Speciation of vanadium in urban, industrial and volcanic soils by a modified Tessier method

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Complete List of Authors:	Orecchio, Santino; University of Palermo, Chemistry Amorello, Diana; University of Palermo Barreca, Salvatore; ARPA Lombardia

UNIVERSITÀ DEGLI STUDI DI PALERMO
DIPARTIMENTO DI SCIENZE E TECNOLOGIE BIOLOGICHE CHIMICHE E FARMACEUTICHE (STEBICEF)

In the paper we report a fractionation study of vanadium in industrial, urban and volcanic area. Also, an attempt is made to estimate the contribution of natural (volcanic) and anthropogenic sources to metal contents in soils from three different types of areas and in particular of the most active volcanic area in Europe: Etna.

The determination of V the solutions obtained by sequential fractionation of soils is not easy: the low concentrations and the presence of interfering substances are the main analytical complications. In particular, high resolution ICP-MS has been applied to the determination of V in various matrices but the quantification of V in soil samples by quadrupole ICP-MS suffers from background problems. One of the innovations of our extraction method consists of the possibility to estimate the concentration of vanadium in the extract solutions of the different steps using voltammetry. The technique is very sensible and accurate. The voltammetric analysis requires few minutes and is inexpensive.

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Speciation of vanadium in urban, industrial and volcanic soils by a modified Tessier method

Santino Orecchio[a*], Diana Amorello[a], Salvatore Barreca[b]

Abstract

Vanadium (V) concentrations in industrial, urban and volcanic soils were sequentially extracted using a modified Tessier's method. The voltammetric technique was used to determine V concentrations in solutions obtained from the various extraction steps. At the reference stations, the V concentrations (sum of four individual fractions) in soils ranged from 0.72 to 0.24 g kg-1 dry weight (d.w.) with a mean value of 0.18 g kg-1 d.w. V concentrations in soils of the Palermo urban area ranged from 0.34 to 2.1 g kg-1 d.w., in the Milazzo (industrial) area between 0.26 and 5.4 g kg-1 d.w. and in the volcanic area near Mt. Etna from 0.91 to 2.9 g kg-1 d.w. When the V concentrations around Mt. Etna were compared with those obtained at the reference stations, it was confirmed that Mt. Etna is a continuous source of V. In all the samples analyzed, the majority of the V (from 94 to 100%) was detected in the fourth fraction.

Introduction

Vanadium (V) is a widely distributed element in the earth's crust and it is present in fossil fuels, especially in petroleum. Total concentrations of V in soil range from trace levels to 400 mg kg^{-1}, with an average of 150 mg kg^{-1} [1]. Natural sources of atmospheric V include continental dust, marine aerosol and volcanic emissions. The masses incoming the atmosphere from each of these sources are unsure. However, continental dust is believed to account for the largest fraction of naturally emitted atmospheric vanadium followed by marine aerosols. Volcanic emissions are negligible if compared with the other two sources [2]. Most anthropogenic V in environmental matrices originates from the use of fossil fuels. During combustion, volatile ashes containing V are deposited in surrounding or faraway areas, where they interact with environmental matrices. Particulate matter is transported by winds and sinks to the ground. Rainwater leaches the ground and transfers soluble compounds into rivers and ground waters.

In general, to understand the toxicological risks associated with an environmental matrix, it is necessary to characterize the fractionation, solubility and bioavailability of compounds present in that matrix [3-5]. A method widely used to assess the bioavailability of metals in soil is the leaching of soil by chemical extractants[6]. Accordingly, single and sequential extraction procedures have been widely applied using several reagents. In particular, sequential extraction procedures provide detailed information on distribution in different association forms, evaluating the mobility and potentially bioavailable metal fractions in contaminated soils[7]. The uptake of vanadium in aquatic plants and animals is reasonably well documented; concentrations of vanadium present in different terrestrial plants have been established by Byerrum[8], while levels present in animals have been established for several species[9].

