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### Release and speciation of uranium in low-ionic-strength groundwaters at an abandoned uranium mine in Val Vedello (Orobic Alp—Italy) by adsorptive cathodic stripping voltammetry

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## Release and speciation of uranium in low-ionic-strength groundwaters at an abandoned uranium mine in Val Vedello (Orobic Alp—Italy) by adsorptive cathodic stripping voltammetry

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Adsorptive cathodic stripping voltammetry (AdCSV) with HDME and a chloranilic acid ligand was used in the trace analysis of uranyl ions at pH = 2 in low-ionic-strength groundwaters around mining areas. Upon optimization, the limit of detection around  $0.10 \mu\text{g L}^{-1}$  was found with linearity up to  $10 \mu\text{g L}^{-1}$ . In the abandoned mining area of Val Vedello (Orobic Alps, Italy), measured uranium concentrations in water ranged from  $0.3 \mu\text{g L}^{-1}$  above the uranium mineralization levels to  $145 \mu\text{g L}^{-1}$  in groundwaters percolating from mine galleries. Such uranium concentrations are related to natural weathering effects of  $\text{CO}_2$  and/or hydrogen carbonate ion on uranium mineralizations under oxic conditions. A marked seasonal dependence was then found, in agreement with literature data on a pre-operational survey dating back to 1980–1981. No significant chemical impact of the abandoned mining activity on groundwater quality could be found. Accordingly, no significant increase in contaminants derived from the heat-burn of explosives, such as chloride and nitrate, in groundwaters from mine galleries was found.

*Keywords:* Uranium; Adsorptive stripping voltammetry; Speciation; Rock weathering; Val Vedello

### 1. Introduction

The investigation of the chemical composition of groundwaters around uranium mining areas is of primary importance, since they can be regarded as the most important pathways for the release and migration of uranium and/or mining-related contaminants into the environment. Typical total uranium concentrations in ground- and surface natural waters were reported to lie in the low  $\mu\text{g L}^{-1}$  range, although concentrations

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may reach much higher values, even in the  $\text{mg L}^{-1}$  range, near mining sites of industrial importance [1, 2]. Consequently, sensitive analytical techniques, in the  $\mu\text{g L}^{-1}$  to sub- $\mu\text{g L}^{-1}$  range, are required for the analytical determination of uranium. Spectroscopic techniques are widely used, from fluorimetry to X-ray fluorescence [3] and to highly sensitive ICP-MS [4]. Such techniques are expensive, and will often require time and specialized technical skill for their operation. Electrochemical techniques have thus been proposed as a viable and less costly alternative for the determination of trace uranium concentrations in fresh and marine waters [5–11]. Adsorptive stripping, differential pulse voltammetric methods may be considered as the ideal candidates for routine determination of uranium(VI) in groundwaters. In fact, very low detection limits may be reached with the conventional hanging mercury drop electrode (HMDE) without requiring the use of modified working electrodes [12]. At the same time, these electrochemical techniques offer interference-free operations from matrix composition. However, the stripping voltammetric technique should be optimized for uranium analysis in low-ionic-strength water samples as in the case of the abandoned mining area in Val Vedello. This is a small, north-facing valley in the drainage area of the river Venina, which is located in the central sector of the Orobian Alps on the southern side of Valtellina near Sondrio (Italy). This site attracted considerable industrial interest at the end of the 1970s, since a large uranium orebody was found on the orographic right side of the valley. This orebody had an average uranium concentration of  $1000 \text{ mg L}^{-1}$  and an estimated extraction yield of 3500 t as  $\text{U}_3\text{O}_8$  [13].

It was shown [14] that these mineralizations can be attributed to late Permian to Triassic geothermal events which leached uranium from Permian ignimbrites and transported it along Permian faults. The main uranium containing mineral is uraninite, which largely consists of  $\text{UO}_2$ , the reduced form of uranium (formal oxidation state +IV). A pre-operational survey was conducted in the Val Venina area, in order to draw a preliminary map of natural radioactivity prior to the start of mining activity [15]. This survey resulted in the finding that pre-operational activities were leading to very low sources of natural contamination. However, industrial mining operations were actually discontinued, because of the opposition of the local communities, and the Val Vedello mine was closed and abandoned at the end of the 1980s.

In this article, a 3-year monitoring programme on uranium release from Val Vedello mine was then undertaken, in order to evaluate seasonal variations of uranium concentration and the possibility of late releases of mine-related contaminants. Finally, a model analysis of uranium speciation was carried out on the basis of the ionic composition of water samples, with the aim of a better understanding of water–rock interactions and chemical mechanisms of uranium release.

