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Analysis of the mobilization of solid loads and heavy metals in runoff waters from granite quarries

Received: 22 December 2005
Accepted: 8 March 2006
Published online: 28 March 2006
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Abstract The cutting operations of dimension stone at quarries produce a large amount of fines that, in turn, cause a negative environmental impact over local surface waters. This article presents a detailed analysis of the mobilized contamination associated with runoff waters in a large granite quarry (~200 ha) which is located in Porriño (Galicia, NW Spain), the most important production centre of dimension stone in Spain. There, an intensive monitoring survey was developed in order to characterize the hydrology of the system as well as the release and transport of pollutants. This was accomplished by means of different control sections for the flow and by the collection of 52 random water samples. Automatic samplers were also used to collect 192 water samples associated with runoff generated by significant rain events. For each of the samples collected, a wide battery of analytic determinations was performed, including solid loads, turbidity, organic pollution,

nutrient and selected metals. Upon careful examination it has been possible to obtain different parameters related to the contamination control, like the “event mean concentration” (EMC), maximum concentrations and specific sediment loads. Moreover, a comprehensive statistical study including parameter correlation and cumulative probability analyses helped to understand the pollutant mobilization behaviour within the quarry system. It can be concluded that mobilized contamination shows the anomalous presence of some metals, whose concentrations are in excess when compared to the natural rock. This excess metal amount must be attributed to an anthropogenic source associated to mining and cutting operations.

Keywords Granite quarries · Runoff water pollution · Suspended solids · Selected metals · Statistical analysis · Spain · Galicia · Porriño

Introduction

Mining and, particularly, the extraction of rock and minerals in open mining have always been considered aggressive activities with a high and negative impact on the environment. Mining operations have, both voluntarily and under pressure from the legislation, implemented an increasing number of measures in order to reduce all the effects and disturbances caused by this

activity on the environment. One of the aspects that have been signalled out as important in minimizing these impacts is reducing water pollution.

This article presents an in-depth study of the quality of runoff waters from a large granite quarry in Porriño (Galicia), which is located at the northwest corner of Spain. The study area is characterized by a large number of quarries that, due to the continuous operation for decades, have merged in a nearly continuous face with a

Fig. 1 View of the work fronts at the granite quarries in Porriño



total surface of around 200 ha (Fig. 1). It extends over the slope of a hill from a height of 298 up to 22 a.s.l.

Dimension stone industry (extraction and, in special, processing) is one of the pillars of the Galician economy and its perspectives in terms of growth along the next decade are very promising. The national income from the exportation of finished granite amounts to 123.8 M€, 60% of which come from Galicia.

From the geologic point of view, the rock mined in the quarries of the Porriño region belongs to the unit called Porriño pluton, a late Hercynian batholith (i.e. unaffected by the main deformations of the Hercynian orogeny) which extends from the north of Porriño to Tuy, in the south, and towards Pontearreas to the east. It is a complex igneous massif made of biotitic monzogranites that develop different facies. Among these, the most notable rock group from a commercial point of view is the world-renowned Rosa Porriño, which is characterized by its striking pink tonality due to the major development of iron oxide-bearing microcline

megacrystals (Sánchez et al. 2005). The chemical composition of this rock is presented in Table 1.

Granite mining operations are spread over several small hydrographic catchments which drain into the Louro river, a tributary of the Miño river. The Louro river has historically been subjected to strong anthropic pressure since it is the site of a booming industrial activity. As a result, the water quality of this river has become in recent years very poor. The effect of the operations involved in granite mining over the Louro river is rooted basically in the flushing and transport of fines caused by the runoff from rainfall. Given the nature of the quarry operations, a significant amount of fine materials are produced and they are not absorbed by the vegetative land cover, as would happen in a natural catchment. These fines, lacking cohesion, are washed away by rainfall and transported by either suspension or saltation, from the higher zones of the catchment to a certain number of drain points, which end up being discharge points into the Louro river.

Table 1 Representative chemical composition of the Rosa Porriño-type granite

	Weight (%)	Element	Concentration (ppm, $\pm \sigma$)	Element	Concentration (ppm, $\pm \sigma$)
SiO ₂	71.9	V	8.8 ± 0.3	Sb	0.23 ± 0.02
Al ₂ O ₃	13.7	Cr	7.8 ± 0.4	Ba	81.2 ± 4.1
Fe ₂ O ₃	2.55	Ni	3.2 ± 0.3	Hg	< 0.1
CaO	0.94	Cu	0.85 ± 0.09	Pb	27.9 ± 0.1
K ₂ O	6.94	Zn	46.0 ± 1.0	U	4.4 ± 0.2
Na ₂ O	3.34	As	3.2 ± 0.1	Mn	~194
MgO	0.25	Se	< 1.2	Rb	~137
TiO ₂	0.20	Mo	1.9 ± 0.1	SrO	~51
P ₂ O ₅	0.05	Cd	0.081 ± 0.005		

The tributary area flowing into each of the drainage catchments depends on the evolution of the mining operations, which means that the concept of “drainage catchment” is somewhat vague in this zone. Catchments in the quarry studied can be divided into two general types: those in which the man actions have completely changed the original surfaces (vegetation, soil structure, natural drainage, etc.) and those which still retain a pseudo-natural surface.

The aim of this study is twofold: first, to analyse and characterize the hydraulics of the quarry system and the hydrologic water balances; second, to identify the main pollutants mobilized in the mine by surface water flows and to assess their impact over natural waters. This has been accomplished by studying both concentrations and mobilized loads (total, dissolved and particulated pollutants).

Materials and methods

Methods

Given the singularity of the study area it is not advisable to use the conventional hydrological models. Although some of such models could potentially provide reasonable answers, it would be very difficult to adequately assess the parameters needed for them as long as the soil uses in the quarry are not typified. Thus, it is preferred to directly record the hydrological parameters, associated flows and contaminant loads over the course of an extended period (10 months).

Attending to specific characteristics of the system, we have developed an adapted methodology for sampling and analysis. Hence, in order to record rainfall, we employed an integrated rain gauge that was installed in a central location of the quarry. To analyse the flows generated along the mining operations, five flow meters were installed to record data at maximum intervals of 2 min.

