

Geochemical comparison of natural and anthropogenic metal fluxes in extreme environments: Mt. Etna volcano (Italy) and Šalek Valley (Slovenia)

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Abstract: Geochemical comparison between some metals (As, Cd, Cu, Pb, Se, V, Zn) emissions from an active volcano (Mt. Etna) and a highly industrialized area (Šalek Valley) showed some interesting similarities: in general, most of the elements emitted into the atmosphere do not return to the Earth's surface and are therefore dispersed into the environment. Exceptions for Šalek Valley are Cd, which probably derives in large part from rock leaching, and in part As and Pb, which fall mostly as ash. Also, Etna's emissions are richer in Cd and Cu, whereas industrial emissions at Šalek Valley are richer in V and Zn. All other metals have similar fluxes in the two types of emissions.

Key words: Trace metals, Mt. Etna, Šalek Valley, metals budget, pollution

Introduction

There are a variety of natural and anthropogenic sources of trace elements into the environment. Both of them are well defined, yet they are difficult to determine and the many estimates of Trace Metals (TMs) budgets have large uncertainties.

The present study focuses on the comparison between two "extreme" environments, Mt. Etna volcano (Italy) and Šalek Valley (Slovenia), that are well representative of a natural and an anthropogenic source of TMs, respectively.

Active volcanoes release significant amounts of metals into the atmosphere, groundwater and the soil by direct input of magmatic fluids. Among volcanoes, Mt. Etna is certainly one of the most important as a natural source of TMs. Etna is the largest strato-volcano in Europe and one of the most active in the world. Mt. Etna is also a densely populated area, with roughly 900,000 people living on its lower slopes (Chester et al., 1995). Etna's activity is characterized by the persistent emission of a huge volcanic plume from its summit craters during both quiescent and eruptive magma degassing (Allard et al., 1991; D'Alessandro et al., 1997). Based on remote sensing measurements, the time-averaged SO₂ emission rate over the last two decades was found to be about 2 Mt/a (Allard, 1997), corresponding to about 10% of the annual global volcanic emissions (Stoiber et al., 1987). Based on the average C/S plume molar ratio, the above SO₂ degassing yields a mean CO₂ output of ~4 to 7 Mt/a from the volcano conduits (Allard et al., 1997). These figures indicate that this volcano alone emits between 5 and 15 % of the estimated global volcanic emissions of carbon dioxide (Gerlach, 1991),

being it one of the greatest emitters of volcanic volatiles on Earth. Fluxes of metals in Mt. Etna summit crater plume range from about 36 kt/a for major species (e.g., K, Na, Al) to 10^{-2} t/a for ultra-trace elements (Buat-Menard and Arnold, 1978; Andres et al., 1993; Gauthier and Le Cloarec, 1998; Aiuppa et al., 2003; Calabrese, 2009), thus indicating that Mt. Etna is one largest volcanic emitter of several metals and trace elements.

Šalek Valley (Fig. 2) is a strongly industrialized area where large amounts of pollutants are released into the environment. Air motion inside the valley normally impedes local accumulation of pollutants in the atmosphere, so most of the industrial emissions, in terms both of gases and of particulates, are carried to nearby areas. Today, ŠV includes three small communities: Velenje (83 km²), Šoštanj (96 km²) and Šmartno by Paka (18 km²) (Pavšek et al., 2000).

The main industrial activity in the ŠV is based on lignite mining and power production. Almost all of lignite mined has been used to produce electricity in the near thermal power plant at Šoštanj (ŠTPP). Burning of lignite to produce electrical power was the leading cause for the environmental pollution of the valley, particularly from the 1960's to the early 1990's. The ŠTPP is actually the biggest air pollutant in Slovenia. From 1991 until 1994 it contributed 99% of the air pollution in the Šalek Valley according to the Register of Pollutants (Ramšak, 1991; Stropnik et al, 1994). The average European SO₂ emission value is 57 kg/a per capita, whereas in 1990 SO₂ emissions in Slovenia were almost twice as much (101 kg/a per capita) and Slovenia ranked 5th in Europe as the highest industrial SO₂ emitter (Sevšek and Jurač, 2006). Apart from SO₂, also NO_x and CO₂ emissions are very high and cause a serious additional problem to environmental hazard.

Results for Mt. Etna

The dominant gaseous species in volcanic plume are Cl, S, and F (from in-tandem filter-pack measurements with base-treated filters), whereas the most abundant metals (in particles) are K, Ca, Mg, Al, Fe, and Ti (1.5 - 50 µg/m³), which are some of the main constituents of basaltic rocks and magmas. Minor and trace element concentrations in volcanic aerosols range from about 0.01 to 1 µg/m³, and can be divided into volatile (e.g. Se, Cd, Tl, Sb) and non-volatile (e.g. U, Th, La, Rb, Ba) elements. In order to estimate the metal fluxes, the metal/sulphur ratios (ranging from 10^{-2} to 10^{-8} , depending on the element) obtained from the summit craters were calculated, and then related to the total sulphur fluxes daily measured by the INGV of Catania using remote sensing techniques. The average fluxes for selected metals during the study period are shown in Tab. 1. These measurements are representative of the quiescent degassing from Mt. Etna and do not account for the contribution from eruptive degassing.