## 2. Experimental

### 2.1 Sample collection

Four water samples, denoted C2–C5, were taken in the 2002–2003 seasons from waters exiting the main galleries in the abandoned uranium mine in Val Vedello (figure 1): the entrance in the tunnels was unauthorized, and drainage water only outside the

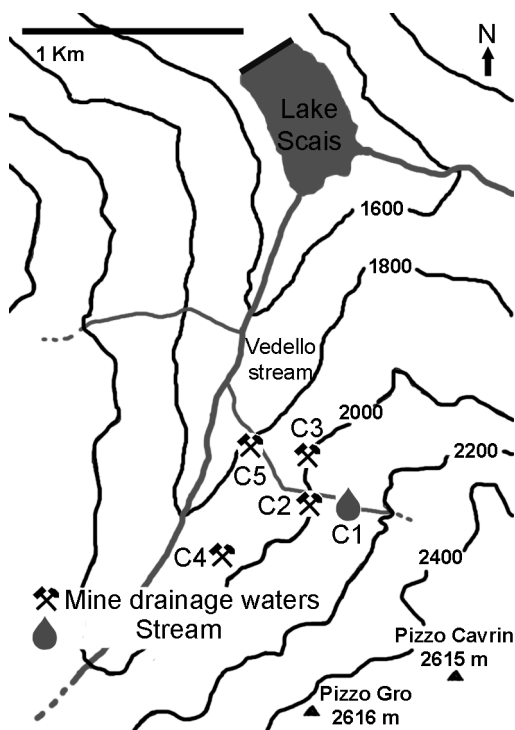


Figure 1. Map of the C1–C5 sampling sites in the Val Vedello mining area (Sondrio, Italy).

galleries could be collected. Sample C1 was collected from a stream at 2140 m a.s.l., probably originating by the melting of high altitude snowfields, above the uranium mineralization levels: the sampling-site location and altitude are reported in table 1. Four more samples were collected during 2004 in the C5 site.

All samples were collected in 1L low-density polyethylene bottles (LDPE, Nalgene). The bottles were previously cleaned by soaking in hot detergent for 24 h followed by 5 M hydrochloric acid for 1 week. After rinsing with several portions of ultrapure water (Millipore Milli-Q System, 18 M $\Omega$  cm resistivity) under a laminar flow hood, bottles were stored filled with Milli-Q water acidified to pH 2 with ultrapure hydrochloric acid (Fluka Traceselect, 36% w/v).

The physicochemical parameters (temperature, pH, and conductivity) were determined *in situ*. Temperature and pH were measured through a portable Hanna HI902C pH meter and conductivity through a Radiometer Analytic Pioneer 6 conductivity meter. Both instruments were calibrated daily in the field following the manufacturer's specifications. The pH scale was calibrated at 7 and 10, and checked at 4.7; no buffer solutions have been added to water samples prior to the actual determination to avoid any possible contamination.

## 2.2 Analytical determinations

The 10 mL samples for the determination of major ions were syringe-filtered in the field (Millipore 0.45  $\mu$ m pore size) and stored in polypropylene vials. The concentration of

Table 1. Sampling site altitude and location (Gauss–Boaga coordinates).

Sample	Altitude m a.s.l.	East	North
C1	2140	1571798	5102267
C2	1970	1571641	5102247
C3	1960	1571641	5102501
C4	1960	1571229	5101989
C5	1803	1571361	5102510

major ions was determined in the laboratory by means of automated ion chromatography with conductimetric detection (IC761 from Metrohm, Herisau, Switzerland coupled with an 813 Compact Autosampler). A Metrohm Metrosep Anion Supp 5-250 column was used for anion separation with a flow of  $0.7 \text{ mL min}^{-1}$  of carbonate/hydrogencarbonate eluent ( $3.2 \text{ mM Na}_2\text{CO}_3 + 1.0 \text{ mM NaHCO}_3$ ). Cations were separated on a Metrohm Cation 2-150 column with an eluent composition of  $4.0 \text{ mM}$  tartaric acid and  $0.75 \text{ mM}$  dipicolinic acid at a flow rate of  $1.0 \text{ mL min}^{-1}$ . The measured limits of detection (LOD) are around  $3 \mu\text{g L}^{-1}$  for anions and  $10\text{--}25 \mu\text{g L}^{-1}$  for cations. Confidence limits for analysis were estimated within 3% for anions and 5% for cations.

The hydrogen carbonate concentration was determined by titration with  $0.01 \text{ M}$  hydrochloric acid with a computer-based automatic titrator developed in our laboratory [16].

