overall rainfall value was recorded in Palazzolo Acreide (1044.6 mm), followed by Siracusa (970.4 mm) and by Augusta (730.4 mm).

In the area of Milazzo (Torregrotta), the highest value

was recorded in the period 10/12/2018 – 16/01/2019 (147.2 mm). In this area the rainfall events were well distributed throughout the study period, except for the driest summer period. The total rainfall amount during the study period was 946.8 mm.

Figure 3 shows the dominant wind direction ($^{\circ}$) and the average wind speed (m s^{-1}), at 2 m above the ground for the weather station of Siracusa, Augusta and Torregrotta, and the average wind speed (m s^{-1}) at 10 m above the ground for the weather station sited in Palazzolo Acreide.

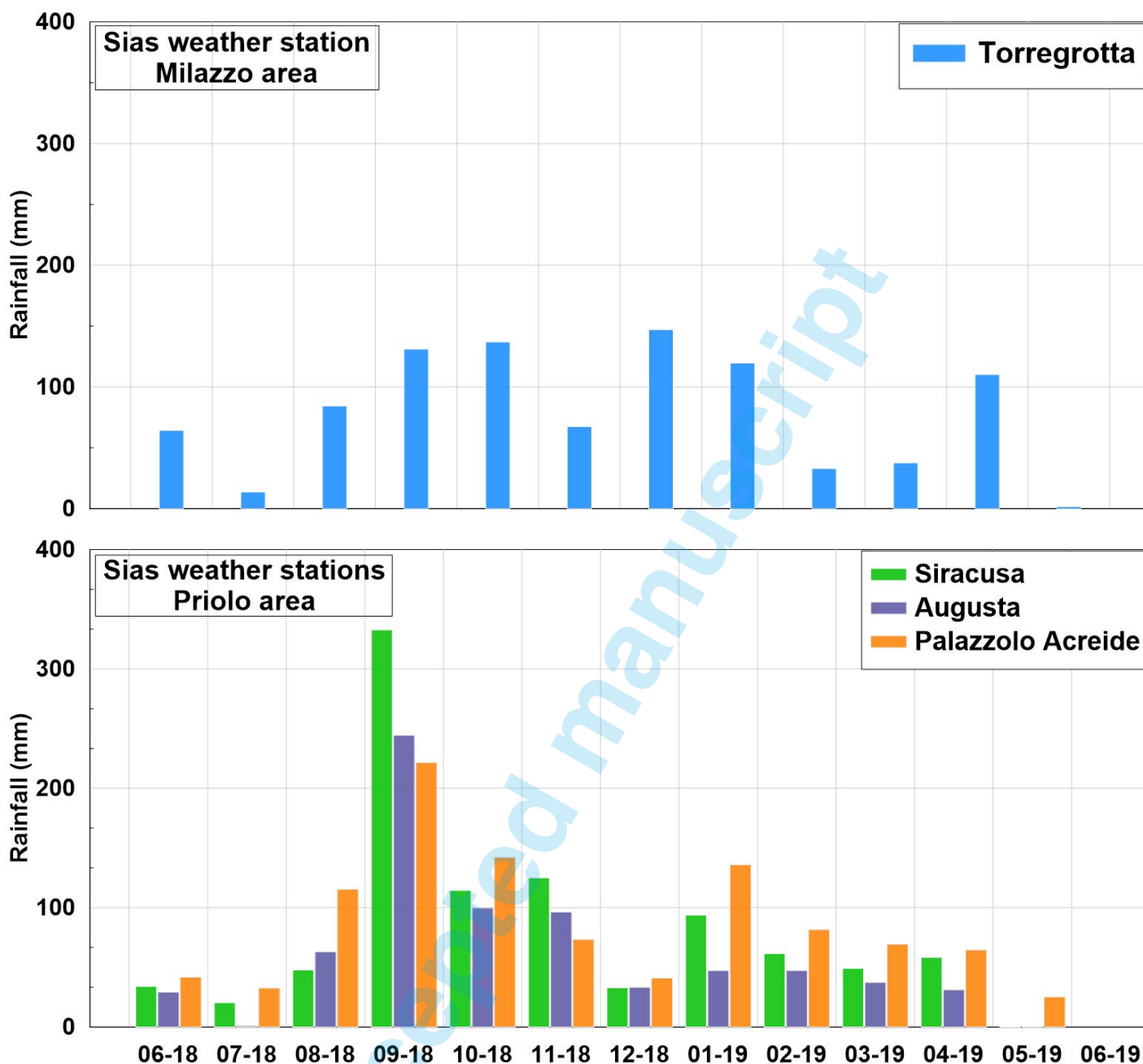


Fig. 2 - Monthly rainfall (mm) in the period June 2018 – June 2019 at Torregrotta, Siracusa, Augusta and Palazzolo Acreide.

In particular, in the period June 2018 - June 2019:

- at the site of Palazzolo Acreide, the wind was characterized by a dominant direction from north-east (0°), and south-west (225°), and a dominant average wind speed between 2.5 and 3.0 m s^{-1} .
- at the site of Siracusa, the wind had two dominant directions (from north and from west), a dominant average wind speed between 0.5 and 1 m s^{-1} and a maximum wind speed between 2.0 and 2.5 m s^{-1} .
- at the site of Augusta, the wind had a dominant direction from the eastern quadrants (90°), with a dominant average wind speed between 0.5 and 1.0 m s^{-1} and a maximum wind speed between 2.5 and 3.0 m s^{-1} .
- at the site of Torregrotta, the wind was characterized by

a dominant south-east direction (135°) and a dominant average wind speed between 1.0 and 1.5 m s^{-1} , with a maximum wind speed between 2.0 and 2.5 m s^{-1} .

MATERIALS AND METHODS

Wet and dry (bulk) deposition samples were collected in the areas of Milazzo (SIN Milazzo) and Priolo (SIN Priolo), during almost one year (from 11/06/2018 to 03/07/2019), according to the guidelines published by the main international agency involved in the monitoring of atmospheric precipitation: EMEP/CCC-Report (2014), ICP-forest (2016) and WMO (2018).

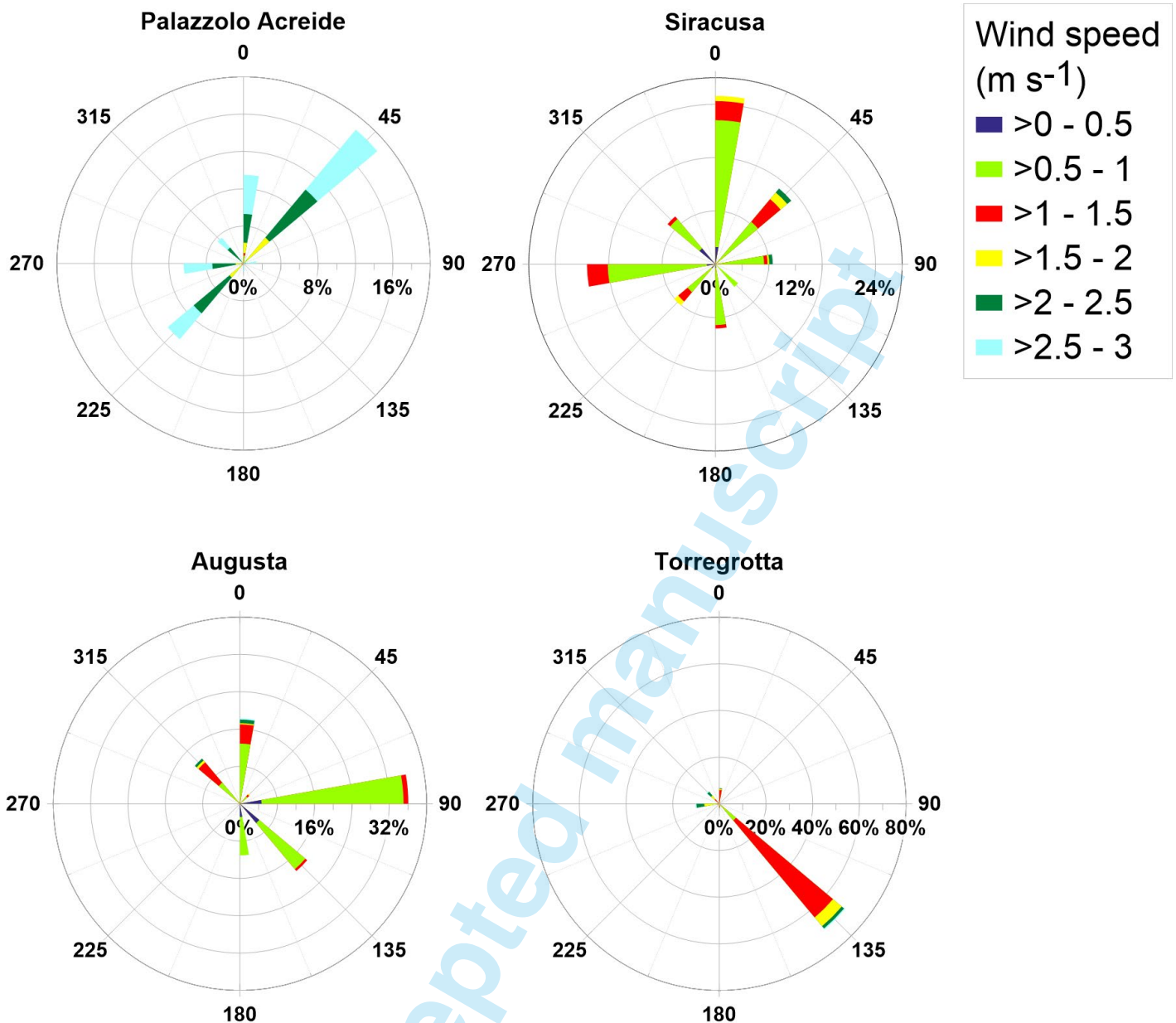


Fig. 3 - Wind direction ($^{\circ}$) and average wind speed (m s^{-1}) at 10 m above the ground at Palazzolo Acreide and 2 m above the ground at Siracusa, Augusta and Torregrotta.