The chemical composition of rainwater from the down-wind sites (TDF, CIT, CDV, and ZAF) exhibits a significant enrichment in all elements analyzed, compared to the up-wind site (INT). The enrichment is most evident for elements like Cu, As, Se and Cd. The rainwater samples with the highest element concentrations were collected at TDF, the closest site to the summit craters. Samples from INT have the lowest element concentrations in the dataset, and the mean values for this site were here considered as representative of the local background. In the attempt to discriminate the contribution of the volcanogenic input, the deposition on the downwind sector has also been calculated by subtracting the values measured at the background site (INT).

Comparison with the whole plume emission values evidences that only a very small percentage of the emitted elements is deposited close to the volcano. As evident from Tab. 1, more than 90% of volcanogenic trace metals are dispersed at regional and/or global scale.

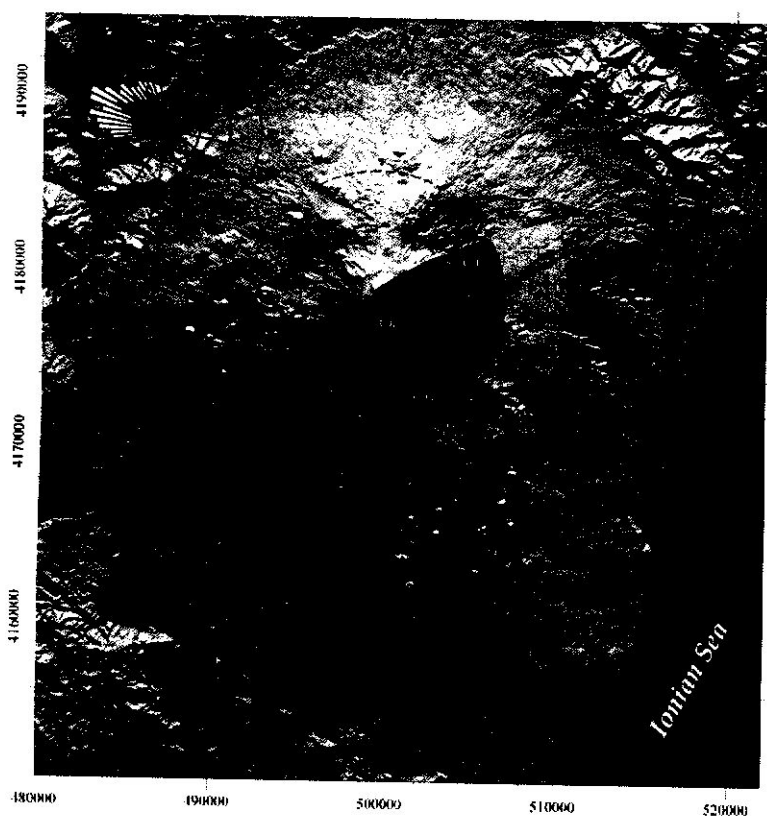


Fig. 1: Map of Mount Etna and location of the sampling sites of bulk deposition (blue triangles): Torre del Filosofo (TDF), Citelli (CIT), Casa del Vescovo (CDV), and Zafferana (ZAF) are the down-wind sites; Intraleo (INT) is the up-wind site. The wind rose highlights the prevailing wind directions, referring to the altitude of the summit for the period 2006-2007 (data from Birgi station)

Tab. 1: Volcanic emissions of selected TMs from Mt. Etna, total deposition on the whole Etna area and percentage of scavenged elements from the volcanic plume (minimum and maximum values are relative to upper and lower estimates)

	Volcanic emissions	Volcanogenic deposition on the whole Etna area (upper estimate)	Volcanogenic deposition on the whole Etna area (lower estimate)	Amount of elements scavenged from the Plume		
	(t/a)	(t/a)	(t/a)	(%)		
As	31	0.3	0.1	0.3	-	0.9
Cd	12.8	0.1	0.1	0.5	-	0.7
Cu	240	2.5	1.5	0.6	-	1
Pb	31	0.3	0.2	0.6	-	0.9
Se	18.9	0.4	0.1	0.8	-	2.2
V	12	1.4	0.4	3	-	12
Zn	90	10	2.9	3.2	-	11

Results for Šalek Valley

Several different types of samples were collected to determine the emissions of pollutants in this area: precipitation, ash, surface and ground water. Attention focused on some metals (As, Cd, Cu, Pb, Se, V and Zn) that are among those with a high impact on the environment as well as on human health.