For uranium analysis, a  $250 \text{ mL}$  aliquot of the sample was vacuum-filtered on a  $0.45 \mu\text{m}$  nitrocellulose membrane from Millipore, using an all-plastic, acid-cleaned system. Samples before and after filtration have been indicated as unfiltered ('unF') and filtered ('F') samples, respectively. All samples were acidified with high-purity hydrochloric acid (Fluka Traceselect, 36%) to pH 2. All the foregoing handling was performed under a laminar-flow hood in order to minimize any contamination.

UV digestion was employed during method optimization. A Metrohm 705 UV-Digester equipped with a 500-W high-pressure mercury lamp was used. Samples were transferred in Teflon-capped acid-cleaned quartz tubes and digested for 1–3 h.

Uranium concentrations were determined by adsorptive cathodic stripping, differential pulse voltammetry using a Metrohm VA 757 Computrace stand connected via a VA Computrace interface module to a personal computer. A standard three-electrode configuration was used with a hanging mercury drop electrode (HMDE) as working electrode, a double junction Ag/AgCl (3 M KCl, saturated AgCl, and 3 M KCl bridge) as reference electrode and a platinum wire as counter-electrode. Uranium standard solutions were prepared by appropriate dilution of the atomic absorption standard stock solution ( $957 \text{ mg L}^{-1}$ , Aldrich), and acidified to pH 2 with HCl. A stock solution of chloranilic acid  $2.5 \text{ mM}$  (99%, Aldrich) was prepared in  $0.01 \text{ M}$  HCl. After a  $10 \text{ mL}$  sample aliquot was transferred into the voltammetric cell,  $80 \mu\text{L}$  of chloranilic acid solution was added and the solution purged with nitrogen for 5 min. The  $[\text{UO}_2]^{2+}$ -chloranilic acid complex was preconcentrated onto the mercury drop for 60 s at an accumulation potential of  $+0.1 \text{ V}$ . A differential pulse scan from  $0.05$  to  $-0.15 \text{ V}$  was then started with the following optimized parameters: pulse amplitude =  $50 \text{ mV}$ ; potential step =  $4 \text{ mV}$ ; pulse time =  $40 \text{ ms}$ ; pulse repetition =  $300 \text{ ms}$ . A quantitative analysis was carried out by the standard addition method.

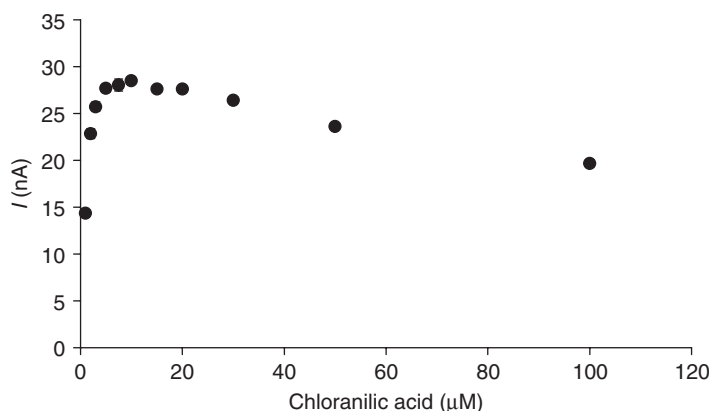


Figure 2. Dependence of analytical signal of a  $10 \mu\text{g L}^{-1}$   $[\text{UO}_2]^{2+}$  solution as a function of the concentration of chloranilic acid.

### 3. Results and discussion

#### 3.1 Uranium analysis

Uranium concentration was measured by adsorptive cathodic stripping differential pulse voltammetry (AdCSV), at pH 2 with chloranilic acid as complexing ligand for  $[\text{UO}_2]^{2+}$  ions [5–11]. In this way, the interfering effects of hydrogencarbonate and/or carbonate ions could be totally removed, since carbonate–uranyl complexes are decomposed at such a low pH. The influence of the concentration of chloranilic acid ligand in uranium analysis was investigated at a constant uranium concentration ( $10 \mu\text{g L}^{-1}$ ) by plotting the voltammetric analytical signal against the ligand concentration (figure 2). As expected, the analytical signal rapidly increased with ligand concentration until a plateau was reached at around 20–30  $\mu\text{M}$ ; a slow decrease was then observed because of surface-site competition between the electroactive uranyl complex and the free ligand. A chloranilic acid concentration of 60–80  $\mu\text{M}$  was chosen for real sample analysis, since we could not exclude the possibility that, even at such low pH values, chloranilic acid might be complexed by trace elements in real water samples, thus reducing the actual free-ligand concentration.