Samples were collected, on a monthly basis, using a network of eleven rain gauges installed at different distances from the industrial areas (Table 1). In the study area of Priolo six pluviometers were installed: two of these (ARP and SIR) were installed in two urban sites in the city of Syracuse, the first on the roof of the ARPA (*Agenzia Regionale per la Protezione dell'Ambiente*) headquarters of the Province of Siracusa, and the second one close to an environmental monitoring station of the Sicily Region, along the main road connecting Syracuse and Priolo; the Melilli (MEL) deposimeter has also been placed close to an environmental monitoring station, adjacent to a public school; another sampler was placed in the periphery of Priolo (PRI), on the roof of the headquarters of the Provincial Civil Protection Department; the fifth pluviometer was placed in the urban site of Augusta (AUG),

on the roof of a private house; the last was installed at Palazzolo Acreide (PAL), an urban area in a rural context, located about 30 km far from the industrial area of Priolo and from the sea coast. In the study area of Milazzo five monitoring stations were installed: three of these in urban sites few kilometers away from the industrial area, in the inhabited areas of Milazzo, Archi and Passo Vela (MIL, ARC and PAV respectively); another pluviometer (GAB) was placed in a primary public school of a small village, *Contrada Gabbia*, located in between the main industrial area; the fifth pluviometer was installed at *Santa Lucia del Mela*, on the roof of a private house, located in a rural area of low density of human activity (more details in the Table 1).

Each rain gauge (Fig. 4) consisted of a 5 L HDPE bottle and a PP Büchner type funnel ($\varnothing$ 240 mm). The bottle

TABLE 1

Sampling sites of the rain gauges used in this study.

ID Site	City	Locality	Site type	Coordinates UTM WGS84	Altitude (m a.s.l.)
SIR	Siracusa	Scalagrega	urban	33 S 523613 4106275	63
MEL	Melilli		urban	33 S 511433 4115107	249
AUG	Augusta		urban	33 S 519388 4120387	28
PAL	Palazzolo Acreide		semi-urban	33 S 491732 4102437	656
ARP	Siracusa		urban	33 S 524666 4104347	76
PRI	Priolo		industrial/urban	33 S 514767 4112657	94
GAB	Pace del Mela	Gabbia	industrial	33 S 527148 4228670	15
ARC	Pace del Mela	Archi	industrial/urban	33 S 524760 4227710	34
PAV	Pace del Mela	Passo Vela	urban	33 S 527271 4226464	107
LUC	S. Lucia del Mela	Contrada Pattina	semi-urban	33 S 524222 4222617	150
MIL	Milazzo		industrial/urban	33 S 520799 4230495	20

was inserted in a 1.5 m high PVC tube to protect it from direct sunlight (CALABRESE *et alii*, 2011). The rain gauges were positioned at about 2.5 m above the roofs of public and private buildings or air quality monitoring stations of “Regione Sicilia”. The collectors were open during the entire exposure period collecting both wet and dry deposition (bulk collectors). All the equipment (funnels and bottles) was cleaned before the field exposure first using a rinse solution of deionized water and then “ultrapure” deionized water and dried under laminar hood for 24h. Afterwards, the collectors were assembled and stored in clean plastic bags until their exposure in the field. About once per month the bottles and funnels were removed and replaced by clean ones. The sampling bottles were carried to the laboratory

and pH and electrical conductivity were measured within 48 hours, by using specific Orion conductimeter and pH meter with a 52-21 combination electrode.

The collected water samples were divided in three aliquots for different analytical determinations. Unfiltered aliquot was used for total alkalinity determination with an automatic Titrator Compact G20, using 0.1M HCl. Filtered (0,45 μm acrodisc filters) aliquot was used for major anions (NO_3^- , SO_4^{2-} , Cl^- and F^-) determination by ion chromatography system (ICS-1100 Dionex) in suppressed mode and equipped with an anion column (AS14A) and a precolumn (AG14A) that works under continuous flow of carbonate-bicarbonate eluent. Filtered and acidified (with Ultrapure HNO_3) sample were stored for the analysis of



Fig. 4 - Picture of the bulk collector installed at the Augusta sampling site; at the top right, a detailed view of the funnel.

major (Ca^{2+} , K^+ , Mg^{2+} and Na^+) and a large suite of trace elements (Al, As, B, Ba, Be, Ce, Cd, Co, Cr, Cs, Cu, Fe, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, U, V and Zn) by inductively coupled plasma optical emission and mass spectrometry (ICP-OES, Jobin Yvon Ultima2 and ICP-MS, Agilent 7500-ce). All the aliquots were stored at 4 °C. To avoid metal contamination during collection and analysis of samples, all plastic ware was washed with ultrapure water of 18 M Ω cm resistance (Milli-Q water-purification system, Millipore). After collection, sample treatment and analysis were carried out in a clean room. Pre-treatment of the samples and chemical analyses were performed in the laboratories of the Dipartimento di Scienze della Terra e del Mare (DiSTeM), Dipartimento di Scienze Agrarie, Alimentari e Forestali and Istituto Nazionale di Geofisica e Vulcanologia (INGV) of Palermo.

RESULTS

The results of the chemical-physical data measured in the collected bulk deposition samples of both the areas and

the main statistical parameters, relative to the major ions, are given in Table 2. The statistical parameters relative to the trace elements of the samples collected in the area of Priolo are given in Table 3.

In the study area of Priolo, the pH values show a high variability ranging from 4.1 to 8.2. The electrical conductivity values ranged from 7 to 396 $\mu\text{S cm}^{-1}$, with a median value of 64 $\mu\text{S cm}^{-1}$. In the study area of Milazzo, the pH values range from 3.9 to 8.3, showing also in this area a high variability. The electrical conductivity values range from 10 to 317 $\mu\text{S cm}^{-1}$, with a median value of 61 $\mu\text{S cm}^{-1}$. The Electrical Conductivity values are generally inversely related with the amount of precipitation in both areas.

The annual volume weighted mean (VWM) concentrations for each ion were calculated using the following equation (LAOUALI *et alii*, 2012):

$$\text{VWM} = \sum_{i=1}^n C_i P_i / \sum_{i=1}^n P_i \quad (1),$$

where, C_i is the concentration of a given ion in the i th sample, P_i is the rainfall depth (mm) during i th sampling

TABLE 2

Main statistical values of the chemico-physical parameters and major ions concentrations, determined on the bulk deposition samples collected in both study areas (number of samples: 71 for the area of Priolo; 60 for the area of Milazzo). Electric conductivity values are in $\mu\text{S cm}^{-1}$. Major ions' concentrations are in mg L^{-1} .