On the other hand, in order to characterize the pollution, we followed two complementary strategies. First, random samples (in both time and space) were taken throughout the quarry in the different control sections. Second, rainfall-runoff events were characterized by means of automatic samplers. An “event” was programmed when there were significant variations in the level measurements of the running flow in the different sections monitored, due to rainfall or an occasional discharge. The threshold level was determined after the post-processing of results during 2 months. The samplers are able to collect up to 24 simple samples. All the samples taken underwent a complete series of analytical determinations, including solid content (dissolved, particulated, etc.), selected metals, organic pollution, nutrients, etc.

To evaluate the differences between the dry season and the rainy season, the equipment was kept in place for 10 months, covering a winter and a summer period. The load associated with the surface flow was obtained from samples taken in periods with no rainy days.

The treatability of the samples was studied in the Environmental Sanitary Engineering Laboratory of the Civil Engineering School in the University of A Coruña.

Control program

The shape and surface characteristics of the several catchments into which the quarry may be split constrains their respective behaviour in a great manner. Therefore, the definition of sub-catchment in this terrain is not a priority owing to the special characteristic of the environment. Given these peculiarities, it is more important to choose adequate checkpoints in order to record water levels, flows and pollution.

The characterization of the flowing surface waters was based on five checkpoints located at the lowest part of the slope where quarrying is carried out. These checkpoints are situated close by, on either side of the road running parallel to the quarries which serve, to some extent as a hydraulic barrier.

Control stations 2, 3 and 4 are located in close proximity to the road and the quarries and, during the dry season, natural flows are nearly null. However, when rainfall events occur, they receive a significant volume of water and contaminant load. All of them collect the waters channelled from the zones having the greatest activity in the quarries and, therefore, they constitute key points to analyse the problem in detail and provide management solutions.

The checkpoints labelled as control stations 1 and 5 are completely different from the above characteristics. They are located in what we can identify as a “rural” area, i.e. an area not affected by the quarry activities where we can find the only permanent watercourse of the system. Although it has variable flows depending on the rainfall and quarry works, the stream has a small, but permanent, water flow and the associated pollution levels are far less when compared with the rest of control stations (Fig. 2).

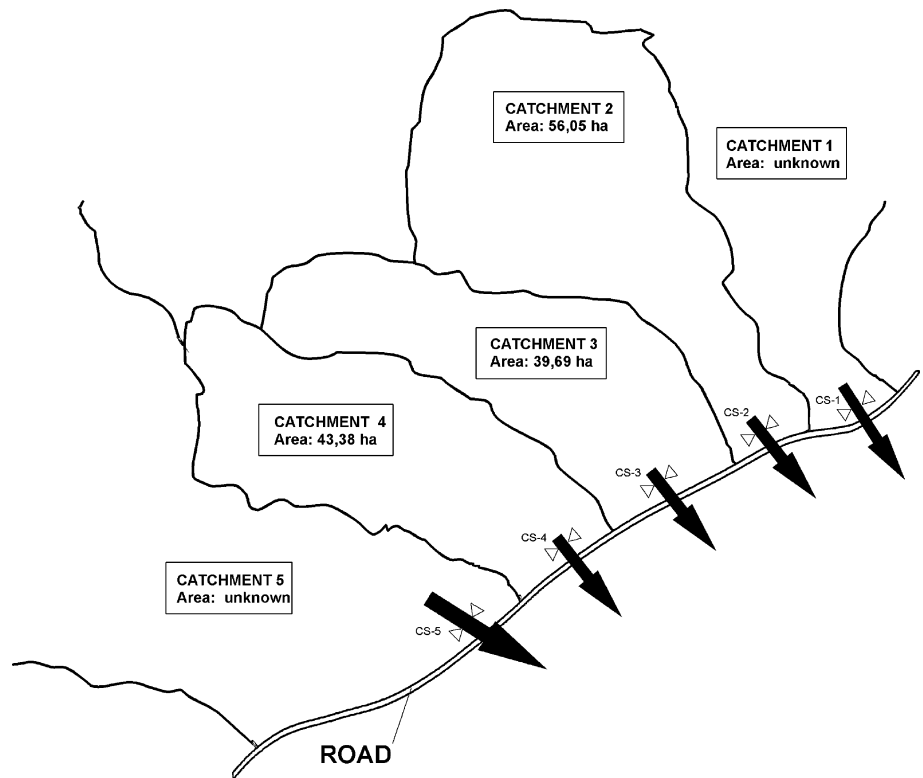
The surfaces of sub-catchments 2–4, where quarry work is carried out, are summarized in Fig. 3.

Different types of equipment were installed in the quarry in order to characterize the hydrology of the system and the concomitant pollution loads. Rainfall was monitored with an aerodynamic rain gauge ARG100 equipped with a pulse register recording data every 2 min. The flows were computed based on the depth measurements taken in the five sections by means of LIT-25 ultrasound sensors and Tinytag Plus dataloggers, which recorded data every 2 min from January



Fig. 2 Location of control station no. 5

Fig. 3 Sketch and area of the catchments with quarry work



until October of 2001. To obtain the circulating flows in the study area, five triangular weir stations were built 60° on the vertex. Sediments accumulated in the lower area of the weirs were removed regularly to prevent distortion in the measurements.

Water samples corresponding to rainfall events or to what was earlier defined as relevant flows were collected with the aid of two SIGMA-900 automatic samplers placed in the five control stations.