The limit of detection of this analytical protocol was calculated with the IUPAC method [17] and it was found to be  $0.10 \mu\text{g L}^{-1}$  with a 60 s accumulation time. Longer accumulation times can be used to decrease the limits of detection; a linear dependence between the analytical signal and deposition time was found between 60 and 500 s, with a slope of  $0.039 \text{ nA s}^{-1}$ . Consequently, an LOD of around 15 ppt ( $\text{ng L}^{-1}$ ) may be estimated with a 500 s accumulation time.

The instrumental response at 60 s accumulation time is linear up to  $10 \mu\text{g L}^{-1}$ ; samples with higher concentrations were properly diluted with 0.01 M HCl in order to remain within the limit of linearity. The confidence limit for uranium analyses was finally estimated to be around 5%.

C1–C5 samples were analysed for uranium content before and after filtration through a  $0.45\text{-}\mu\text{m}$ -pore-size membrane (see section 2). The uranium concentration was very low in C1 samples, always below  $0.30 \mu\text{g L}^{-1}$  for all sampling campaigns. This result is to be expected in a site located above the uranium mineralization levels, where the uranium

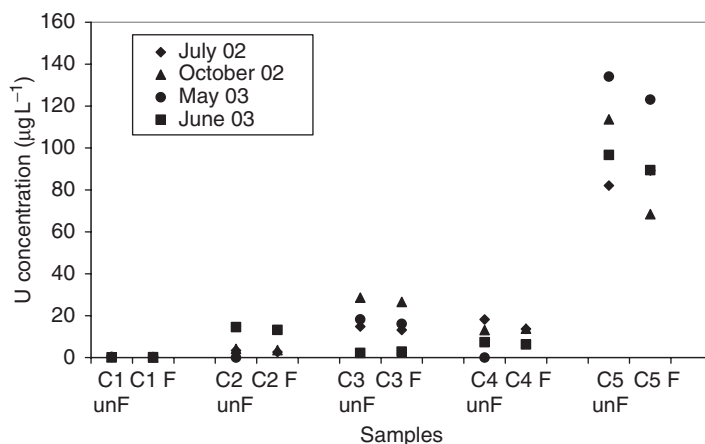


Figure 3. Uranium concentrations in unfiltered (unF) and filtered (F) water samples at the C1–C5 sites.

contents in rocks are significantly decreased. Samples collected in the C2, C3, and C4 sites, which are located outside the main galleries, show uranium concentration values in the 2–15  $\mu\text{g L}^{-1}$  range. The C5 site is located at the bottom level of the mine galleries, and this collects all the waters percolating through the uranium mineralization levels; accordingly, the concentration of uranium is the highest, reaching 82.1–134  $\mu\text{g L}^{-1}$  in the unfiltered sample, and 68.4–123  $\mu\text{g L}^{-1}$  after filtration. The results for both filtered and unfiltered samples are reported in figure 3.

It has to be evidenced that uranium contents in filtered samples appear to be always lower than in unfiltered samples, although the difference may be statistically significant only in C5 samples. This difference is proposed to be related to the presence of insoluble complexes of  $[\text{UO}_2]^{2+}$  with particulate organic matter. The effect of adsorption of  $[\text{UO}_2]^{2+}$  onto inorganic particulate matter, primarily iron and/or manganese oxy-hydroxides, may be disregarded. In fact, not only is the presence of large amounts of hydrogencarbonate ion necessary for the oxidative dissolution of  $\text{UO}_2$  to uranyl carbonato-complexes, but it has a negative effect on U(VI) adsorption on iron hydroxides because of the low affinity of such anionic complexes with basic surface sites [18].

Regarding the ‘dissolved’ ( $<0.45 \mu\text{m}$ ) fraction, the presence of organic complexes of uranium cannot be excluded. Uranyl complexes with humic and fulvic acids are well known in the literature [19], and they may originate suppression or enhancement of the analytical signal. However, no matrix effect is claimed in  $[\text{UO}_2]^{2+}$  determination with chloranilic acid [5]. The effect of oxidative digestion under UV irradiation was thus investigated, in order to evidence any possible interference of humic/fulvic acid in the uranium determination under our experimental conditions. Samples were treated in a UV digester, in the presence or absence of hydrogen peroxide that is used as a radical initiator: the results are displayed in figure 4. It is immediately evident that no UV pre-treatment is needed for low-ionic strength, high-altitude freshwater samples, thus confirming that a low organic-carbon content does not compete with chloranilic acid for complexation and adsorption onto the mercury electrode. Preliminary results from this research group indicate that UV digestion is instead required to achieve accurate