Priolo area	LOQ	Minimum	1 st quartile	Median	Mean	3 rd quartile	Maximum	Weighed mean
pH		4,15	6,19	6,70	6,53	7,15	8,25	
Electric conductivity (EC)		7	23	44	64	69	396	
F	0,01	<LOQ	0,01	0,03	0,10	0,08	0,88	0,04
Cl	0,02	0,56	3,12	6,19	10,9	10,4	124	7,88
NO ₃	0,02	<LOQ	0,56	1,07	2,55	2,63	25,0	1,08
SO ₄	0,02	0,69	2,28	3,68	5,07	6,43	23,1	3,03
Na	0,10	0,40	1,66	2,98	5,38	5,04	60,2	3,91
K	0,05	0,08	0,14	0,27	0,62	0,64	6,58	0,26
Mg	0,01	0,08	0,34	0,60	0,88	0,99	7,68	0,60
Ca	0,10	0,36	1,52	3,23	4,65	6,02	26,1	2,49
Si	0,01	0,01	0,05	0,09	0,15	0,19	0,63	0,11

Milazzo area		Minimum	1 st quartile	Median	Mean	3 rd quartile	Maximum	Weighed mean
pH		3,92	5,75	6,31	6,44	7,43	8,32	
Electric conductivity (EC)		10	29	38	61	64	317	
F	0,01	<LOQ	0,03	0,05	0,06	0,07	0,20	0,04
Cl	0,02	1,27	3,69	7,01	12,7	13,4	95,1	9,47
NO ₃	0,02	<LOQ	<LOQ	0,93	1,64	1,93	11,1	1,00
SO ₄	0,02	1,08	2,45	3,65	5,23	5,52	27,1	3,25
Na	0,10	0,75	1,80	3,27	6,20	6,82	39,2	4,67
K	0,05	0,09	0,17	0,23	0,61	0,63	6,33	0,27
Mg	0,01	0,12	0,37	0,58	0,90	1,00	5,19	0,65
Ca	0,10	0,44	1,26	1,97	3,91	4,42	30,7	2,05
Si	0,01	0,01	0,05	0,08	0,18	0,17	1,74	0,10

TABLE 3

Main statistical parameters of the trace elements ($\mu\text{g L}^{-1}$) determined on the bulk deposition collected in the study area of Priolo (number of samples: 71).

Priolo	LOQ	Minimum	1 st quartile	Median	Mean	3 rd quartile	Maximum	Weighed mean
Li	0,01	0,01	0,06	0,13	0,18	0,22	1,22	0,11
B	0,5	0,9	3,0	4,5	5,4	5,9	24,6	4,0
Al	0,5	2,1	9,8	20,9	28,3	37,3	152	17,3
Ti	0,01	<LOQ	0,00	0,12	0,28	0,28	3,21	0,12
V	0,05	0,30	0,54	0,78	1,03	1,03	5,73	0,64
Cr	0,01	0,01	0,04	0,06	0,09	0,09	0,92	0,05
Mn	0,01	0,01	0,37	0,81	7,98	3,11	123	1,42
Fe	0,1	0,1	1,6	2,9	5,5	5,1	66,9	3,7
Co	0,01	<LOQ	0,02	0,03	0,06	0,05	0,60	0,03
Ni	0,01	0,01	0,13	0,24	0,46	0,43	2,82	0,23
Cu	0,1	0,1	0,6	1,3	3,0	2,3	42,9	0,9
Zn	0,5	0,9	4,7	9,9	16,8	13,9	181	8,8
As	0,01	0,02	0,06	0,1	0,11	0,13	0,48	0,07
Se	0,05	0,05	0,11	0,14	0,18	0,21	0,64	0,13
Rb	0,01	0,04	0,13	0,28	0,55	0,70	6,31	0,22
Sr	0,1	1,7	5,9	13,5	24,4	36,1	102	13,1
Mo	0,01	0,03	0,09	0,18	0,22	0,30	0,92	0,13
Cd	0,005	<LOQ	0,007	0,013	0,021	0,020	0,141	0,012
Sn	0,005	<LOQ	<LOQ	<LOQ	0,006	0,006	0,050	0,004
Sb	0,01	0,01	0,02	0,06	0,09	0,11	0,48	0,07
Te	0,001	<LOQ	<LOQ	<LOQ	0,002	<LOQ	0,025	<LOQ
Cs	0,001	<LOQ	<LOQ	0,003	0	0,007	0,019	0,002
Ba	0,05	0,18	2,29	4,39	7,75	8,18	75,60	4,68
Tl	0,005	<LOQ	0,005	0,009	0,019	0,018	0,164	0,010
Pb	0,005	<LOQ	0,023	0,048	0,246	0,125	6,330	0,098
Bi	0,001	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
U	0,001	0,001	0,002	0,003	0,005	0,005	0,038	0,003

period and n is the total number of samples with valid concentrations for the ion.

The concentrations of the major ions (on VWM basis) decrease in the order of $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- \gg \text{F}^-$ for anions and $\text{Na}^+ > \text{Ca}^{2+} \gg \text{Mg}^{2+} > \text{K}^+ > \text{Si}$ for cations in both the study areas. Chloride has a relative abundance of 42.3% in the area of Priolo and 42.5% in the area of Milazzo, followed by HCO_3^- , with a relative abundance of 35.5% in the area of Priolo and 38.2% in the area of Milazzo, by SO_4^{2-} with a relative abundance of 16.2% in the first area

and 14.6% in the second one, by NO_3^- with a relative abundance of 5.8% in the area of Priolo and 4.5% in the area of Milazzo and finally by F^- with a relative abundance of 0.19% in the first area and 0.16% in the second one.

As for the cations, Na^+ has a relative abundance of 53.1% in the area of Priolo and 60.3% in the area of Milazzo, followed by Ca^{2+} with a relative abundance of 33.8% in the first area and 26.5% in the second one, by Mg^{2+} with a relative abundance of 8.1% in the area of Priolo and 8.4% in the area of Milazzo, by K^+ with a relative

abundance of 3.5% in both areas and finally by Si with a relative abundance of 1.5% in the first area and 1.9% in the second one.

The most abundant trace elements, on VWM basis, are Al and Sr ($> 10 \mu\text{g L}^{-1}$). Boron, Mn, Fe, Zn, Ba are one order of magnitude lower ($< 10 \mu\text{g L}^{-1}$), whilst other trace elements are more than two orders of magnitude lower (Li, Ti, V, Ni, Cu, Sr, Rb and Mo between 0.1 and $1 \mu\text{g L}^{-1}$; Cr, Co, As, Cd, Sb, Tl and Pb between 0.01 and $0.1 \mu\text{g L}^{-1}$; Cs and U $< 0.01 \mu\text{g L}^{-1}$). Tin and Te had more than 50 % of values below detection limit while Bi was always below that limit.

DISCUSSION

SEAWATER CONTRIBUTION

Due to the closeness of the study areas to the seacoast, a high load of Na^+ and Cl^- can be observed at all sites. These two ions show a high positive correlation ($R^2 = 0.989$) along the Na^+/Cl^- ratio (0.558 by weight) of the seawater (Fig. 5) indicating that sea-derived CCN and/or direct sea-spray deposition strongly contribute to the chemical composition of the precipitation, while human activities and geogenic dust have a negligible influence on these ions.

Contributions of sea salt ionic concentrations to deposition are commonly estimated by calculating the excess concentrations of K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} with respect to sea salt using Na^+ or Cl^- as a reference. The former is often preferred because significant contributions of Cl^- may sometimes derive from anthropogenic sources (KEENE *et alii*, 1986) and/or volcanic gases (AIUPPA *et alii*, 2001; AIUPPA *et alii*, 2002; AIUPPA *et alii*, 2005). Although rarely Na^+ may partially derive from geogenic source, we used the reference ratios of this ion to calculate the seawater contribution (KEENE *et alii*, 1986). The sea salt

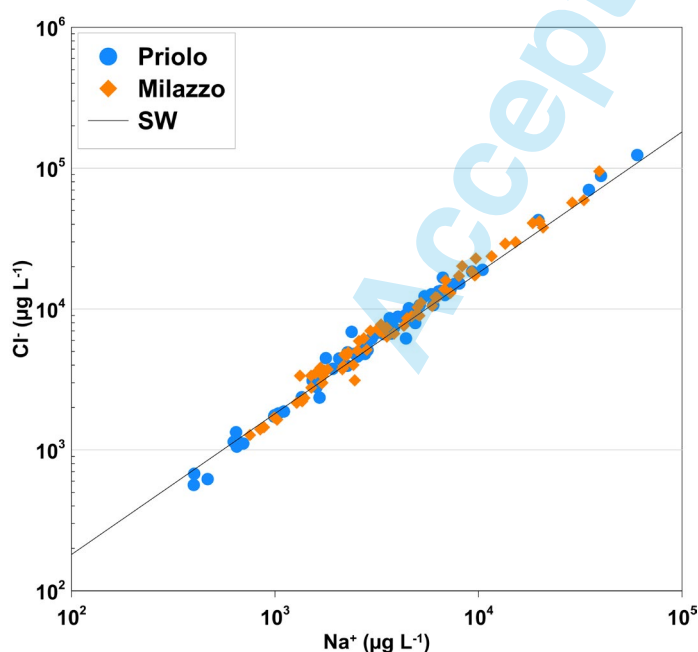


Fig. 5 - Binary plot of chloride ($\mu\text{g L}^{-1}$) vs. sodium ($\mu\text{g L}^{-1}$) concentrations in rainwaters.

fractions of any of these species, X, with respect to Na^+ are:

$$[\text{X}]_{\text{marine}} = [\text{Na}]_{\text{rain}} \times [\text{X}/\text{Na}]_{\text{seawater}} \quad (2),$$

where $[\text{X}]_{\text{marine}}$ is the sea salt contribution of X in mg L^{-1} , $[\text{Na}]_{\text{rain}}$ is the concentration of Na^+ in the sample (mg L^{-1}) and $[\text{X}/\text{Na}]_{\text{seawater}}$ is the seawater concentration ratio (KEENE *et alii*, 1986).