Polluted soils are an important source of V to aquatic environments [10] and the amount of metal that can be transferred to the water is related to the stability and solubility of several possible V species formed with the soil components (carbonates, oxides, sulfides, organic compounds, etc.). This means that knowledge of the total V concentration in polluted soils is important but not sufficient to evaluate the environmental risks and the toxicological consequences of V pollution if these data are not supported by information on the chemical species present. The amounts of different V species in soils depends on the physical and chemical properties of the substrate, such as the pH, organic and inorganic content, redox potential and other factors. For example, under anaerobic conditions, most V compounds are transformed into VO^{2+}, one of the more soluble, and hence more hazardous, V species in water.

The partitioning of vanadium in groundwater and soil is influenced mainly by pH, redox potential and the presence of particulate. The vanadium oxidation states vary between −1 and +5 [11-13]. Most minerals of vanadium are V(V) compounds[1] . In solution, vanadium generally exists as the vanadyl ion (V^{4+}) in reducing conditions, the vanadate ion (V^{5+}) in oxidizing conditions or adsorbed onto particulate matter[14] . The formulas of the vanadyl species most commonly reported in water are VO_2^+ and $VO(OH)^+$ and the vanadate species are H_2VO_4 and HVO_4^{2-} [14] .

In this paper, we report on the fractionation of V in soils from industrial, urban and volcanic areas. The V fractionation used a modified Tessier's sequential extraction method [15] , which allowed us to recognize metals in four different fractions: a) exchangeable V; b) V bound to carbonates; c) V bound to iron and manganese oxides and hydroxides; and d) V bound to the soil organic fraction and/or sulfides.

The extracted vanadium forms are related to the reagents used and may be different from the forms that exist in the solid phase [16,17].

Several analytical techniques are available for determining total element contents in environmental matrices. These are mainly spectrophotometric methods such as inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ET AAS) [1,4, 18-21]. However, the determination of V in the solutions obtained by sequential fractionation of soils is not easy. Specifically, low V concentrations and the presence of interfering substances are the main analytical complications [20]. High resolution ICP-MS has been applied to the determination of V in several matrices [20] but unfortunately, the quantification of V in soil samples by quadrupole ICP-MS is affected by background

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[a] *Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche, Università degli Studi di Palermo, Viale delle Scienze, I-90128, Palermo, Italy.*
[b] *ARPA Lombardia, Milano, Italy Address here.*

problems. The possible interfering species in ICP-MS analysis of soil V were $_{35}Cl_{16}O$, $_{38}Ar_{12}CH$ and $_{34}S_{16}OH$. Several undesirable polyatomic ions in the background mass spectra could also be obtained during ICP analysis if dissolution requires HF, HCl or H_2SO_4. The main innovation of this paper was the estimation of V concentrations in each extraction solution using voltammetry.

Metals in the environment can be associated with emissions from domestic heating and automotive traffic as well as industrial sources and the contribution from each of these sources need to be differentiated.

Experimental

2. Materials and methods

2.1. Reagents and standards

All reagents were of analytical reagent grade. The solutions were prepared using ultra-pure Milli-Q water. The calibration standards of V were prepared by making appropriate dilutions of a concentrated V solution (1000 ± 1 μg mL^{-1} in 5% HNO_3 (v/v)) of ammonium metavanadate (99.9%). Blank calibration solutions were also used as a zero calibration for each fraction. All diluted standard solutions containing V were stabilized by adding HNO_3. The analysis using voltammetry requires about 5 min. The quality of the results and applicability of the method to real samples were checked by analyzing a blank solution of each fraction spiked with a known amount of determinant and several soil samples collected from reference sites spiked with known amounts of the analyte. All chemicals used for the extraction procedure were purified by re-crystallization or by treatment with Chelex 100 resin (Sigma Aldrich, Milano, Italy). To prevent contamination of tools, instruments and other materials, only clean glassware and high purity reactants were used. To avoid contamination of the solutions, different glassware was used for standard and sample solutions.