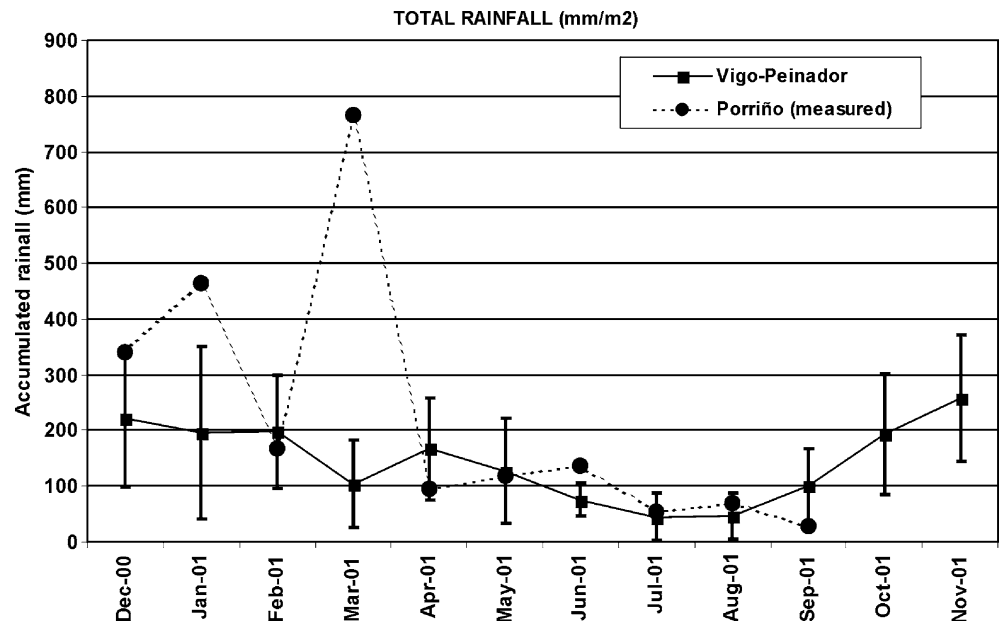
Results

Hydrological characterization

The weather station of the Vigo-Peinador airport, located in the vicinity of the quarries, provides data that were used as a basis for comparison with our ARG100 time series record (Fig. 4).

Based on that comparison, we can observe that the period analysed may be considered as particularly rainy, with a cumulative value of $2,238.8 \text{ L/m}^2$ for the 10 months covered (annual average of $1,700 \text{ L/m}^2$). Thus, the transport of pollutants to the receiving water system has been characterized within the context of heavy and continuous rainfall, as well as during sporadic rainfall events.

Fig. 4 Comparison of the rainfall recorded in the quarries studied and the mean monthly precipitation with the standard deviation, recorded in a nearby meteorological station (Vigo-Peinador airport, 1982–1993)



An interesting piece of information is the unit volume contributed by each catchment, in other words, the volume of runoff water per millimetre of rainfall. This gives us an idea of the size of the catchment and is the basic element in the design of infrastructures (Table 2).

As can be seen, catchment 5 generates a substantial amount of the total volume. This is of interest insofar as, taking into account the lower pollution levels measured, the water from catchment 5 must undergo some sort of natural attenuation during its circulation through the permeable catchment. However, in station 3 the mean flow is very low, although during some events it may increase considerably. These differences are illustrated in Fig. 5, which allows us to corroborate the low permeability of catchment 3, with a small storage capacity, which is common to catchment 4. However, the behaviour of catchment 5 is different owing to the existing vegetation, which produces a certain low permeability there and the presence of a base flow as discussed earlier.

From the hydrologic data records and taking into account the hydromorphologic properties of each catchment it is possible to assess a global water balance through the use of an integrated descriptor or coefficient.

We will call this coefficient as “mean runoff coefficient” and can be computed from the total volume registered in the control sections and the total rainfall volume.

It is evident that the values of the so defined mean runoff coefficients do not correspond to an impervious catchment. Hence, the retentions in the watercourses, the infiltration through fractures or epidermal (i.e. sub-surface) flows in some areas, will determine the complex hydrological balance in this type of catchments.

Characterization of pollution

The pollution generated in the catchments studied is mobilized and transported towards the receiving water system according to two different ways: (a) during dry periods and (b) during rainfall events. In the dry periods, the flows generated mainly come from the quarry activities described in previous sections.

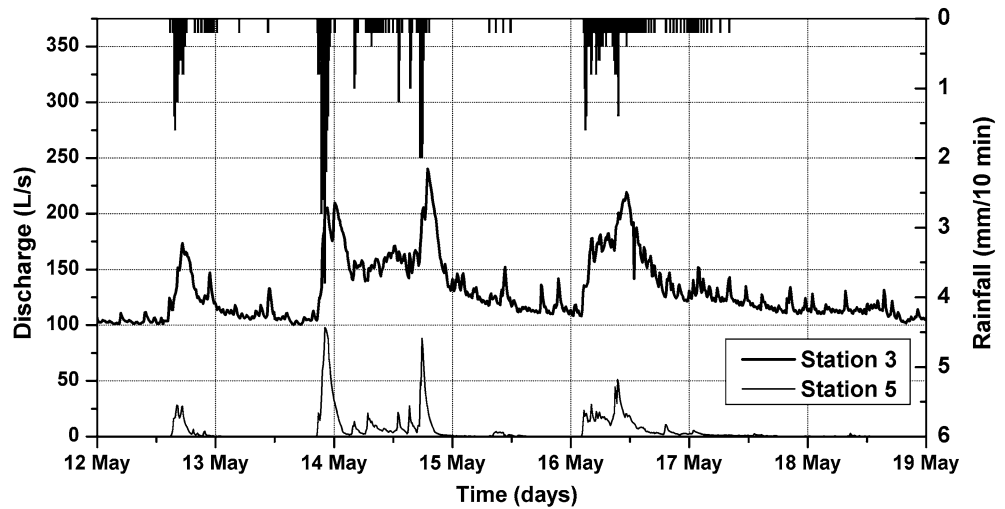
In view of these mobilization schemes, two strategies were established for their characterization and analysis. The first entailed the collection of random samples in all the control sections in a number that would be repre-

Table 2 Volumes, flows and computed “mean” runoff coefficient in the area under study (10 months)

Sub-catchment	Total volume (m ³)	Maximum flow (L/s)	Mean flow (L/s)	Cumulative rainfall K (mm)	Area A (Ha)	Total rainfall volume (m ³) (T = KA)	“Mean” runoff coefficient (TV/T)
1	297,472	358.28	14.89	1,188	Unknown	Unknown	–
2	83,073	95.03	5.87	998	56.054	559,418.9	0.15
3	69,556	101.14	3.03	396	39.689	157,168.4	0.44
4	26,309	95.76	1.18	396	43.378	171,776.9	0.15
5	2,262,578	691.75	98.43	1,695	Unknown	Unknown	–

Cumulative rainfall is different between control sections, related to the time interval where level transmitters worked properly

Fig. 5 Comparison between water flows recorded in stations 3 and 5



sentative of the pollution during the dry periods. The other strategy focused on the evolution of the pollutant fluxes during rainfall events or the appearance of unusual flows (occasional discharges) in the control section where the random samples reflected the highest levels of pollution.