The non-sea salt fraction of X can then be calculated by:

$$[\text{X}]_{\text{nss}} = [\text{X}]_{\text{rain}} - [\text{X}]_{\text{marine}} \quad (3),$$

where $[\text{X}]_{\text{rain}}$ is the concentration of species X in the collected deposition, and $[\text{X}]_{\text{nss}}$ is the non-sea salt contribution of species X in mg L^{-1} .

The ions with the highest non sea salt component are NO_3^- (99% of the total load), Ca^{2+} (91.8%) and SO_4^{2-} (72.8%). The ions mostly derived from a marine source are Cl^- (93.7% of the total load) and Mg^{2+} (71.8%).

ACID-BASE EQUILIBRIA

Cloud water in equilibrium with the atmospheric CO_2 would have a pH value of 5.65 (ARSENE *et alii*, 2007). Acid species such as H_2SO_4 , HNO_3 , HCl , HF or organic acids are able to shift the pH to lower values. The main sources of these acid compounds are anthropogenic and volcanic activities (BERNER & BERNER, 1987). In areas where alkaline components (NH_3 , dust, etc.) in the atmosphere are limited or absent these compounds bring to severe impact on the environment and buildings due to the highly acid deposition (SEINFELD & PANDIS, 1998). This problem has long known as “acid rain” and although in recent years the anthropogenic emissions drastically decreased, in many parts of the world it is still effective (XING *et alii*, 2017).

In our samples the values of pH are inversely related with the amount of precipitation. The higher pH values in less rainy periods are the result of the relatively higher influence of the dry deposition. Due to the lower amounts of water inside the samplers, post-deposition interactions with the atmospheric aerosol particles, like geogenic dust and sea aerosol, the concentrations of the dissolved ion increase and as a consequence also the buffering process leading to higher pH values (Fig. 6).

The ratio $(\text{H}^+)/(\text{nssSO}_4^{2-} + \text{NO}_3^-)$ can be used to evaluate the magnitude of the rainwater neutralization; if the acidity caused by H_2SO_4 and HNO_3 is not neutralized, this ratio is close to 1. In the present study, an average $(\text{H}^+)/(\text{nssSO}_4^{2-} + \text{NO}_3^-)$ ratio of about 0.076 was estimated, which suggest that the 92.4% of the acidity due to SO_4^{2-} and NO_3^- was neutralized. The extensive neutralization of the acidity is probably due to the transported alkaline dust particles, which have a buffering role in the rainwater (ARSENE *et alii*, 2007).

The neutralization factors of different chemical component of interest can be obtained using the equation (POSSANZINI *et alii*, 1988):

$$\text{NF}_x = [\text{X}] / [\text{nssSO}_4^{2-} + \text{NO}_3^-] \quad (5),$$

where $[\text{X}]$ denotes the chemical component of interest, with all the concentrations in meq L^{-1} . The highest NF corresponds to nssCa^{2+} with a value of 1.91; nssMg^{2+} and nssK^+ have very low NF with values of 0.16 and 0.065 respectively.

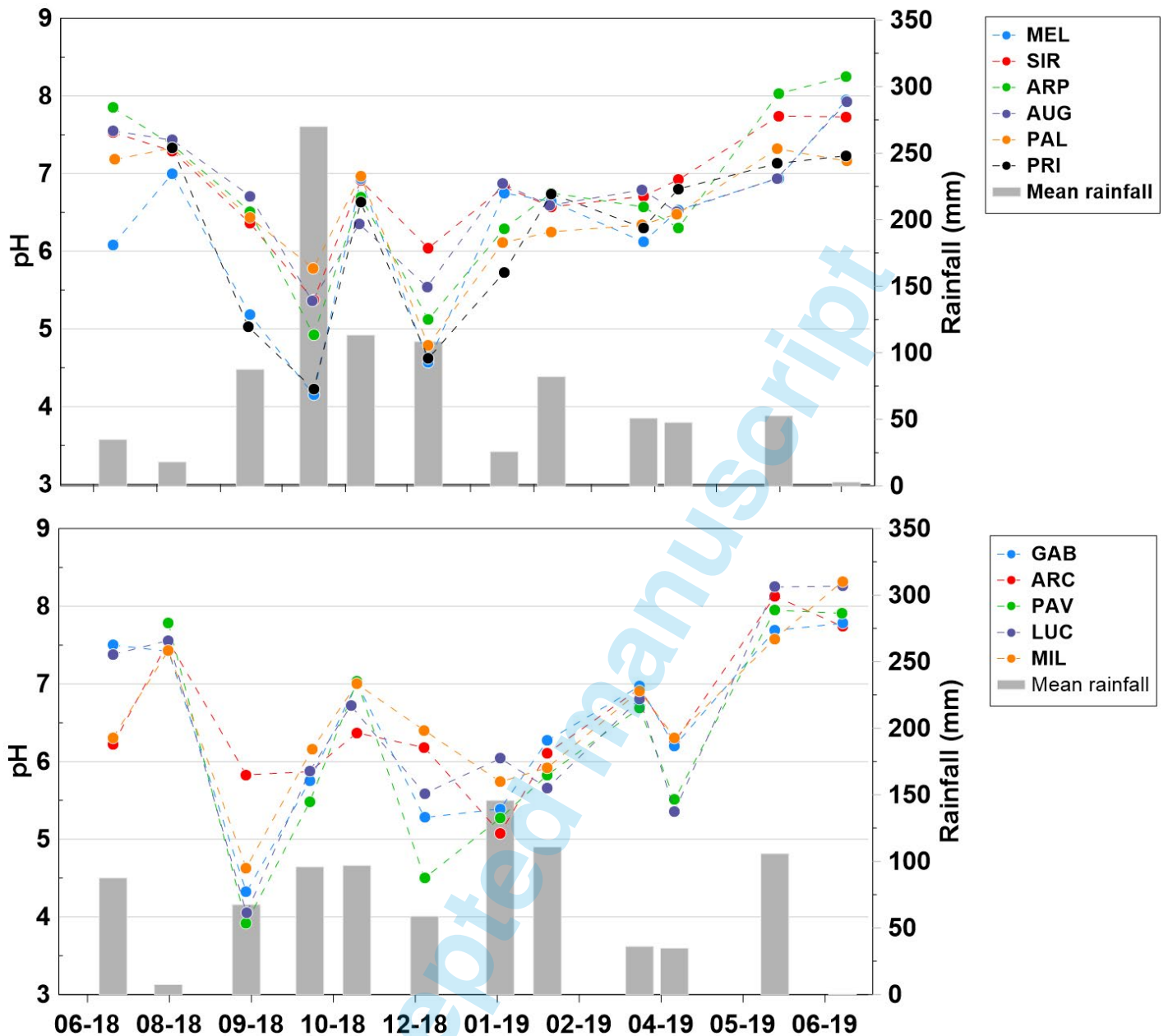
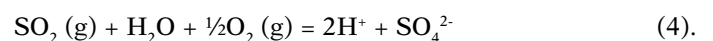


Fig. 6 - Temporal variations of pH values and rainfall amounts in the area of Priolo and Milazzo.

Figure 7 presents the correlation between pH values and nssCa^{2+} and between nssCa^{2+} and nssSO_4^{2-} , in both the study areas. Rainwater samples characterized by high load of nssSO_4^{2-} for which we could expect low values of pH, have also high load of nssCa^{2+} , so the acidity due to the SO_4^{2-} is neutralized by the high load of Ca^{2+} ; on the contrary, low concentrations of nssCa^{2+} correspond low pH values, because the buffering process is less effective. The good positive correlation between nssCa^{2+} and nssSO_4^{2-} , with a R^2 value of 0.795 confirm the importance of crustal (mainly carbonate) material in the rain neutralization process. Previous authors evidenced widespread acid-rain neutralization by atmospheric carbonate dust over the entire Mediterranean basin due both to Saharan dust (LOYE-PILOT *et alii*, 1986) and to the widespread outcrop of limestone formations (AL-MOMANI *et alii*, 1995) and this is also the case of the

study area. 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 alii*, 1995; AL-MOMANI *et alii*, 2008; AVILA & ALARCON, 1999; KITA *et alii*, 2004; D'ALESSANDRO *et alii*, 2013).