2.2. Site and sampling stations

Twenty-three soil samples were collected in Sicily (Fig. 1) in areas characterized by different natural and anthropogenic V sources. Three of the sampling sites (Ce21, M10 and M12) were chosen as reference sites to avoid anthropogenic sources of V, because they were located far from industrialized, urbanized or cultivated areas. Four soil samples (PA17–PA20) were collected in the Palermo urban area (Fig. 1a) to characterize urban pollution; thirteen soil samples (M2–M16) were collected in the Milazzo area (Fig. 1b) to characterize heavy metal pollution from several industrial activities; and six samples (Ct22–Ct27) were collected in the Mt. Etna area (Fig. 1c) to characterize V associated with volcanic activity.

Palermo is a heavily populated city (about 850,000 inhabitants) with a heavy load of vehicular traffic and major craft activities within the city area. It is characterized by conspicuous air pollution [22-24] . The town is situated on the north-western coast of the island (Fig. 1a) along the wide bay Piana di Palermo and is overlooked by Mt. Pellegrino (600 m above sea level). It is delimited on the NE by the Tyrrhenian Sea and it is surrounded by mountains 500–1000 m above sea level.

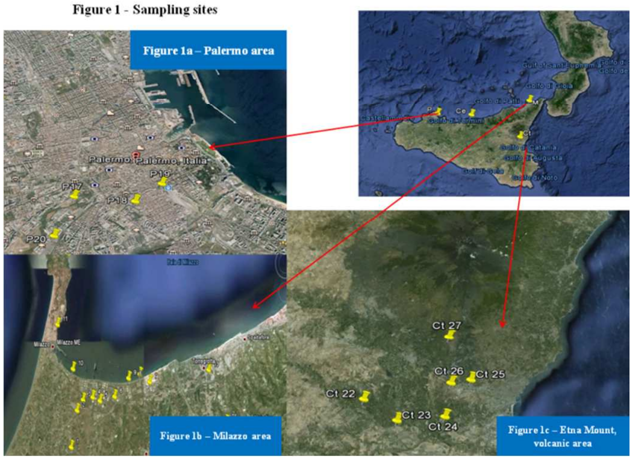
The area of Milazzo is placed along the North Mediterranean coast of Sicily (Fig. 1b). The economy of Milazzo relies mainly on a petrochemical complex, a power plant, several mechanical industries and agricultural activities. The oil refinery covers an area of about 200 ha. The refinery can handle a wide range of crudes and produces a wide variety of petroleum products.

Mt. Etna (Fig. 1c) is one of the most active volcanoes in the world and, during the last 5000 y, has been continuously active and has erupted volcanic products essentially composed of lavas and gaseous materials. It is the highest mountain in Italy south of the Alps and covers an area of 1,190 km^2 with a basal circumference of 140 km.

Soil samples were taken using a plastic trowel at a depth of 0–5 cm. The samples were transferred into polythene bags, transported to the laboratory and were preserved at −20 °C until further processing. At each sampling site, eight samples were collected within a distance of 50–100 cm. In the laboratory, the samples were dried at 105 °C overnight. Twigs and stones were removed. After homogenization, the soil samples were sieved through a 2-mm sieve. Representative samples were obtained after quartering.

The repeatability of the sampling was preliminarily checked by analyzing for total V in four different soil samples collected from different points in the same area (4 m × 4 m). The batch to batch sampling standard deviation (about 7%) was similar to the analytical reproducibility.

Figure 1 - Sampling sites



2.3. Metal sequential extraction procedure

In order to optimize the extraction procedure, previous work [3] paid particular attention to determine the reaction conditions of each extraction step. The following fractions were separated:

Fraction a (exchangeable V): about 2.5 g (dry weight) of < 2-mm sieved soil sample was treated with 40 mL of 1 M sodium acetate solution for 1 h under continuous stirring. The residue was separated from the solution by centrifugation. The supernatant was acidified with 0.5 mL of nitric acid and brought to volume with the extracting solution.