With the automatic sampler used, in some cases, we were able to obtain as many as 24 samples during one event. The time interval between samples used in this study (5 min between the first 12 samples and 15 min between the following ones) made it possible to follow an event for 4 h.

Both the 52 random samples as well as the 192 samples taken during a rainfall event were analysed (APHA et al. 1992), resulting in a large number of pollution parameters: pH, turbidity (NTU), conductivity (EC, $\mu\text{S}/\text{cm}$), nitrites (mg/L), nitrates (mg/L), ammoniacal oxygen (mg/L), chemical oxygen demand (COD, mgO_2/L), total solids (TS, mg/L), total dissolved solids (TDS, mg/L), total suspended solids (TSS, mg/L), total volatile solids (TVS, mg/L), total fixed solids (TFS, mg/L), fixed dissolved solids (FDS, mg/L), volatile dissolved solids (VDS, mg/L), fixed suspended solids (FSS, mg/L), volatile suspended solids (VSS, mg/L), sedimentable solids (Ssed, mL/L), total carbon (TC, mg/L), inorganic carbon (TIC, mg/L), organic carbon (TOC, mg/L) and some selected metals: aluminium (Al, mg/L), iron (Fe, mg/L), chromium (Cr, $\mu\text{g}/\text{L}$), manganese (Mn, $\mu\text{g}/\text{L}$), nickel (Ni, $\mu\text{g}/\text{L}$), copper (Cu, $\mu\text{g}/\text{L}$), zinc (Zn, $\mu\text{g}/\text{L}$), arsenic (As, $\mu\text{g}/\text{L}$), cadmium (Cd, $\mu\text{g}/\text{L}$), mercury (Hg, $\mu\text{g}/\text{L}$) and lead (Pb, $\mu\text{g}/\text{L}$). Relations: $\text{TS} = \text{TDS} + \text{TSS}$, $\text{TS} = \text{TVS} + \text{TFS}$, $\text{TDS} = \text{FDS} + \text{VDS}$, $\text{TSS} = \text{FSS} + \text{VSS}$, $\text{TC} = \text{TIC} + \text{TOC}$.

Random samples taken at the beginning of the study underwent the complete series of analytic determinations, examining the possible presence of different species of nitrogen to determine whether or not they could be used as a tracer of fecal waters. A thorough analysis

of the solids was carried out to detect the possible presence of organic components that would allow us to justify part of the high COD measured and which would also serve as an indicator of fecal waters. After we evaluated the presence of organic pollutants and verified their low levels, we decided to focus these analytical determinations on the remaining solid fractions. The resulting values shed light on the pollution mobilized from the standpoint of both concentrations and mobilized loads.

To facilitate the interpretation of the mobilization of the pollutant loads, a specific methodology was used. The basic tools on which this methodology is based are the computation of a parameter called “event mean concentration” (EMC), the balance of loads crossing the control section and statistical analysis (correlation matrices, accumulated probability analysis, etc.).

The variability of the events and the way in which they occur may be very high. This is why some authors (Sansalone and Cristina 2004) propose an approach that includes working with mean concentrations weighted with the flow to obtain an EMC. Its mathematic expression would be as follows:

$$\text{EMC} = \frac{\int_0^t q(t)c(t)dt}{\int_0^t q(t)dt},$$

where EMC is the “event mean concentration”, $q(t)$ is the instant flow in the hydrograph and $c(t)$ the concentration for each time.

Since random variables are involved, the analysis of these variables may be done using probability distribution functions. This technique requires the selection of a specific probability function and then it is necessary to verify the fit of the data arranged according to this type of distribution. In this study we tested different types of

probability functions, particularly those known as log-normal, logistic, extreme value and weibull. In all the probability analyses carried out, the log-normal distribution provided the best fit to our data measurements and the parameters used, although the weibull function also provided a good fit in some specific analyses. In general, lognormal function is the one recommended in the literature as one of the most suitable for the analyses of phenomena related to hydrology and pollution (Butler and Davies 2000).

The different functions were fitted by means of the maximum likelihood method, used as a parameter for goodness of fit, the Anderson–Darling statistic, unbiased with regard to the number of points used. The lower the value of this statistical parameter, the better the fit. A number close to 1 indicates a good fit, while a value greater than 2 is clearly a poor fit. The corresponding confidence interval was associated with each curve having a 95% significance level. This resulted in two curves that accompany the regression line on both sides. The fit is considered to be more reliable, when the interval between curves is smaller.

Random samples

Random samples were collected in the five control stations at different times to determine the evolution of the pollutants, during both the rainy season and the period without rainfall. The values obtained in control station numbers 3–5 are presented in Table 3.

Of note are the extreme pH values measured in some of the samples: 10 pH units in station 3 and 11.3 in station 4. The value of 2.7 pH units obtained in station 5 is clearly abnormal and may be accounted for owing to the industrial discharge unrelated to the mining activities.

In the random samples from stations 3 and 4 the COD values obtained show maximums of 272 and 154 mg/L, respectively. Station 5 exhibits significantly

lower COD values. The values corresponding to the different forms of nitrogen are negligible.

The suspended solids have relatively high mean values in stations 3 and 4, as high as 3,887 mg/L. The mean dissolved fraction of solids accounts for less than 10% of the total solids (station 4). Station 5 once again exhibits much lower values for solids, with a mean value of 243 mg/L, and with a ratio between TS and TDS around 50%. The values corresponding to carbon, in its different forms, although scarce, confirm the low incidence of pollution from wastewater of domestic origin (operators, workers, etc.).