HF and HCl emitted by volcanoes by either passive degassing or eruptive activity, due to their high solubility, are rapidly dissolved in the rainwater, forming F^- and Cl^- (AIUPPA *et alii*, 2005). The volcanic SO_2 , once emitted in the atmosphere, is oxidized through complex processes, which may follow several paths. The more plausible process of SO_2 dissolution and oxidation in precipitation is according to the following reaction (STEFANSSON *et alii*, 2017):



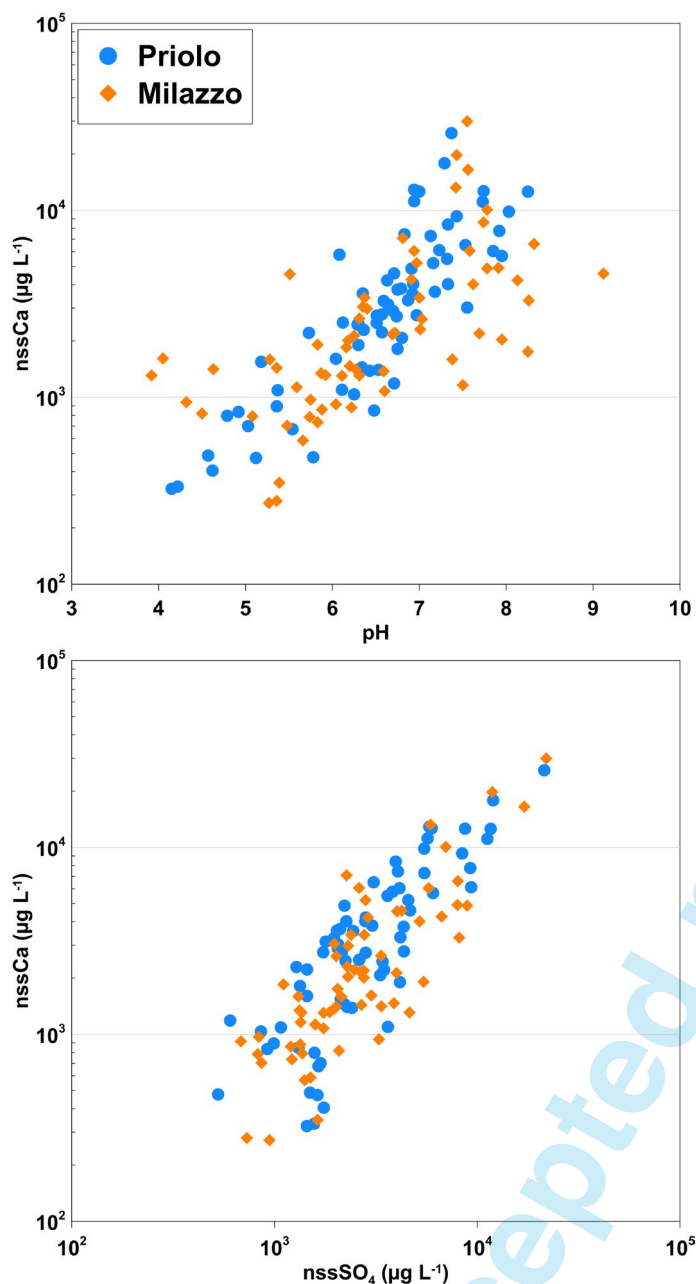


Fig. 7 - Binary plots of nssCa^{2+} ($\mu\text{g L}^{-1}$) vs. pH, and nssCa^{2+} ($\mu\text{g L}^{-1}$) vs. nssSO_4^{2-} ($\mu\text{g L}^{-1}$).

While the volcanic gases strongly contribute to the acidity of precipitations, volcanic ash may represent a source of buffering cations (AIUPPA *et alii*, 2005; CALABRESE *et alii*, 2011).

IMPACT OF THE 24TH DECEMBER 2018 MT. ETNA ERUPTION ON BULK DEPOSITION CHEMISTRY

In recent years many studies evidenced the impact of volcanic emissions on rainwater around active volcanoes (HARDING & MILLER, 1982; JOHNSON & PARNELL, 1986; KAWARATANI & FUJITA, 1990; AIUPPA *et alii*, 2001, 2005; CUOCO *et alii*, 2013). The first studies took in account only major

ions and acidity, while more recently also trace elements were determined and discussed (CALABRESE *et alii*, 2011; MATHER *et alii*, 2012; CANGEMI *et alii*, 2017; LIOTTA *et alii*, 2017; STEFANSSON *et alii*, 2017). Most of these studies considered deposition samples taken within few tens of km of radius from the volcanic vents. The bulk deposition samples of Priolo were collected at distance between 60 and 80 km from the Etna craters, and in the period straddling the eruptive event they were characterized by high concentrations of Fluoride (up to 0.88 mg L^{-1}). Fluoride in rainwater directly derives from the dissolution of hydrofluoric acid emitted by volcanic activity.

Meteorological reports and satellite images support this hypothesis. During the eruptive period (from 24th to 30th December 2018), the prevailing winds blew from the North direction and there were light rainfalls in the monitored sites (between 0.2 mm in Siracusa and Augusta, and 1.6 mm in Palazzolo Acreide). As a consequence, gases and particles of Etna's plume were carried for long distance from the emission point, and they were deposited as dry and wet deposition also in the area of Priolo. During the eruption event and in the following days, the plume reached distances of more than 300 km from the emission point (Malta Island) (Fig. 8).

The concentrations of fluoride over time, in both the study areas are shown in Fig. 9. In the Priolo area a strong fluoride enrichment is clearly observable in the rain collected after the Christmas's eruption (F^- ranging from 0.4 to 0.8 mg/L), and to a lesser extent in the samples of July 2018 and July 2019 at the Siracusa sampling sites (ARP and SIR). These fluoride values sharply contrast with the median of the whole period in this area ($\sim 0.03 \text{ mg L}^{-1}$). The same enrichment is not visible in the samples from the Milazzo area that shows a median value of 0.04 mg L^{-1} , and only some slightly higher value (from 0.1 to 0.2 mg L^{-1}). Several anthropogenic sources may be a significant source of fluorine to the atmosphere. The most important industrial processes that release gaseous fluorine compounds are: aluminium smelting, coal burning, phosphate fertiliser and cement production, and brick and ceramic firing (WEINSTEIN & DAVISON, 2003). There are only few local possible anthropogenic fluorine sources. In the area of Milazzo there is widespread brick production that could explain the slightly higher median value. In the area of Priolo there is a cement factory between 8 and 10 km to the closest sampling sites (AUG, MEL and PRI). But these sites never showed F^- concentrations higher than 0.2 mg L^{-1} except immediately after the Mt. Etna eruption. Apart from small anthropogenic contamination from local sources and from the European background of industrial emissions (PREUNKERT *et alii*, 2001), higher values in the Central Mediterranean area are probably always connected to volcanic activity. The Etnean emissions may, therefore, also explain the higher than average F^- concentrations found in some of the samples collected in August 2018 and in July 2019 in the area of Priolo. The satellite images from OMI Volcanic SO_2 Image Archive by NASA (<https://so2.gsfc.nasa.gov/index.html>) show in those periods enhanced SO_2 emissions with the plume directed towards the south (Fig. 10). Furthermore, contemporaneous ash emissions have been described in the reports about the Etnean volcanic activity issued by the Istituto Nazionale di Geofisica e Vulcanologia (<http://www.ct.ingv.it/index.php/monitoraggio-e-sorveglianza/prodotti-del-monitoraggio/>