Fraction b (V bound to carbonates): soil from step a was treated with CH_3COONa/CH_3COOH solution at pH ~ 5 and the suspension was stirred for 4 h. A new residue was obtained after centrifugation. The supernatant was acidified with 0.5 mL of nitric acid and brought to volume with the extracting solution.

Fraction c (V bound to Fe and Mn oxides): soil from step b was treated with a solution of 0.04 M $NH_3(OH)Cl$ in 25% CH_3COOH (v/v) under stirring at 96 °C for 6 h, until the free iron-manganese oxides were completely dissolved. The residue was separated from the solution by centrifugation. The supernatant was acidified with 0.5

mL of nitric acid and brought to volume with the extracting solution.

Fraction d (V bound to organic matter and or sulfide.): the residue of step c was mineralized in a microwave digestion unit (Milestone, mod. mls 1200 mega) by adding 6 mL of HNO_3 and 1 mL of 30% H_2O_2. A new residue was obtained after centrifugation and solution removal. To reduce the extraction time, step d of Tessier's original procedure was substituted with the mineralization procedure as described above.

2.4. Quantitative analysis

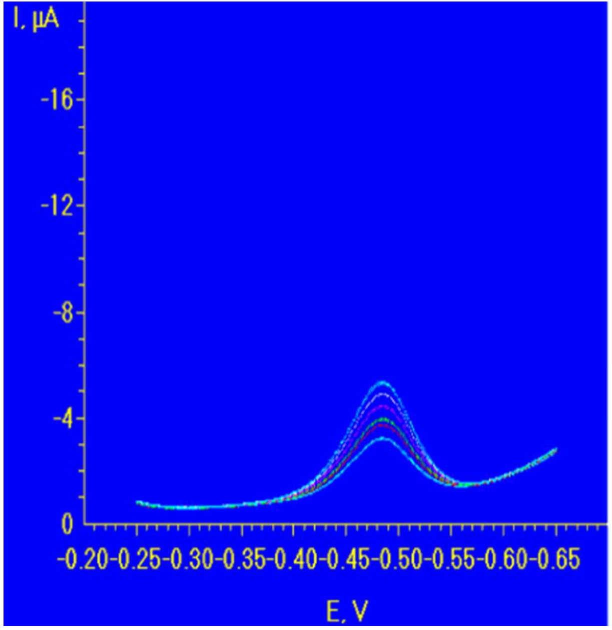
At the end of each extraction step, the resulting solutions were treated with nitric acid in order to transform all the vanadium, whatever may have been the original form in the solution obtained from the extraction, in the pentavalent vanadium. By voltammetry we measure V(V).

The solutions obtained from each stage of the soil extractions were analyzed by adsorptive stripping voltammetry using a Polarograph Model 433 (Amel Srl, Milano, Italy).

Voltammetric curves of solutions obtained from a sample is reported in Figure 2.

Samples were analyzed by standard addition method [25,26], whereby volumes of the metavanadate standard solution were added directly to a known volume of solution obtained by extraction of samples. This method was used because sample matrix and possible interferences could also contribute to the analytical signal, a situation known as the matrix effect, thus making it impossible to compare the analytical signal (in our case current) between sample and standard using the traditional calibration curve approach. Using standard addition method, as in our case, by the intercept (negative) on the calibration curve, the employed mass of soil and the dilutions, we calculate the concentrations of vanadium in the different samples. Under optimal conditions, a very good linear correlation (R = 0.999) (Figure 3) was obtained between the monitored voltammetric peak currents and metal concentrations.

Figure 2 Voltammetric curves for vanadium



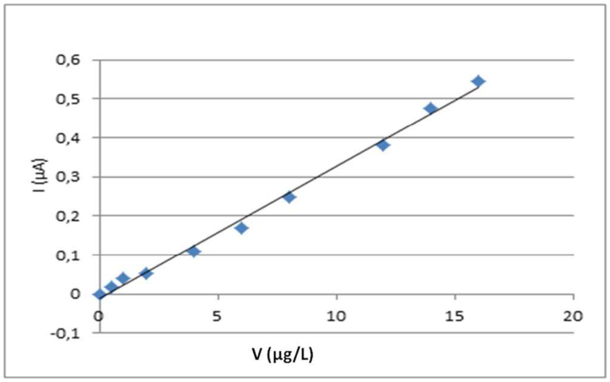


Figure 3 – Calibration curve for vanadium

The instrument parameters are reported in Table 1.