Samples associated with rainfall events

The samples analysed to characterize pollution associated with rainfall events were collected in both the wet and dry stations. Moreover, the automatic samplers were installed in stations 3–5, since in the first two stations our aim was to analyse the situation in locations without a base flow, whereas in station 5 we were interested in determining the evolution of the pollution in an important natural flow. On the basis of the criterion described, 11 events were characterized and a total of 192 samples were analysed. However, in the subsequent analysis, only eight events, considered to be significant on the basis of the results, were selected. The values obtained for solids and COD are given in Table 4.

The EMC obtained in control stations 3 and 4, with values for suspended solids between 4 and 36 g/L, is a clear indication that, in the flows generated during rainfall events, large loads of solids are mobilized. For the most part, they are suspended solids, while the dissolved fractions in stations 3 and 4 account for less than 5% of the total solids, and in most cases, they are under 2%. Control station 5 continues to show ratios of around 50% between dissolved solids and total solids.

Table 3 Characterization of the pollution of the random samples in stations 3–5

	Station 3 (n = 10)		Station 4 (n = 11)		Station 5 (n = 10)	
	Mean	Max	Mean	Max	Mean	Max
pH	8.9	10.0	7.5	11.3	5.9	7.1
Turbidity (NTU)	920.0	4,090.0	1,252.4	5,300.0	182.0	775.0
EC (mS/cm)	505.5	2,610.0	260.4	1,458.0	184.4	1,164.0
COD (mgO ₂ /L)	107.7	272.0	45.2	154.0	16.2	53.0
TS (mg/L)	4,116.4	15,106.0	2,266.8	6,456.0	242.7	964.0
TDS (mg/L)	229.6	620.0	228.9	736.0	125.5	610.0
TSS (mg/L)	3,886.8	14,486.0	2,037.9	5,981.0	117.3	354.0
TVS (mg/L)	127.4	348.0	50.0	72.0	83.3	406.0
TFS (mg/L)	3,348.0	11,118.0	1,041.3	2,342.0	120.0	260.0
FDS (mg/L)	130.8	152.0	202.0	724.0	83.7	222.0
VDS (mg/L)	40.2	71.0	18.0	34.0	104.0	558.0
FSS (mg/L)	3,217.2	10,968.0	839.3	1,618.0	113.7	426.0
VSS (mg/L)	87.2	292.0	32.0	60.0	26.7	132.0
Ssed (ml/L)	24.5	96.0	3.6	26.0	31.0	31.0

Table 4 Event mean concentrations, maximum concentrations and total load mobilized in the eight events analysing solids and COD

Station	3	3	3	4	4	5	5	5
Date	09/Feb	03/Sep	15/Aug	16/Jul	20/Jul	17/Mar	30/Mar	28/Sep
Total event volume (m ³)	405	500	125	12	27	2,811	1,833	126
Event mean concentration (mg/L)								
TS	4,433	4,010	23,592	23,309	37,082	148	107	3,296
TSS	4,251	3,853	23,366	22,922	36,726	69	52	3,201
COD	137	96	1,230	48	296	15	8	139
Maximum concentration (mg/L)								
TS	16,284	12,092	52,734	30,086	55,410	282	306	8,204
TSS	16,108	11,904	52,406	29,682	55,076	196	190	8,054
COD	312	158	2,600	102	560	105	16	281

If we compare the mean event concentrations with the runoff volumes that cross the control section during the sampling period, it is clear that the events with the highest volume have the lowest concentrations and vice versa.

The mean COD values analysed on the basis of the EMC reflect the same order of magnitude as the measurements in the random samples, with maximum values of up to 300 mg/L, with the exception of event August 15th in station 3, where the EMC was 1,230 mg/L, a very high value in these types of runoffs.

Selected metals were only analysed in three events detailed in Table 5, providing the minimum, maximum and mean value of all the samples collected.

Finally, a specific analysis of solid loads per area has been done with five significant events (Table 6). The suspended sediment loads registered in stations 3 and 4, the most altered and those with more activity, range between 0.14 and 0.59 kg/min ha, with a mean value of 0.29 kg/min ha. This value is interesting because it allows carrying out an estimate of the sediment loads that would be necessary to manage in sedimentation ponds or in treatment facilities.

Discussion

This section details the discussion developed with the probability analysis and the relations between the

different parameters presented, using the Minitab program and following the methodology explained in Results.

Accumulated probability curves of all random sample values

Figure 6 shows the fit to a lognormal accumulated distribution function of the values corresponding to COD, TDS and TSS, of all the random samples in all the stations. They represent the overall phenomenon of the water pollution produced in the quarry zone, as it cannot be separated into catchments or situations with or without rainfall.

The three pollution parameters presented reflect a good fit to the lognormal distribution. The more vertical the line obtained, the lower the variation in the concentration values generated. A different behaviour was seen between parameters TDS and TSS. While the latter presents a variation of three orders of magnitude, the TDS generally remains around a magnitude of 10² mg/L. This behaviour indicates that the dissolved fraction is quite constant and is not significantly influenced by accumulation times, runoff volumes or any other factor.

The COD values show a variation of around one order of magnitude but the maximum values are acceptable for discharge towards natural aquatic systems.

Table 5 Concentration of selected metals in three rainfall events

	Station 3 (n = 11)			Station 4 (n = 11)			Station 5 (n = 17)		
	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max
Al (mg/L)	29	526	1,397	32	114	282	51	99	153
Fe (mg/L)	51	999	2,678	38	186	514	71	138	302
Cr (µg/L)	31	456	1,306	ND	ND	ND	ND	ND	ND
Mn (µg/L)	824	14,415	39,109	416	1,875	5,398	1,002	1,942	3,670
Ni (µg/L)	27	442	1,288	7	29	72	15	22	45
Cu (µg/L)	81	822	2,589	23	61	186	58	82	130
Zn (µg/L)	1,045	13,039	28,840	221	1,258	4,093	775	999	2,225
As (µg/L)	17	237	631	21	37	63	ND	24	34
Cd (µg/L)	2	7	15	ND	ND	ND	ND	1	4
Hg (µg/L)	3	4	5	4	4	4	ND	1	4
Pb (µg/L)	87	1,188	3,370	31	129	345	109	146	222

Table 6 Specific sediment load relative to five events in control stations 3 and 4

Suspended sediment discharge during events					
Station	3	3	3	4	4
Date	09/Feb	09/Mar	15/Aug	16/Jul	20/Jul
Sampling interval (min)	245	245	125	20	171
Total sediment discharge (kg/min)	7.3	8.2	23.6	14.6	6.0
Specific sediment discharge (kg/min ha)	0.18	0.21	0.59	0.34	0.14

Accumulated probability curves of the event samples in control stations 3, 4 and 5

First of all, results of parameters COD, TDS and TSS, corresponding to every sample in all of the events (Fig. 7), are presented. Since the values of the three control sections were taken at the same time, it is possible to see that the values for TDS again show a homogeneous behaviour with values of around 10^2 mg/L, which reflects their stability when faced with any hydrological or mining operation situation.