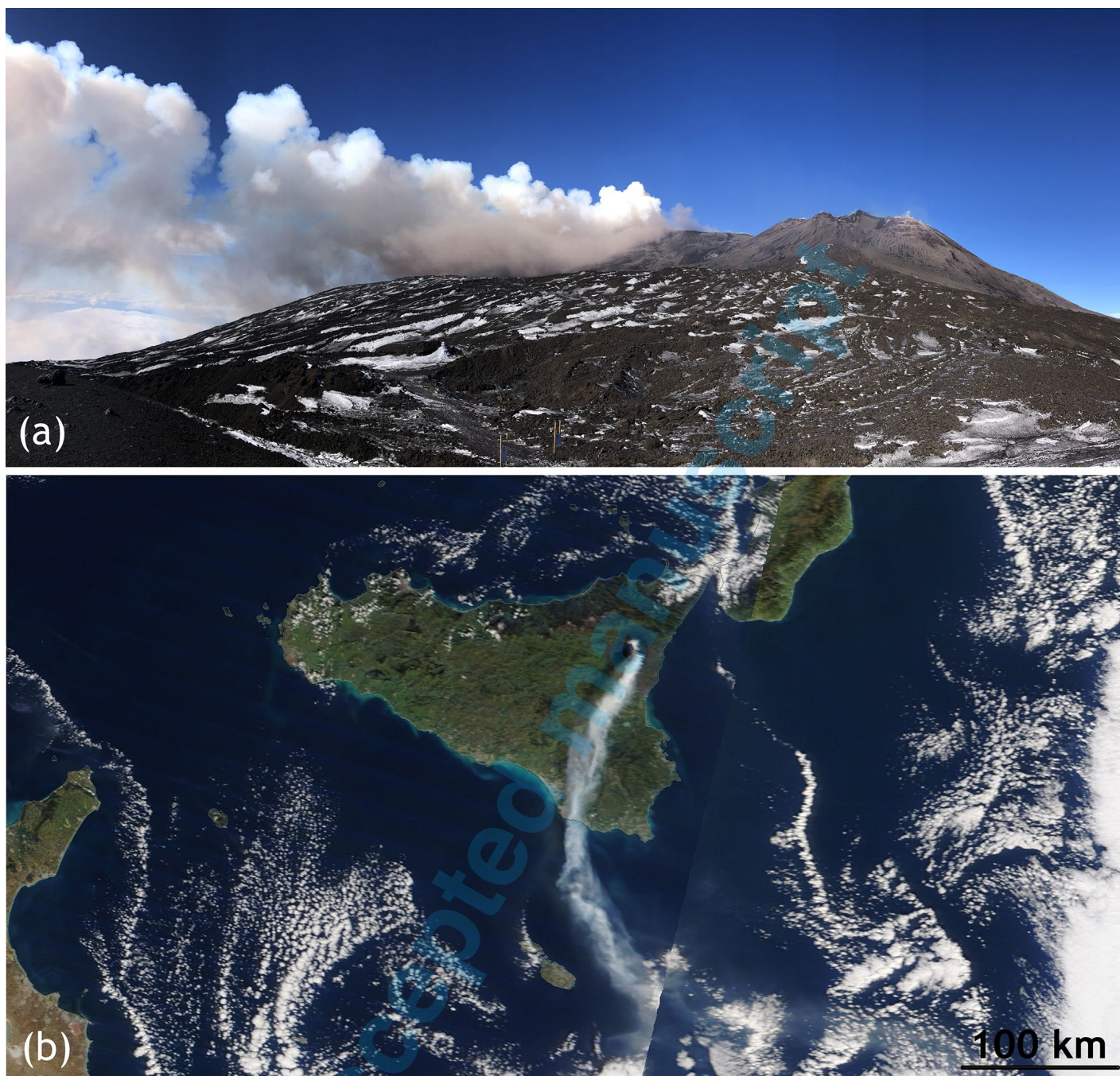


Fig. 8 - Photo of Mt. Etna craters during the eruptive event – Ph. Sergio Calabrese (a) and satellite image of Sicily taken by MODIS (Moderate Resolution imaging Spectroradiometer), on the 27th of December 2018 (b). The plume of Etna going to south and reaching the island of Malta is clearly visible.

bollettini-settimanali-multidisciplinari). Although both gas and ash emissions were quantitatively lower with respect to the Christmas eruption, as clearly visible in Fig. 10, nevertheless they may be responsible of the observed anomalous F⁻ values.

The bulk deposition samples collected after the eruption show a relative enrichment in fluoride and sulphate with respect to the F⁻/Cl⁻ (7×10^{-5}) and SO₄²⁻/Cl⁻ (0.14) weight ratios in the seawater. Fluoride and sulphate are among the ions showing the most remarkable volcanogenic contribution in rainwater close to active volcanoes (AIUPPA *et alii*,

2001, AIUPPA *et alii*, 2006; BELLOMO *et alii*, 2003, CALABRESE *et alii*, 2011). In order to evaluate if F⁻/Cl⁻ and SO₄²⁻/Cl⁻ characteristic ratios in bulk deposition are consistent with the plume signatures, the ratios typical of Etna's plume were plotted (Fig. 11). In the plots, F⁻/Cl⁻ and SO₄²⁻/Cl⁻ ratios in the bulk deposition samples fall between the ratios of seawater and the ratios of Etna's plume, suggesting a volcanic contribution in the composition of the collected rainwaters at least for fluoride.

Although chloride has a volcanic origin, it is difficult to discriminate the volcanic contribution from that of

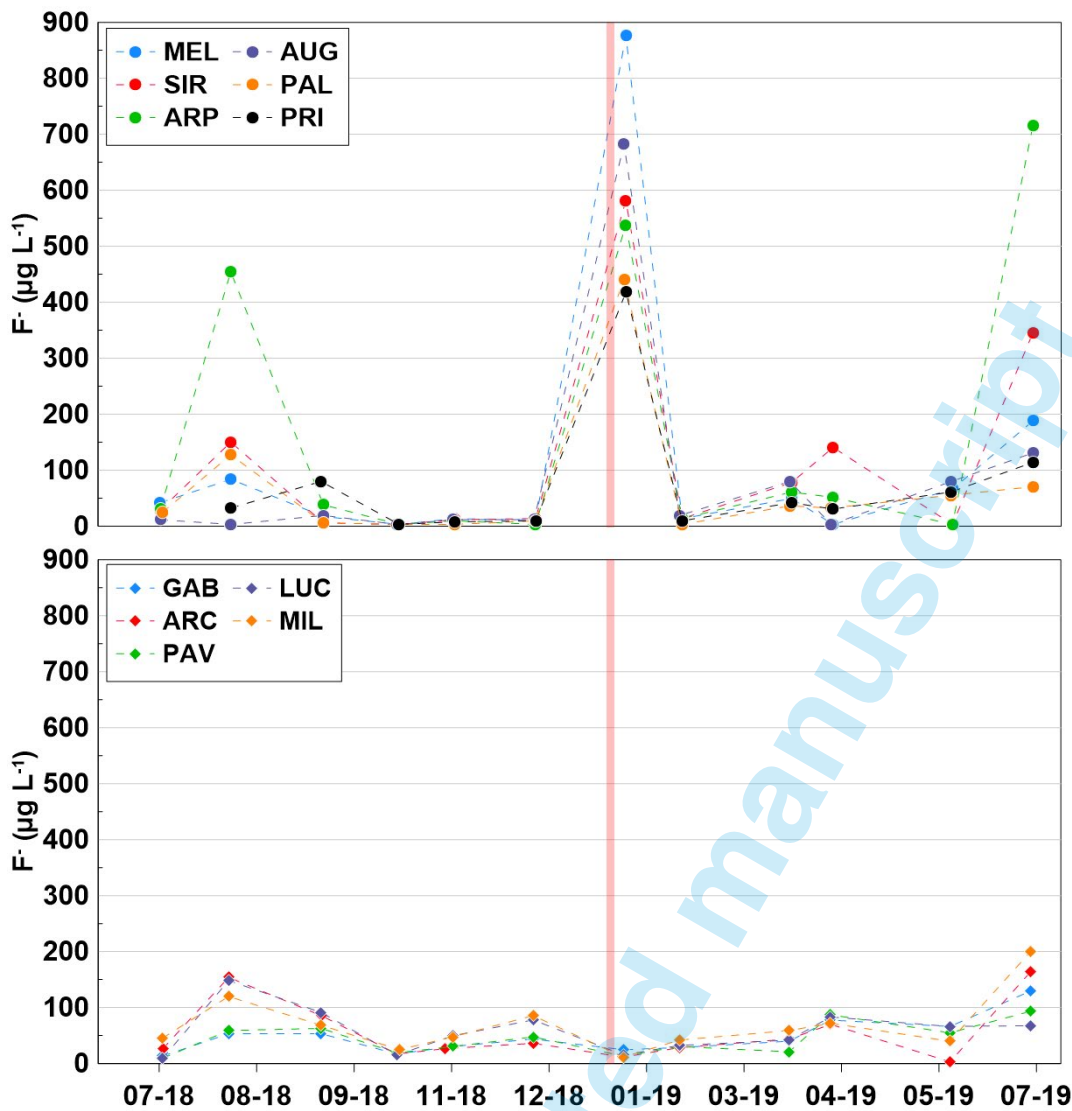


Fig. 9 - Temporal variations of F^- ($\mu g L^{-1}$) concentrations in the samples collected both in the area of Priolo and Milazzo. The red line represents the Christmas's eruption of Mt. Etna.

seawater, which is the main source of this ion in areas located close to the coast. The rainwater samples of the Priolo study area, affected by the Christmas's Etna eruption, have an average percentage of nss-chloride of about 15%, which is higher than the average calculated for all the remaining bulk deposition samples of the same area (5%). This possibly evidences a volcanic contribution but not as significant as for fluoride. Sulfate is another ion that may derive from SO_2 , one of the major components of volcanic plume gases. As seen before, the non-marine component of SO_4^{2-} is always prevailing in all collected samples. This is due to the presence of a large anthropogenic component for SO_4^{2-} . The samples collected immediately after the eruption do not show an anomalously high SO_4^{2-}/Cl^- ratio and fall between seawater and Etna's plume (Fig. 11b). Many samples show much higher ratios reaching the values of the latter ratio. This is due to the fact that anthropogenic sources show SO_4^{2-}/Cl^- ratios much higher than the volcanic one. On the basis of the chemical composition it is difficult to discriminate between different non-marine sources (anthropogenic or volcanic). The effect of the described eruption is also shown by the high concentrations of some trace elements. The strong compositional differences

between the sample collected after the eruption and the periods before and after can be recognised in Al, Cd, Tl and Te. The mean concentrations of these elements in the samples collected in the area of Priolo, excluding the sample collected just after the Christmas's eruption, are: $24.0 \mu g L^{-1}$ for Al, $0.016 \mu g L^{-1}$ for Cd, $0.010 \mu g L^{-1}$ for Tl, while Te was always below $0.0026 \mu g L^{-1}$. The mean concentrations of the same elements in the samples collected immediately after the eruptive event are: $74.9 \mu g L^{-1}$ for Al (maximum $152 \mu g L^{-1}$), $0.086 \mu g L^{-1}$ for Cd (maximum $0.141 \mu g L^{-1}$), $0.120 \mu g L^{-1}$ for Tl (maximum $0.164 \mu g L^{-1}$), and $0.014 \mu g L^{-1}$ for Te (maximum $0.025 \mu g L^{-1}$), therefore showing a strong enrichment, of even an order of magnitude (Fig. 12).