Voltammetric measurements were carried out in a 30 mL glassy electrochemical cell. A three-electrode cell system was completed by means of a hanging mercury drop electrode (HMDE) with a graphite electrode as auxiliary electrode and Ag|AgCl|KCl (sat.) as reference electrode.

V determinations, after dilution, were carried out in aqueous buffered solution ($CH_3COOH–CH_3COONa$ 0.1 M at pH 4.5) (reagent for analysis; Carlo Erba, Milan, Italy) as supporting electrolyte and chloranilic acid (alcoholic solution 0.2%; Carlo Erba). Chloranilic acid forms a complex with V which is absorbed at the mercury drop at −150 mV. Subsequently, a potential scan from −300 to −650 mV in the differential pulse mode was applied to the working electrode, and the current was measured at −0.48 V (versus Ag/AgCl) (Figure 2); the current intensity was proportional to the V concentration.

Quantitative measurements were performed using the standard addition procedure. To minimize the matrix effects, the blanks were prepared with the same matrix derived from the sequential extraction.

The accuracy of the method for each fraction was evaluated by analyzing three replicate simulated solution samples prepared by

Table 1 - Operating parameters for the stripping analysis of the solutions obtained from particulate samples.

Technique	**AdSV**
Initial potential (mV)	-300
Final potential (mV)	-650
Potential scan rate (mV/s)	20
Potential of deposition (mV)	-150
Cycle (n°)	2
Deposition time (s)	100
Stirring rate (r.p.m.)	300
Size of the drop (a.u.)	30
Delay time before potential sweep (s)	5
Working electrode	Hanging mercury drop electrode
Auxiliary electrode	Glassy carbon
Reference electrode	Ag/AgCl/KCl (sat.)
Flowing gas	N2 (99.998%)
Electrolyte	HAc-NaAc pH 4.8
Reagent	Chloranilic acid 0.2% + KBrO3

adding known amounts of V to each solution used in the extraction. The accuracy, as evaluated by the recovery percentage, ranged between 92 and 102%. Relative standard deviations of the three V analyses were about 8%.

Reproducibility of the analytical method was tested by three replicate analyses of the same soil. The relative standard deviation ranged from 3.2 to 20%. A blank was run every 5 samples. All the reported data were blank corrected.

Results and discussion

The results of V analysis in the sequentially extracted fractions from soil samples are reported as the average of three complete analyses in Table 2. In the three reference stations, the V concentrations in soils (sum of four individual fractions) ranged from 0.072 to 0.24 g kg^{-1} d.w. with a mean value of 0.18 g kg^{-1} d.w. (Figure 4).

V concentrations (sum of four individual fractions) in soils of the Palermo urban area ranged from 0.34 to 2.1 g kg^{-1} d.w., in the Milazzo area between 0.26 (station M15) and 5.4 g kg^{-1} d.w. (station M9) and in the area near Mt. Etna from 0.91 to 2.9 g kg^{-1} d.w. (Figure 3). The lowest values of total V (0.072 g kg^{-1} d.w.) were found at stations M10 (Milazzo) and Ce21 (Cefalù), while the highest concentrations were measured in stations M3 (5.4 g kg^{-1} d.w.), M9 (4.6 g kg^{-1} d.w.) and M5 (4.4 g kg^{-1} d.w.). The last three stations were located (Figure 1b) near industrial plants (refinery and power plant) in the coastal area of Milazzo characterized by heavy industrial activities.