The fit of the TSS values is poor, but interesting in terms of the three sections that present actual data. Although other functions found better adjustments, for example weibull distribution with an Anderson–Darling statistic of 1.61, the lognormal one is presented to maintain coherence with the rest of the results, and also following recommendations in the literature. No evidence was found to change the lognormal distribution. A minimum asymptotic value (around 10–20 mg/L) and a maximum asymptotic value (around 50,000 mg/L) can be seen. The mean value of the samples associated with the event is estimated at 2,000 mg/L.

The values for COD concentrations range between 5 and 2,500 mg/L, with a mean value roughly equivalent to 100 mg/L, with a good fit of the lognormal function. Contrary to the numbers detected in random samples, it is important to notice the high values measured during events, clearly problematic for the receiving waters.

Accumulated probability curves of selected metals in control stations 3–5

Figure 8 displays the same analysis for selected metals, with the comparison of the results for iron, copper and zinc with random and event samples. These three metals were selected due to the special characteristics of their presence in the runoff waters, as was shown in previous results (Table 5) and will also be detailed later.

All the metals were clearly fitted to the Anderson–Darling (AD) statistic under 1.5. It is interesting to note that all the results show a similar behaviour pattern, with straight lines having similar slopes. The data occur in a parallel fashion in the analysis of random and event samples, which means that their presence has a certain

Fig. 6 Accumulated probability curves of the random samples (COD, TDS and TSS)

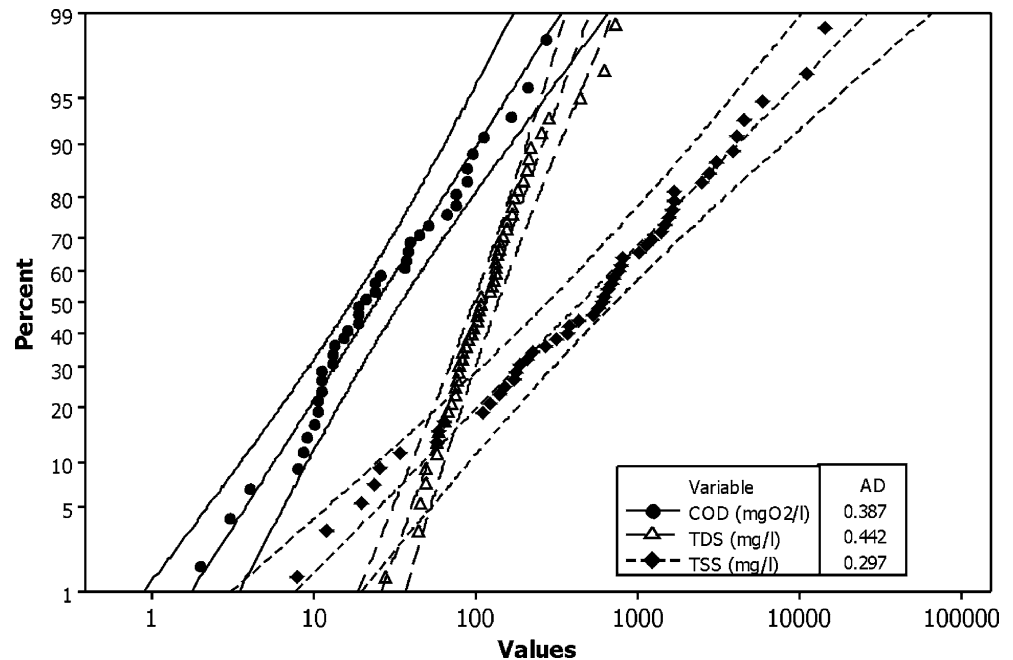
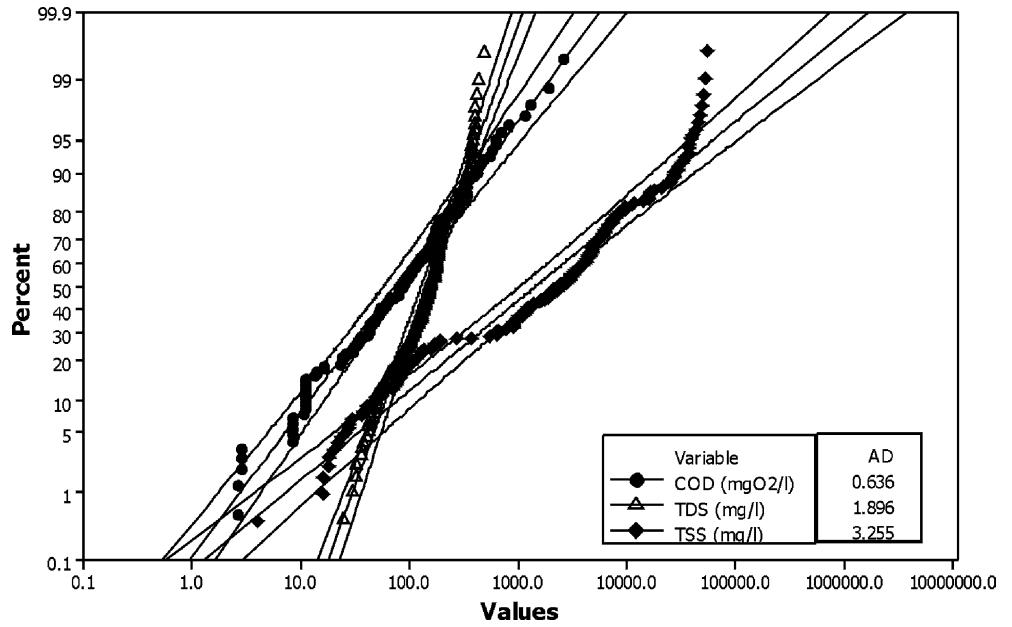


Fig. 7 Accumulated probability curves of the samples associated with events (COD, TDS and TSS) (stations 3–5)



proportionality, having values of an order of magnitude greater between them.