While Cd, Tl and Te are highly volatile elements typically enriched in volcanic emissions, Al is a refractory element that was probably released by the dissolution of the related volcanic ashes. This probably depends on the low solubility of the element. It is worth noting that the highest concentrations are found in the samples with the lowest pH favouring Al dissolution.

The study area of Milazzo, due to the prevailing winds from the North direction during the period of the Christmas's eruption, has not been affected by the plume

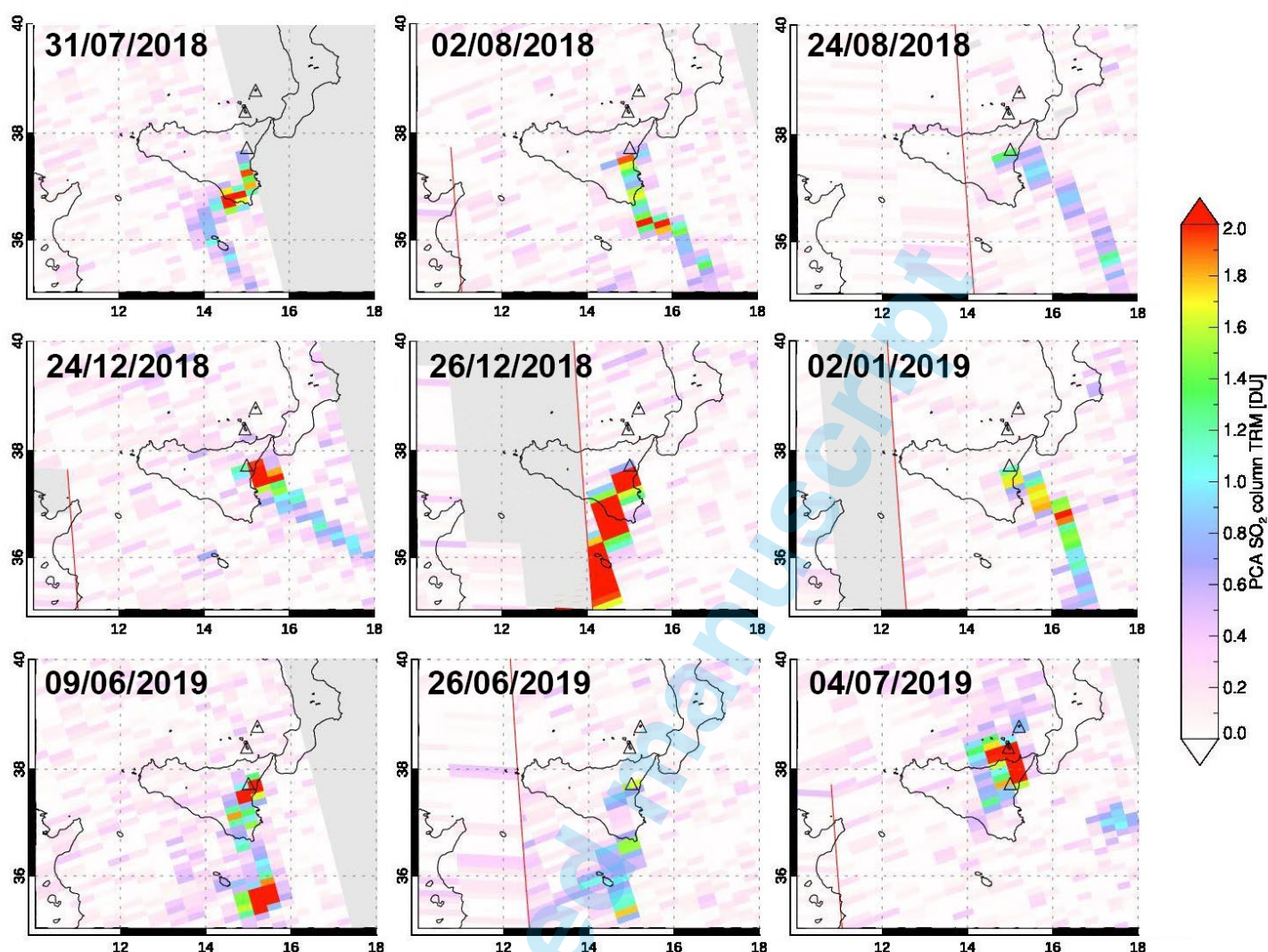


Fig. 10 - SO₂ emissions (expressed in Dobson Unit of the column) from Mt. Etna ad Aeolian Islands, relative to three different sampling periods in which bulk deposition samples were affected by the volcanic emissions. Sketches are from OMI Volcanic SO₂ Image Archive by NASA.

and therefore the signature of the eruption is not visible in the samples collected in that area, as shown by the mean values of the selected trace elements: 22 $\mu\text{g L}^{-1}$, 0.021 $\mu\text{g L}^{-1}$, 0.021 $\mu\text{g L}^{-1}$ and <0.012 $\mu\text{g L}^{-1}$ for Al, Cd, Tl and Te respectively.

A good correlation between F concentrations and Te, Tl, and Cd concentrations of the samples of Priolo area can be observed in plots in Fig. 13. Samples with a high F concentration also show a high concentration of the trace elements taken as a reference of the signature of the volcanic activity of Mt. Etna in bulk deposition samples. The samples in red are those related to the sampling carried out immediately after the Christmas's eruption.

CONCLUSION

The bulk deposition of the two areas around major industrial plants of Eastern Sicily show the imprint of three main sources. The most obvious is seawater due to the

closeness of the areas to the coast. Sea-derived CCN and/or direct sea-spray deposition strongly contribute to the chemical composition of the precipitation, as suggested by high load of Na⁺ and Cl⁻ in all the samples and by the high positive correlation along the Na⁺/Cl⁻ ratio of the seawater.

Another source is represented by anthropogenic activities causing high concentrations of NO₃⁻ and nssSO₄²⁻. The third one is typical of the Mediterranean area and consists of geogenic dust both of local (mainly limestones outcrops) and of regional origin (Saharan dust). The third source is responsible for the high nssCa²⁺ concentrations and for the extensive neutralization of the rainwater whose pH values are mostly above 5.65 (81%) and up to 8.3.

One more source can be identified with volcanic emissions, and the Etna eruption of the 24-30 December 2018 offered a good opportunity to collect rain samples strongly affected by volcanogenic elements. The chemical composition of the bulk deposition collected in the Priolo area, located between 60 and 80 km downwind from the volcanic source showed significant enrichments of several