Station	Fraction a	Fraction b	Fraction c	Fraction d	Total
Ce21	0.72	0.37	0.61	$2.8\bullet10^{2}$	$2.8\bullet10^{2}$
M10	0.5	1.2	2.8	68	72
M12	2.6	2.4	9.4	$2.3\bullet10^{2}$	$2.4\bullet10^{2}$
M2	0.9	0.6	6.4	$1.2\bullet10^{3}$	$1.2\bullet10^{3}$
M3	1.3	0.3	11	$4.6\bullet10^{3}$	$4.6\bullet10^{3}$
M4	6.3	2.4	6.2	$2.1\bullet10^{3}$	$2.1\bullet10^{3}$
M5	6.8	4.4	1.6	$4.4\bullet10^{3}$	$4.4\bullet10^{3}$
M6	3.6	3.3	3.8	$3.1\bullet10^{3}$	$3.1\bullet10^{3}$
M7	4.0	0.4	1.1	$1.2\bullet10^{3}$	$1.2\bullet10^{3}$
M8	4.9	2.0	16	$20\bullet10^{3}$	$2.0\bullet10^{3}$
M9	7.5	1.4	1.6	$5.4\bullet10^{3}$	$5.4\bullet10^{3}$
M11	8.1	1.5	1.4	$3.1\bullet10^{2}$	$3.2\bullet10^{2}$
M13	6.2	1.0	6.8	$6.6\bullet10^{2}$	$6.8\bullet10^{2}$
M14	11	3.9	2.0	$7.4\bullet10^{2}$	$7.5\bullet10^{2}$
M15	5.7	3.1	2.3	$2.4\bullet10^{2}$	$2.6\bullet10^{2}$
M16	19	3.9	3.0	$2.1\bullet10^{3}$	$2.2\bullet10^{3}$
PA17	8.5	1.5	3.5	$3.3\bullet10^{2}$	$3.4\bullet10^{2}$
PA18	11	2.7	8.1	$1.1\bullet10^{3}$	$1.2\bullet10^{3}$
PA19	5.2	2.8	2.6	$9.1\bullet10^{2}$	$9.2\bullet10^{2}$
PA20	2.0	5.8	2.9	$2.1\bullet10^{3}$	$2.1\bullet10^{3}$
Ct22	9.5	1.9	2.1	$2.0\bullet10^{3}$	$2.0\bullet10^{3}$
Ct23	3.6	1.9	4.0	$2.3\bullet10^{3}$	$2.4\bullet10^{3}$
Ct24	4.9	6.1	2.8	$1.7\bullet10^{3}$	$1.8\bullet10^{3}$
Ct25	6.2	1.5	8.4	$1.7\bullet10^{3}$	$1.7\bullet10^{3}$
Ct26	54	4.3	7.6	$2.9\bullet10^{3}$	$2.9\bullet10^{3}$
Ct27	12	2.6	5.2	$8.9\bullet10^{2}$	$9.1\bullet10^{2}$

Table 2 - Concentrations (mg Kg-1 d.w.) of vanadium in soil samples collected in Milazzo, Palermo and Etna Mount areas.

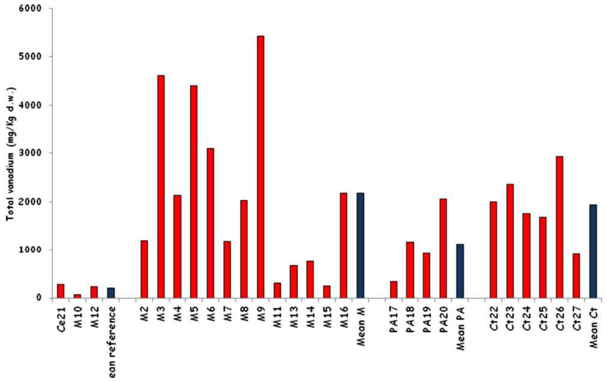


Figure 4- Total vanadium (mg/Kg d.w.) (sum of individual fractions)

In Palermo urban soils (Figure 1a) the lowest total V concentration was measured at station P17, located in a large square (Piazza Indipendenza), a green and open area where the traffic is severe and slow. In this square it is possible that the lush vegetation that covers the surface assimilate or uptake the pollutants and limits the concentration of pollutants in the soil. The highest V concentrations were measured in stations P20 (2.1 g kg^{-1} d.w.) and P18 (1.2 g kg^{-1} d.w.), both located on roads characterized by high traffic density.