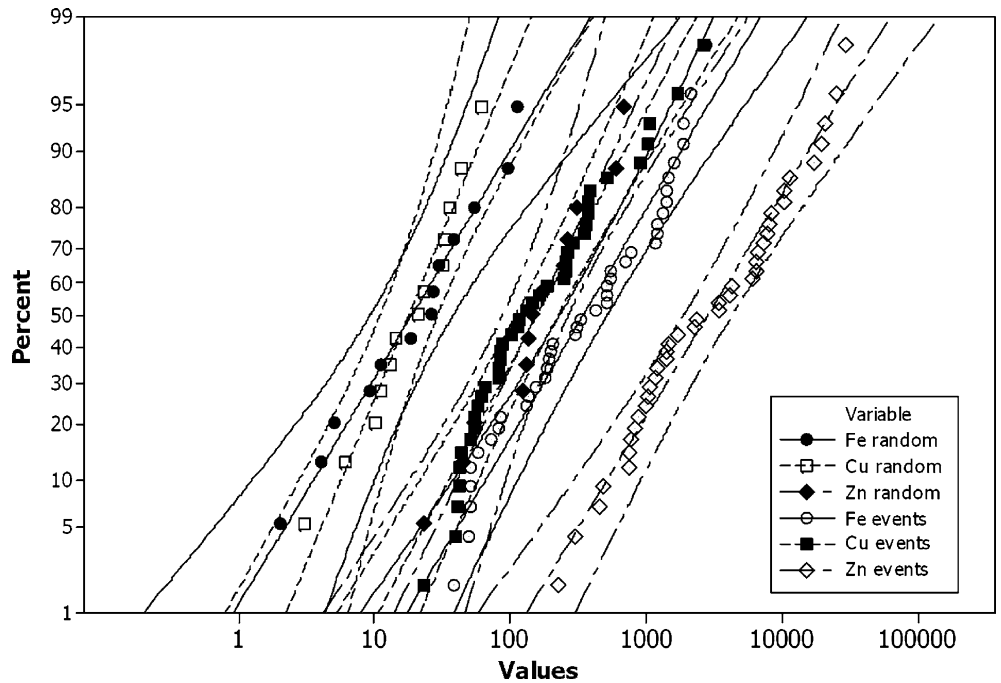
The results also show low and high concentrations in certain intervals, which means that there was a considerable gap in the values analysed, associated with the samples from control stations 3 and 4, and control station 5, respectively. Moreover, this behaviour is similar to that obtained analysing suspended solids in random and event samples (Figs. 6 and 7).

Correlations

We have performed a correlation study including the analysis of the random samples considering first all the sections together and, second, all the samples associated with events.

In the correlation matrix obtained with the random samples, the following aspects may be underscored:

Fig. 8 Accumulated probability curves of iron (Fe, mg/L), copper (Cu, µg/L) and zinc (Zn, µg/L) in random and event samples



- Turbidity correlates with COD with a value of 1, similar to the TS and SS. Therefore, the COD is associated with the quantity of total solids and the SS, which represent the majority. Conductivity correlates with 0.83 of the TDS and VDS, which is consistent. In spite of the fact that the samples were often collected during the dry season, they show an interesting correlation (0.86) between SS and Ssed. We may also highlight that the pH had no correlation with any other element.

In the correlation matrix obtained with the samples associated with the events (3–5) the following aspects are worthy of mention:

- The pH correlates with the VDS, but not the FDS. This may be attributed to the volatilisation of bicarbonates and carbonates in the dissolved solids tests. Turbidity decreases in value in correlation with the COD (0.53), but it remains of interest as regards the SS (0.93). The conductivity decreases in relation to the TDS (0.53) but it remains of interest with the SDV. The correlation of the COD is high in relation to the FSS (0.83). In order to assure this relation, a laboratory experiment was carried out using an artificial suspension of 4 g/L with material from the sedimentation ponds. Three types of sample preparation were done: drying at room temperature and in a drying chamber at 40 and 550°C. COD obtained were 31.6, 36.9 and 0, respectively, that confirms the COD origin is organic matter, and perhaps oxidation of certain compounds such as Fe-II to Fe-III.

In the samples associated with events, the selected metals were also analysed which gave rise to the following aspects. The metal concentrations do not correlate with the dissolved solids, which would indicate that they generally appear in particulate form. This behaviour coincides with the highest correlations of the SS with all the metals (greater than 0.9, between 0.9 and 0.85), less than Ni (0.73) with Cu (0.59) and Zn (0.76), which show anomalous behaviour.

The metals Al, Fe, Cr, Mn, As and Pb are all inter-correlated with values close to or greater than 0.9, which would point to a common origin, in principle, the mineral matrix. In contrast, Ni and Cu do not exhibit a similar correlation and Cu reached values under 0.6. Zn presents an intermediate value of around 0.8 with all of them except Ni (0.28) and Cu (0.22), which would suggest sources coming from the outside or different from the mineral matrix.

Analysis of the anomalous presence of some selected metals

The characterization of pollution from the standpoint of the origin of the metals is another aspect of interest in this paper. Table 1 shows the chemical composition repre-

sentative of the rock being mined in the quarries under study. Moreover, as seen in the section above, water pollution due to transport owing to rainfall presents certain behavioural patterns, which, from the point of view of statistics, translates to correlations between parameters and/or elements. However, it is not easy to interpret these correlations; so, in order to understand the origin of the pollution, it is necessary to use other discrimination techniques. Figures 9 and 10 present the comparison between the representative composition and the measured concentrations for the metals being studied in this paper, with random and event samples, respectively.