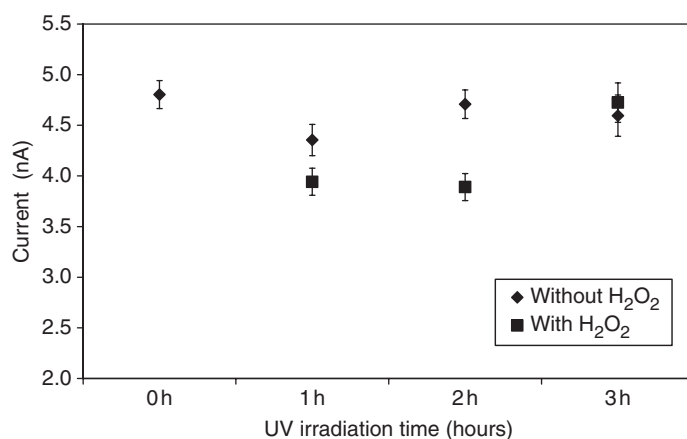


Figure 4. Effect of UV irradiation time on the analytical signal of a  $3 \mu\text{g L}^{-1}$   $[\text{UO}_2]^{2+}$  solution with chloranilic acid ligand.

results for high-ionic-strength, high-organic-content freshwater samples, such as those found in the lower course of the Venina river.

When hydrogen peroxide is added in the analytical protocol of sample digestion, a full 3 h treatment is required, since shorter irradiation times lead to an actual decrease in the analytical signal. On the basis of the known chemistry of the uranyl ion, the formation of peroxy or hydroxy-peroxy uranyl complexes is expected via reaction with  $\text{H}_2\text{O}_2$  and/or with OH and/or OOH radical species formed during UV irradiation [20]. Such peroxy complexes will probably react with chloranilic acid, leading to a decrease in the analytical signal of uranium, and will require long irradiation times for their complete decomposition.

### 3.2 Major hydrochemical features

A detailed investigation of ionic composition of water samples has been undertaken, in order to find chemical correlations with rock weathering and uranium speciation. As can be expected from the remote, high-altitude location of the uranium mine, all water samples show a low ionic strength, with a specific conductivity ranging between  $10 \mu\text{S cm}^{-1}$  (at the C1 station) and  $130 \mu\text{S cm}^{-1}$  (at the C5 station), as can be seen in table 2. Moderate variations in fluxes (winter reduction, spring increase, and late summer decrease) point to a fast groundwater recharge system. Although temperature shows a minor seasonal dependence, no definite conclusion can be made, as water flows in contact with air for some time before exiting the tunnel.

All C2–C5 samples are characterized by the predominance of hydrogen carbonate as the major anion (almost all of the alkalinity is accounted for by this anion as the pH varies between 7.30 and 8.26) and of calcium and magnesium cations; these three ions account for over 90–95% of the overall ionic balance. This enrichment is the result of the chemical interactions of water percolating inside mine galleries with the crystalline basement by 'Morbegno gneiss' and conglomerate constituted by clasts derived from low-grade metasediments and for leucochratic metaintrusives and porphyritic acid Permian volcanics. Considering alkalinity as a marker to indicate



the extent of rock weathering, we may propose the following trend among the four sites:  $C5 > C3 > C4 > C2$ , in good agreement with specific conductivity data (table 2).

Water samples collected at the C1 site show instead a complete different chemical behaviour; the alkalinity, calcium, and magnesium concentrations, as well as the specific conductivities, are about one order of magnitude lower. On the contrary, other ions of environmental significance, primarily nitrates and chlorides, do not show significant differences with respect to C2–C5 sites, within each sampling campaign. Such chemical behaviour may thus suggest that the C1 site collects all melting water from snowfields located at a higher altitude above the mineralization levels. These ions are suggested to derive from the deposition of particulate matter of continental origin; the extreme variability of Na/Cl ratio is in agreement with the absence of significant contribution of sea-salt spray of marine origin. Accordingly, water samples collected in May 2003, at the beginning of snow melting after the dry and polluted 2002–2003 winter season, are characterized by the highest concentrations of chloride and nitrates, and the presence of ammonium ion. Ammonium may be regarded as a typical seasonal marker of long-range, global anthropogenic impact, such as industrial pollution and farming activity. We were unable to detect it in the other sampling campaigns, since it is a short-lived species, which is decomposed to gaseous dinitrogen and nitrate ions via microbial and/or metal catalysed oxidation with oxygen and/or hydrogen peroxide during hot season. Moreover, ammonium ion may also be used as an *in situ* tracer of hydrological, high mountain circuits. Its presence in all sampling sites in May 2003 campaign suggests that melting waters recharge the groundwater system percolating through uranium mineralization levels and are responsible for uranium weathering inside mine galleries. This ‘tracking’ role of ammonium was also highlighted by some of us in a karst groundwater system in the Dolomites (northern Italy) [21].