In the Milazzo area, low V levels were measured in stations M11–M15 sited in green areas, away from sources of emissions of industrial plants, where motor vehicle traffic is practically zero. In particular, stations M11 and M12 are located near the coast of a well-ventilated isthmus.

High V concentrations (mean = 1.9 g kg^{-1} d.w.) were measured in samples collected in the Mt. Etna volcanic area (Figure 1c). The concentrations of total V ranged from 0.91 to 2.9 g kg^{-1} d.w. and, excluding station Ct27 (total vanadium 0.91g kg^{-1} d.w.), located in a green area on the slopes of Mt. Etna, were quite constant.

A comparison of the V concentrations measured in the volcanic area and those obtained in reference stations confirmed that Mt. Etna is a continuous source of V injected into the atmosphere and settled in the surrounding soils, similar to the results of previous studies where higher levels of V were observed in ground-water samples collected in several sites in Mt. Etna compared with other Italian areas [10].

Treatment of data with Surfer 7 (Figure 5) shows the spatial distribution of total V in the Palermo area.

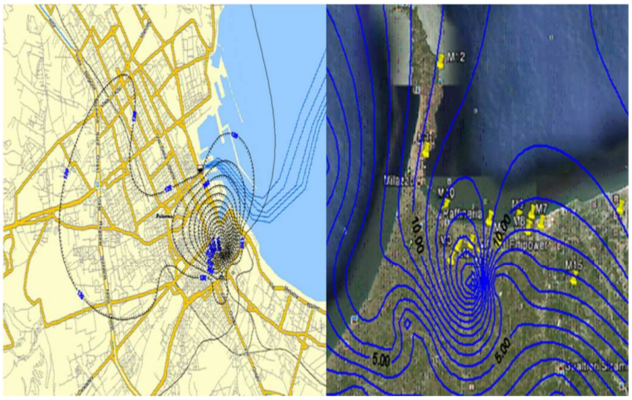


Figure 5- Spatial distribution of total Platinum (left) and Vanadium (right) in Palermo area.

The highest V concentrations were found in the historical town centre characterized by narrow streets and frequented by heavy vehicular traffic. For comparison, we also report the spatial distribution of platinum in the same area[23] (Figure 5). It is interesting to note that the two distributions are similar.

Figure 6 shows the spatial distribution of total V in the Milazzo area. The highest V concentrations were located near the industrial plants. For Mt. Etna, the highest V concentrations were restricted to the top of the volcano (Figure 7).

The results of the V analysis (g Kg^{-1}) in soil sequential fractionation solutions are shown in Table 2. These data were calculated as the average of three determinations and histograms of the data (mean values) of the first three V fractions were also reported in Figure 8

to provide an overview of the V distribution in the soils of the three stations. In all samples, including those taken as reference samples, the majority of the V (from 94 to 100%) was present in the fourth fraction. This fraction is usually related to bioaccumulation and consists of V adsorbed on organic matter or in the form of sulphide or compounds soluble in nitric acid. In this form, the metal is temporarily fixed but during the natural process of mineralization, it can sometimes be passed to one of the other fractions or to natural waters.

Figure 6- Spatial distribution of Vanadium in Milazzo area

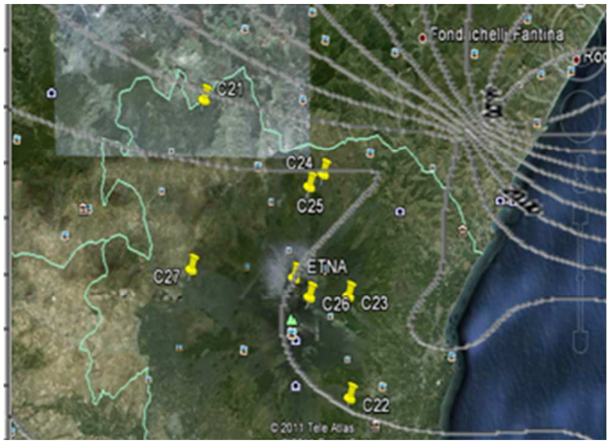


Figure 7- Spatial distribution of Vanadium in Etna Mount area

Figure 8 – Percentages of vanadium in each fraction (excluding the fourth) of the sequential extraction of soils