The results were compared with those from the gas and particulate emissions released from the ŠTPP (Tab. 2). The net balance between sources (coal burning and industrial emissions) and sinks (ash fall, precipitation, surface water runoff and ground water outflow) of these elements shows that only a negligible part of Cu, Se, V and Zn returns to the surface in the Valley, whereas a large portion of As and Pb returns and Cd is even in excess in the surface or sub-surface environment, thus pointing to input of this element from natural sources, such as rock leaching or transboundary air transport from nearby areas.

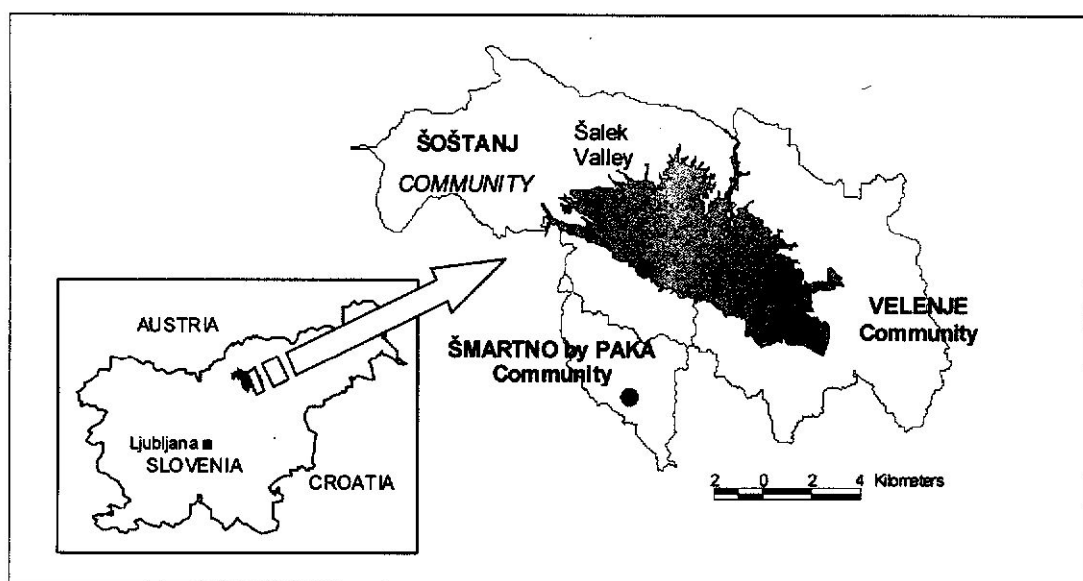


Fig. 2: Location of Šalek Valley

Tab. 2: Fluxes and net balance for some trace metals in the Šalek Valley. Net balance is the difference between sources (Coal + TEŠ) and sinks (Ash + Precipitation + surface runoff + ground water outflow) of metals

	Coal ¹	Industrial emissions (TEŠ) ²	Ash ³	Precipitation ^{4,5}	Surface water runoff ⁶	Ground water outflow ⁷	Net balance
	(t/a)	(t/a)	(t/a)	(t/a)	(t/a)	(t/a)	(t/a)
As	34.8	0.87	20.7	$1.1 \cdot 10^{-5}$	0.1	0.15	14.82
Cd	0.86	0.434	1.7	$5 \cdot 10^{-6}$	0.1	0.26	-0.67
Cu	53.4	6.1	n.d.	$4.7 \cdot 10^{-5}$	1.5	0.56	58.94
Pb	70.4	4.34	59.3	$3.4 \cdot 10^{-5}$	0.2	0.77	14.67
Se	12.2	3.5	0.62	$8 \cdot 10^{-6}$	0.1	n.d.	15.08
V	220	4.34	n.d.	$1.5 \cdot 10^{-5}$	0.4	0.09	224.25
Zn	470	6.5	n.d.	10	2.9	123.8	352.7

¹ Rožič, 2002; ² Pacyna and Pacyna, 2001; ³ Stropnik et al., 1994; ⁴ Druks and Svetina, 2002; ⁵ Svetina et al., 1996; ⁶ Svetina et al., 1993; ⁷ Giammanco et al., 2008

Conclusions

Mt. Etna is an important natural source of trace metals at the regional and in some cases at the global scale, as only a small percentage of the emitted volcanogenic elements returns to the Earth's surface close to the volcano (0.1-1% for volatile elements, and 0.5-10% for refractory elements).

Etna's emissions are about two or three orders of magnitude higher than the local anthropogenic emissions for several elements (e.g. Zn, Cu, Se, Hg, Cd, Ni, Cr). However, when comparing some metal emissions (As, Cd, Cu, Pb, Se, V, Zn) from Mt. Etna with the anthropogenic ones from a highly industrialized area such as Šalek Valley, we observe that the input of As, Pb, Se to the environment is similar, input of Cd and Cu is greater at Mt. Etna, but input of V and Zn is greater at Šalek Valley. As for Mt. Etna, also in Šalek Valley most of the selected elements do not return in large amounts to the surface, except for Cd and in part As and Pb, all of which falling mostly as ash.

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