### 3.3 Uranium speciation and seasonal variability

It is interesting to note that the dissolved uranium concentrations strongly correlate with the alkalinity of the samples. The correlation coefficient  $r$  between the uranium concentrations in C2–C5 samples and the alkalinity is 0.89 ( $n = 14$ ). The C1 sample was not considered, as this site is located at a higher altitude than the mineralization levels. This large positive correlation is well explained by the dissolution kinetics of  $UO_2$ . High levels of hydrogen carbonate were indeed demonstrated to increase the oxidative dissolution kinetics of synthetic  $UO_2$  [22]. The field data presented in this study strongly enforce these findings. Moreover, they suggest that an enhanced uranium export from mine galleries and rock dumps is to be expected when the hydrogen carbonate concentration is high. The geological setting of the catchment is thus supposed to play a major role in dissolving uranium minerals and thus uranium fluxes. Carbonate containing rocks leading to hydrogen carbonate-rich waters will enhance  $UO_2$  weathering and thus uranium release in the hydrological circuit. On the other hand, catchments with low amounts of carbonate rocks are less prone to uranium enrichment.

Carbonate-uranyl complexes are found as predominant species of uranium in solution, although the presence of organic matter competing for uranium complexation cannot be ruled out. Computer calculations of uranium speciation (Visual MINTEQ,

Table 2. Analytical and physicochemical data of water samples collected at the C1–C5 sites of the Val Vedello mining area.

Site	Data	T (°C)	pH	Conductivity ( $\mu\text{S cm}^{-1}$ )	Na <sup>+</sup> <sup>a</sup>	NH <sub>4</sub> <sup>+</sup> <sup>a</sup>	K <sup>+</sup> <sup>a</sup>	Ca <sup>2+</sup> <sup>a</sup>	Mg <sup>2+</sup> <sup>a</sup>	Cl <sup>-</sup> <sup>a</sup>	NO <sub>3</sub> <sup>-</sup> <sup>a</sup>	SO <sub>4</sub> <sup>2-</sup> <sup>a</sup>	Alkalinity <sup>a</sup>
C1	July 2002	5.5	6.70	11.56	0.011	<LOD	<LOD	0.056	0.043	0.002	0.033	0.014	0.050
C2	July 2002	2.7	7.50	53.60	0.024	<LOD	<LOD	0.202	0.254	0.003	0.042	0.058	0.417
C3	July 2002	2.4	7.79	83.20	0.028	<LOD	0.003	0.238	0.517	0.003	0.036	0.054	0.763
C4	July 2002	2.4	7.69	80.90	0.028	<LOD	<LOD	0.238	0.513	0.004	0.037	0.050	0.771
C5	July 2002	5.7	8.00	116.30	0.077	<LOD	0.003	0.360	0.668	0.005	0.031	0.118	1.060
C1	October 2002	4.1	7.10	16.60	0.017	<LOD	0.005	0.051	0.037	0.004	0.032	0.010	0.055
C2	October 2002	3.7	7.55	60.10	0.028	<LOD	0.003	0.244	0.287	0.005	0.045	0.035	0.474
C3	October 2002	4.8	7.80	94.10	0.036	<LOD	0.005	0.312	0.692	0.005	0.036	0.036	0.902
C4	October 2002	3.0	7.48	71.10	0.027	<LOD	0.002	0.315	0.368	0.004	0.037	0.072	0.531
C5	October 2002	6.0	8.15	133.60	0.095	<LOD	0.006	0.397	0.791	0.007	0.027	0.073	1.257
C1	May 2003	2.7	8.60	19.87	0.017	0.067	0.009	0.140	0.083	0.050	0.053	0.038	0.130
C3	May 2003	3.0	8.10	79.00	0.054	0.051	0.029	0.278	0.532	0.060	0.052	0.058	0.750
C5	May 2003	5.0	8.26	118.10	0.104	0.053	0.006	0.466	0.860	0.048	0.044	0.119	1.120
C1	June 2003	3.0	7.29	11.89	0.003	<LOD	<LOD	0.063	0.036	0.010	0.015	0.018	0.074
C2	June 2003	2.0	7.30	49.90	0.019	<LOD	0.007	0.205	0.262	0.011	0.038	0.054	0.457
C3	June 2003	5.0	7.61	73.40	0.026	<LOD	<LOD	0.233	0.478	0.014	0.037	0.042	0.597
C4	June 2003	2.4	7.44	59.10	0.023	0.006	<LOD	0.252	0.295	0.010	0.034	0.086	0.422
C5	June 2003	4.6	8.18	105.70	0.077	<LOD	<LOD	0.362	0.679	0.014	0.035	0.111	0.978

<sup>a</sup>Concentrations are reported as meq L<sup>-1</sup>.