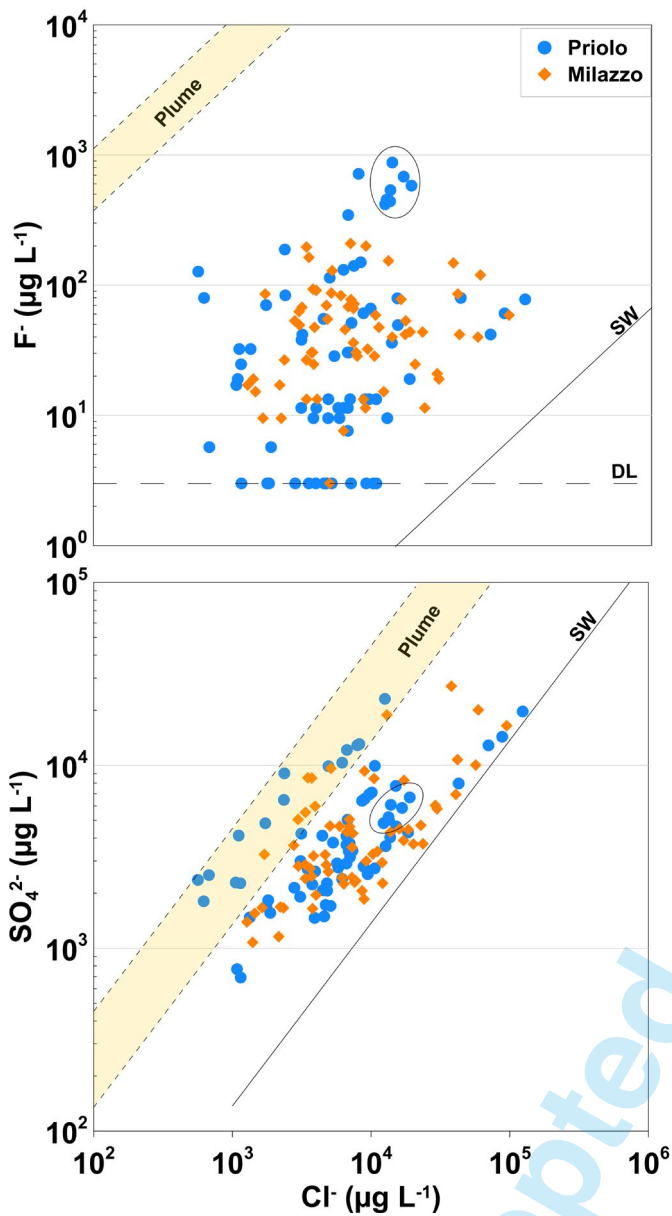


Fig. 11 - Binary plots of F^- and SO_4^{2-} ($\mu g L^{-1}$) vs. Cl^- ($\mu g L^{-1}$) concentrations in rainwater. Sea water ratios and Etna's plume ratios (Aiuppa *et alii*, 2005) are also plotted. The circle evidences the samples collected immediately after the 24th December 2018 eruption. SW = seawater ratio; plume = range of the Mt. Etna emissions; DL = detection limit.

volcanogenic elements. These samples were characterized by high concentrations of fluoride deriving from HF, a gas typically abundant in volcanic emissions. The effect of the eruption on the atmospheric deposition was also recognised in the high concentrations of some trace elements, such as Al, As, Cd, Tl and Te. The results of this study showed that volcanic eruptions might have relevant effect on the composition of rainwater even at great distances from the point of origin.

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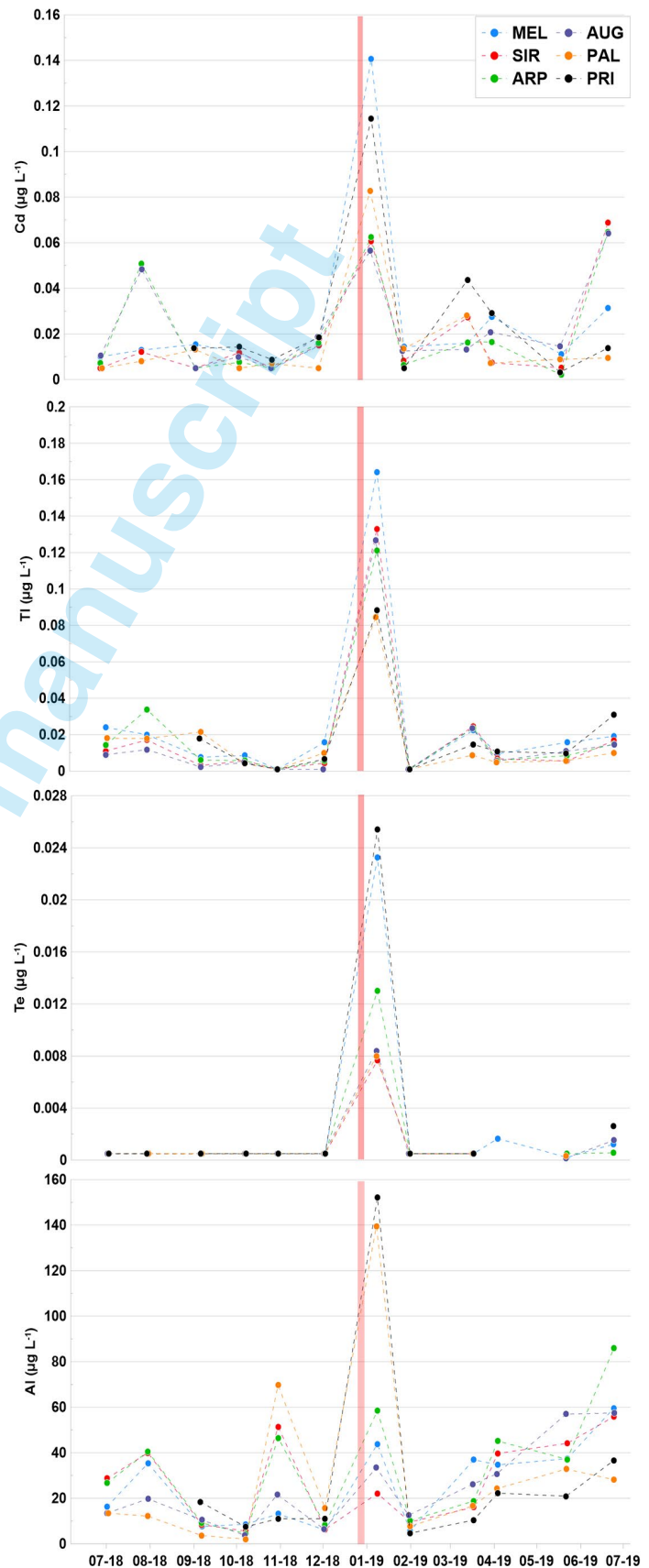


Fig. 12 - Temporal variations of Cd ($\mu g L^{-1}$), Tl ($\mu g L^{-1}$), Te ($\mu g L^{-1}$) and Al ($\mu g L^{-1}$) in the samples collected in the study area of Priolo. Red line corresponds to the Mt. Etna eruptive event.

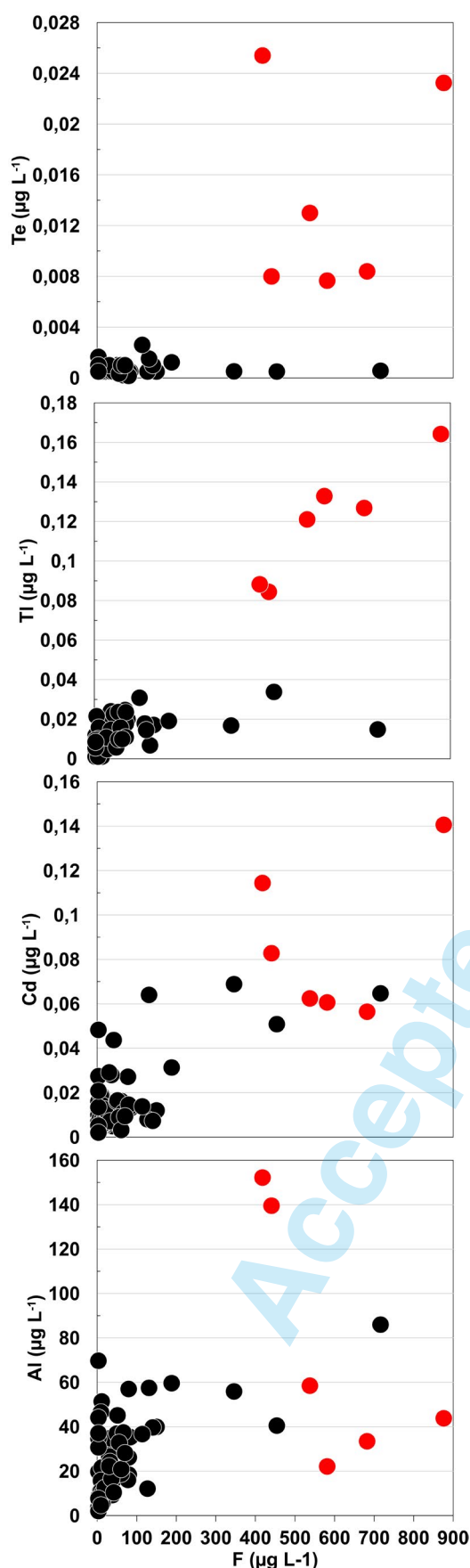


Fig. 13 - Binary plots of F vs. Te, Tl, Cd and Al. Red circles are relative to the samples collected just after the Christmas's eruption of Mt. Etna.

Gianni Attard (Protezione Civile Priolo), Giuseppe Maimone, Emilio Sofia, Alebrando Fortunato, Palma Rosa Legrottaglio (I.C. Secondo Milazzo - Luigi Rizzo, Milazzo), Don Palmiro Prisutto (Augusta) and Sebastiano Gianfriddo. The paper was substantially improved following constructive and insightful reviews from Franco Tassi and one anonymous reviewer, to whom we are very grateful. This work was supported by the project: "Centro Internazionale di Studi Avanzati su Ambiente, ecosistema e Salute umana - CISAS", funded by CIPE-MIUR- CUP B62F15001070005.

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