Preliminary analyses had shown that in the soils in this study, organic matter was present only at trace levels and sulphides were absent. Consequently it is possible that V was present in these soils in other forms that are soluble in nitric acid, such as V_2O_3, even if, from the chemical point of view, with excess oxygen, the pollutant formed during combustion is expected to be V_2O_5. If the stoichiometric conditions of combustion are not optimal, as often occurs in industrial processes, together with the presence of carbonaceous substances, V can be released in the form of V_2O_3 and/or vanadium sulfide, which, being insoluble in the chemicals used during the first three extraction phases, are extracted in the fourth fraction.

The V fractionations of contaminated soils collected at Milazzo and Palermo were similar, while considerable differences were found with the fractionations of soils sampled in the volcanic area and the reference stations. In the reference stations, the percentage of V (mean of three stations) in the exchangeable fraction was low (about 19%) compared with those measured in the soils collected at Milazzo (48%), Palermo (38%) and in the volcanic area (65%). V in this fraction can be released easily by ion-exchange processes and leaches very easily when the environmental conditions are disturbed by changes in pH, salinity or other factors. V in the exchangeable fraction plays a very important role in the evaluation of the environment and acts as a pollution indicator because of its environmental mobility and bioavailability. Usually the weakly linked V forms, particularly those retained on the soil surface by relatively weak electrostatic interactions, are included in this operational fraction. The content of V in the exchangeable fraction indicates the amount of V accessible for organisms, which, in our case, does not depend on the total concentration of the element in soil.

The fraction b, consisting of V associated with carbonates or precipitated with carbonates, in percentage terms, was similar in all monitored areas and ranged from 13% (Mt. Etna volcanic area) to 19% (reference stations) of the total metal. This fraction is sensitive to pH changes, and V release can be achieved through dissolution of a fraction of the solid material at low pH values.

In the soils examined in the present study, Fe–Mn oxides (fraction c) played a minor role in binding V; in the three areas the percentages were almost equal and ranged from 4.3% (reference and Palermo area) to 5% (Volcanic area). In oxygen-free (reducing) conditions, V will pass into solution because of iron and manganese reduction.

Conclusions

Vanadium (V) is a pollutant associated with airborne particulates originating from fossil fuel combustion and from volcanic activities. Although the total concentration of V is still useful in many areas, knowledge of V speciation is of primary importance because the toxicity, mobility, bioavailability and bioaccumulation of this element depend on the chemical species present.

To the best of our knowledge, this is the first report on the fractionation of V in soils from industrial, urban and volcanic areas.

The concentration of V found in the exchangeable fraction was high in the volcanic area and this is a natural phenomenon. This indicates a constant amount of V accessible for plants, which does not depend on the total concentration of this element in soil. The low percentages of V in fraction b in all investigated soils showed that the element does not form carbonates, but in this fraction is present in other forms. The oxidizable fraction of V was the dominant form in all areas. The fourth fraction constituted the most important source of potentially available V and provided information for pollution estimation in these areas.

The present study demonstrated that the voltammetric analysis of V in the soils was an excellent method for the determination of trace amounts of this pollutant. In conclusion, the above system offers a practical method for the subsequent determination of V without any interference because of the close reduction potential of other species present in the matrix. The method has several advantages over other available methods, including high sensitivity, high selectivity, simplicity, speed and low cost.

The higher amounts of V detected in soils from the investigated areas compared with the control sites are diagnostic of conspicuous air contamination.

The fractionation study carried out on V of Milazzo soils could provide very useful information when a remediation strategy for this area is required.

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