In the previous figure, filled circles represent the mineral matrix concentration, and boxes include the 75% measured concentrations for all samples (central line is the mean value, little black box is the median). Lines outside the boxes cover 95% of measured values, and external asterisks are outliers.

Preliminary approach can lead to the conclusion that when the concentration coincides with the mean concentration of the granite, then the element in question has been incorporated into the transport, primarily through the granite itself. Such is the case for random samples of Al, Cr, Cd and Pb. However, there are cases in which the concentration is clearly higher than what would pertain to the same element in the granite (e.g. in the cases of Fe, Mn, Ni, Cu, Zn, As and Hg), in some cases with a variation of around one order of magnitude. This would suggest that there are external contributions to the granite, whose origin must be attributed to the different elements of the productive cycle (machinery, tools, etc.).

Some differences can be found with the event samples analysed (Fig. 10). There is only an important enrichment of anthropic contributions in the context of the productive cycle of the granite in some metals (Fe, Cu,

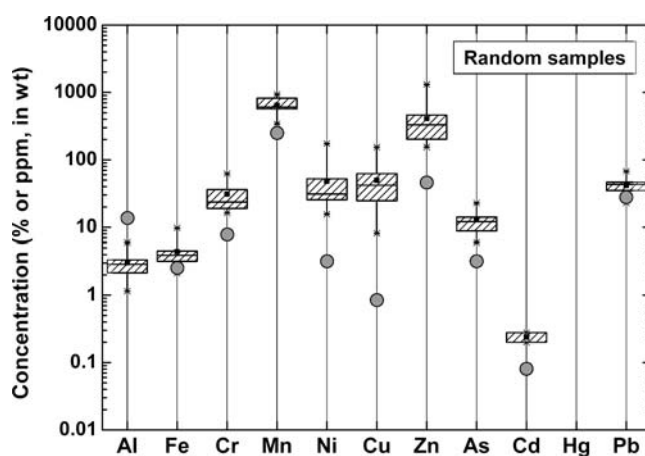


Fig. 9 Random samples. Comparison between the representative composition of Rosa Porriño granite and measured concentrations for selected metals. The concentrations of Al_2O_3 and Fe_2O_3 are expressed in wt%, the rest of the metals in ppm

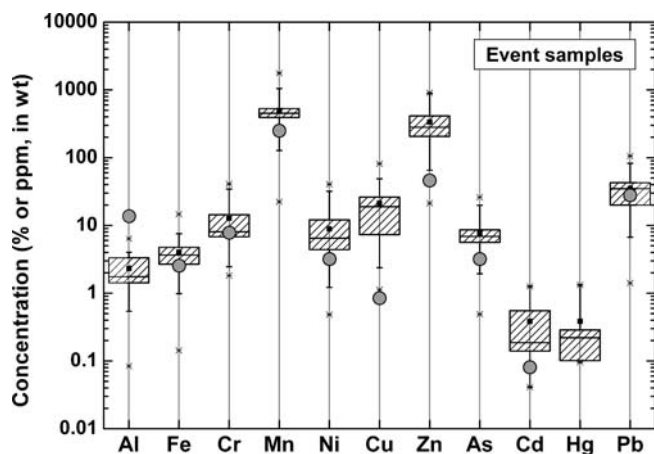


Fig. 10 Event samples. Comparison between the representative composition of Rosa Porriño granite and measured concentrations for the selected metals. The concentrations of Al_2O_3 and Fe_2O_3 are expressed in wt%, the rest of the metals in ppm

Zn), with low concentrations of Cd and null values for Hg.

In this case it is interesting to note that the concentration tends to be lower than in the random samples. Under these circumstances, the sudden contribution of water will lead not only to a greater mobilization of fine materials from the quarries, but also to a minor anthropic contribution. Because of that, this anthropic contribution of some selected metals is greater in dry periods than in significant events.

Conclusions

The most important conclusions drawn in the article are listed as follows in the same order as the presentation of the results.

First of all, it must be noted that the year under study was especially rainy, with a precipitation of $2,239 \text{ L/m}^2$ in 10 months, as compared to an annual average of $1,700 \text{ L/m}^2$. The total volumes in the time period analysed, in terms of both unit flows and

maximum and mean flows recorded, reflect that some of the sub-catchments (2–4) only transport water during the rainy season, while sub-catchment 5 retains an important base flow. Specific rates of accumulate rainfall-runoff per hectare have been obtained, with values of 0.15 and 0.44. These numbers do not correspond to a completely impervious catchment, which indicates the complex hydrological behaviour of this type of catchment.

The analyses of the samples collected along the field survey show that the main source of pollution came from suspended solids, which originate from the inorganic mining activity. The COD is also a pollutant, with values that cannot be considered negligible, but it always appears associated with suspended solids.

Maximum concentrations in control sections have been measured, with values up to $55,000 \text{ mg/L}$ of suspended solids and $2,600 \text{ mg/L}$ of COD. EMCs have reached $36,700 \text{ mg/L}$ in suspended solids and $1,230 \text{ mg/L}$ of COD. Suspended sediment discharge registered in catchments 3 and 4, the most altered and those with more activity, range between 0.14 and 0.59 kg/min ha , with a mean value of 0.29 kg/min ha .

In the random samples as in those associated to events it is proven that the dissolved fraction is homogeneous, reflecting stable values in any hydrological situation or productive cycle of the catchment. A high correlation between suspended solids and metals, except Ni, Cu and Zn, has been detected. Also, poor correlations were obtained among these three metals, pointing to the existence of an external source from the representative composition of the existing granite.

This conclusion is reinforced with the statistical analysis of measured concentrations of selected metals compared with the mineral matrix of Rosa Porriño granite. There are significant increases of some metals in random samples, in particular Fe, Mn, Ni, Cu, Zn, As and Hg. In event samples the excess of concentration in Mn, Ni, As and Hg disappears, but maintains the hypothesis of anthropic contributions in Fe, Cu and Zn.

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