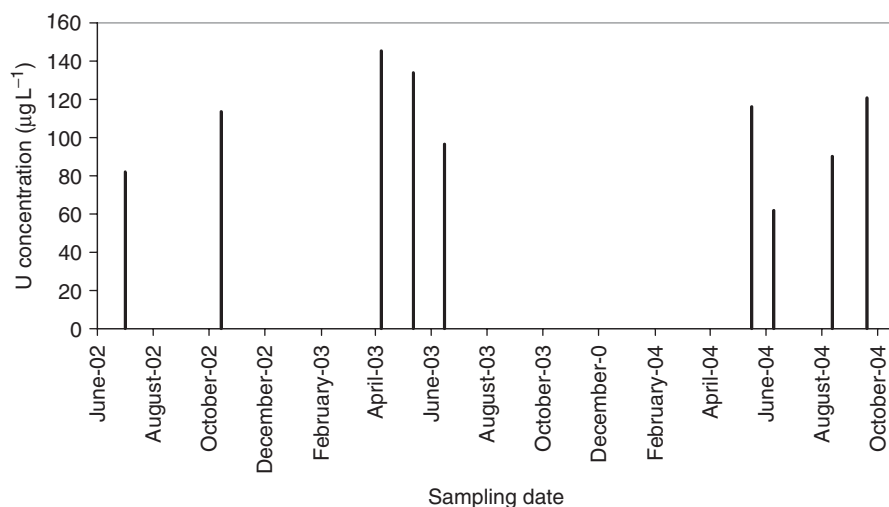


Figure 5. Seasonal variations of uranium concentration in water samples at the C5 site.

version 2.12, 2002, compiled by Jon Petter Gustafsson) indicate in fact that uranium species are the  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  and  $[\text{UO}_2(\text{CO}_3)_2]^{2-}$  anions, accounting for about 70% and 30%, respectively (C5 sample). Similar results, and in particular the predominance of tricarbonato complexes at natural pH, have also been reported for mining-related waters in Germany [1] and by structural studies [23].

It is also interesting to note the peculiar trend in uranium concentration in different seasons; the results for C5 samples are summarized in figure 5. The concentration of uranium follows a marked seasonal dependence; in spring, when wet precipitations and snow melting are strongly reduced, the uranium concentration reaches the highest values:  $145 \mu\text{g L}^{-1}$  in April 2003 and  $116 \mu\text{g L}^{-1}$  in May 2004. During the late spring and summer, the uranium concentration decreases to  $80$ ,  $100$ , and  $60 \mu\text{g L}^{-1}$  in July 2002, June 2003, and June 2004, respectively. In autumn, the uranium concentration increases again to  $120 \mu\text{g L}^{-1}$ , reaching values similar to those found in the spring. The water-input variation explains these changes in uranium concentration found at the C5 site. It should in fact be recalled that  $\text{UO}_2$  dissolution is under kinetic control: a larger water input causes a dilution effect as the weathering reaction is slow with respect to the residence time of water in contact with rock and soils. Accordingly, uranium concentrations are higher during the spring and possibly winter, decrease during the summer, and increase again in the autumn. On the other hand, during late spring and summer, snow melting and abundant rainfalls introduce large amounts of water in the catchment, causing a marked decrease in uranium concentration. Finally, snow precipitation and the start of freezing in autumn lead to a reduced water intake and thus to an increase in uranium concentration. The  $\text{UO}_2^{2+}$  concentration is thus halved between spring and summer. No data could be collected during the winter because of the difficulties in reaching the mining area in this season: it may be expected that even higher concentrations could be reached during this period.

It is important to show that the same trend of uranium concentration was observed and reported in an early paper [10], which outlined a preliminary map of natural

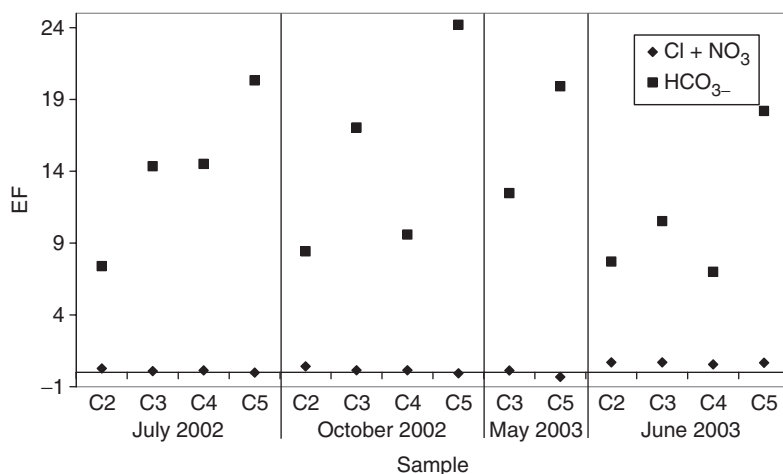


Figure 6. Seasonal variations of enrichment factors (EF) for  $\text{HCO}_3^-$  and  $\text{Cl}^- + \text{NO}_3^-$  ions in water samples at the C2–C5 sites.

radioactivity on the Val Vedello mining sites during the year 1980–1981, before the start of mining activity. In that article, uranium concentrations have been reported to range between  $48$  and  $160 \mu\text{g L}^{-1}$ , a concentration interval which exactly overlaps our present findings in the 2002–2003 season. Our results may thus suggest an overall ‘natural’ origin of uranium in Val Vedello groundwaters, which is no longer associated with the abandoned mining activity.

In order to gain more insight into the residual environmental impact of the abandoned mining activities, we took advantage of the peculiarity of C1 sampling station to lie above uranium mineralization levels. The C1 sample can be regarded as an environmental blank, and its chemical composition is almost independent of any local anthropic impact. Enrichment factors (EF) have been calculated for C2–C5 sites, being defined as  $([C_n] - [C1])/[C1]$  where  $[C_n]$  represents the molar concentration of any major ion for the C2–C5 sites and  $[C1]$  the molar concentration of any major ion for the C1 site. Three representative ions have been considered, namely hydrogen carbonate, chloride, and nitrate, and data are reported in figure 6. The hydrogen carbonate ion was indicative of natural weathering effects, where chlorides and nitrates are instead related to the residual impact of mining activity via leaching of by-products generated after the rapid intensive heat-burn of explosives [24]. This assumption is based on the evidence that no human or farming activities, which could contribute to chloride, nitrate, and, occasionally, nitrite levels in water [25], are located above the mining area in Val Vedello. The cumulative EFs for the sum of  $\text{Cl}^- + \text{NO}_3^-$  are always quite small, between  $-0.10$  and  $0.95$ , if they are compared with EF for hydrogen carbonate, which is in the  $5$ – $22$  range. EFs for hydrogen carbonate are highest in the C5 site, which correlates exactly with uranium concentration levels in water. Instead, no definite trend is observed for the sum of chlorides and nitrate, since EFs are coincident for the four C2–C5 sites within each sampling campaign. This observation is therefore in full agreement with the absence of any residual polluting impact of mining activity after they were abandoned more than 20 years ago.

#### 4. Conclusions

The determination of trace uranium contents in low-ionic-strength groundwaters such as those found in the abandoned mining area of Val Vedello near Sondrio (Italy) was successfully carried out by means of adsorptive stripping voltammetry with chloranilic acid ligand. With low-organic-content samples, no ultraviolet or oxidative pretreatments are needed, thus confirming data reported by Sander and Henze.

A 2 year monitoring programme was thus undertaken to investigate seasonal variations on uranium content of groundwaters in different locations of the mining activity. The uranium concentration was always highest at the C5 sampling site, which collects all the waters percolating through the galleries. The concentration range covers an interval between 80 and 145  $\mu\text{g L}^{-1}$ , and correlates well with literature data on a pre-operational survey, dating back to 1980–1981, aimed to outline natural radioactivity levels prior the starting of the mining activity. In agreement with such results, we may suggest that in the 2002–2004 seasons, the uranium concentration in water is essentially due to the natural weathering effects of  $\text{CO}_2$  and/or the hydrogen carbonate ion on uranium mineralizations under oxic conditions. Moreover, we did not find any significant increase in chloride or nitrate concentrations in groundwaters from mine galleries.

In conclusion, it can be suggested that no significant chemical and geochemical impact of the abandoned mining activity may be found after 20 years from pre-operational surveys.

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