Characterization of polluted runoff in a granite mine, Galicia (Spain)

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Abstract

Mining works in the quarries of Porriño council, in the Northwest of Spain, consist in the block extraction of Pink Granite Porriño. The sawing and processing induce the presence of huge amount of fine sediment (silts and clays). The quarries extend over an area of about 10 hectare and they are subdivided in six sub-basins, where water flows carrying these sediments until the Louro River.

Fig. 1. Porriño granite quarries

The main objective of this research is to analyse and find solutions for the sediment loads carried in normal and extraordinary events of rainfall. Instrumentation to measure the main variables consisted in a rain gauge inside the quarries, and the construction of five control stations with triangular weirs, allowing to determine water discharges. During nine months, and every two minutes, these vari-

ables were registered, permitting a relationship between rainfall and discharges in each sub-basin. Total rainfall of 2239 millimetres showed a year of high levels of rainfall in the region.

Measurements of sediment loads and the consequent contaminations were analysed through samples of flowing water in the five stations. These samples were collected in normal situations, up to 55, and also in extraordinary rainfall events, through the operation of two automatic samplers, that collected 24 samples when a certain depth was exceeded in the stations. With a frequency of five and fifteen minutes, 11 extraordinary events were collected, with 192 samples.

With all this data relation of water and solid discharges was obtained. Metals were also measured in the majority of the samples, analysing the impact of the quarries work. The contamination was obtained with different indicators, such as event mean concentration (EMC), normalized mobilization of sediments, and statistical analysis (matrix correlations, accumulated probability analysis, etc.). The main conclusion is the high degree of correlation between the contamination parameters and the suspended sediments. Values of 52.000 mg/l were obtained in some cases, COD´s higher than 820 mgO_2/l, and turbidity around 9100 FTU.

The solution proposed to the company that financed the research was the design of sedimentation ponds including a chemical active treatment. These structures with retention times around three hours did not achieve water quality good enough for returning to the natural aquatic system. With a process of coagulation, flocculation and clarification, good water even for reuse was obtained.

1 System description and problems

Extraction activity in the granite mining sector is the main economic richness in the region of Porriño (Pontevedra, Spain). This open-pit mining produces an impact on the environment that will be presented here in those aspects relative to the pollution of runoff.

The granite exploitations in Porriño extend over several small hydrographic sub-basins that are tributaries to the Louro River, a tributary itself to the Miño River, with an overall extension of about 10 ha. The Louro River has always suffered a high anthropic pressure from this very industrialized area. The water quality reached very deficient values in the past years. The main pollution impact on the river is the flushing of fine sediments in the surface runoff. The granite quarries produce a huge quantity of fine sediments that can not be retained as the basins are highly degraded, with no vegetation cover, as could be the case in a natural basin. These non-cohesive fine sediments are flushed by the runoff and transported, either by suspension, or by saltation, from the highs of the basins to several drainage points.

The tributary area for each drainage point changes with the time evolution of the quarry exploitation, and thus the concept of basin is a little diffuse. This peculiar and changing morphology of the area is one of the most important goals in this study, for it neither being natural nor artificial in a strict sense, and for its geometry not being standard hydrographic basin like.

The sources of pollution that appear in the open-pit mines are the result of the different industrial activities or processes held in them. Thus it is very important to typify the activities in the extraction fronts (drilling, wire sawing, block handling, residue extraction, machinery movements), the activities in their surroundings (erosion of the roads, wastewater generation, machinery cleaning water, settling tanks, incidental spills of oil and petrol) and those complementary works such as crushing and concrete plants.

It is important to emphasize that the basins are very different from each other, due to their particular soil impermeability. In several basins there is a small amount of accumulation in the soil, and then a delayed runoff due to subsurface flow. In other cases, there is only runoff in rain time. The pollution level and the management strategies for its control in both cases are quite different, as the subsurface water has a relative small contamination level, even sometimes under the permitted maximum levels for spills, but a direct runoff is far from this situation.

The principal objectives of this study have been separated in three main blocks:

- Hydrologic-hydraulic objectives: Analysis and characterization of the rainfall-runoff relationship for the different precipitations along the year.
- Pollution objectives: Analysis of the pollution load detected on discrete samples in transient events associated to the same flowrate, developing methods to characterize these events.
- Proposal of solution (storage, settling, treatment, and reuse) to guarantee the best management practices from an environmental point of view.

2 Planning and methodology

Analysing a hydrologic system in order to obtain the rainfall-runoff relationship can take two ways:

- Build a conceptual model of the rainfall-runoff based on the different soil uses, to establish the transformation rule from rainfall to runoff.
- Register a large campaign of in-situ data for both rainfall and runoff measurements.

As said, these are quite peculiar basins and thus, conventional rainfall-runoff models cannot be used here. Even in that case, as the soil uses are not typified, the parameters in that model cannot be previewed. On the other hand, models involving pollution (solids and other) are not still validated by experience. The choice was then to register a large campaign of events (10 months) measuring rainfall, runoff and pollution loads, to establish the runoff flowrate, pollution loads and pollution highest concentrations for every millimetre of rainfall.

A methodology was established for each of the objectives presented in the first section of this paper.

- A tipping bucket rain gauge and five flowrate metering stations were installed at the area, logging measures each two minutes.
- Random discrete samples of the runoff water were caught at every section in order to typify the pollutants. A large analysis array was performed for them, including solid particulates, metallic elements, organic pollutants, nutrients, etc.
- On behalf of evaluate the different behaviour of the system in both dry and wet periods, the measurement equipments covered ten months, including both winter and summer. During this time, discrete 'events' were monitored using automatic samplers. We mean here 'event' for a substantial increase of the flowrate due to rainfall or an incidental spill.
- The load associated to subsurface flow has been measured in samples not corresponding to rainy days.

The treatability of the samples has been studied at the Civil Engineering School in A Coruña. Sedimentation columns, Jar-tests and filtration essays have been carried for them. Granulometry of the solid loads has also been measured with a Coulter laser analyser.

Fig. 2. Location of control points

As conceptual rainfall-runoff models cannot be used, defining sub-basins in this area is no longer meaningful, and the selection of the points to allocate measuring stations is then critical. Five were identified in the lower part of the hillside where the quarries stand. They are on both sides of the road parallel to the mines. The location of the rain gauge (P) and the stations 1 to 5 can be seen on figure 2. From the quantity and quality point of view of the spills, stations 3 to 5 are the most important. Station 3 is attached to the road, with nearly null natural flowrate, but with substantial water level and pollution in rain time. This station collects the runoff for one of the zones with hardest mining work in the present time, and therefore this is a key station for any study or solution proposal. Station 4 is the only one located inside the quarries.

This control point was placed on a small stream that collects the runoff from the highest parts of the near hillside. As station 3, has nearly null flowrate in dry time, but its position inside the exploitations made it another key station. Station 5 is the only one with an enduring natural flow, and although it increases in rain time, its surrounding vegetal soil set the pollution levels at a lower values than the other points.

Due to the nature of the problem for us to study, equipment for both hydraulics and pollution measuring were installed.

The flowrate was measured at the stations with V-notch weirs and ultrasonic level indicating transmitters (Greyline LIT25) and registered with single channel dataloggers (Geminy Tynitag Plus) every two minutes from January 2001 to October 2001. In the upper part of the quarries hillside, a tipping bucket rain gauge (ARG100) was installed, also with a single channel datalogger. With both measures, rainfall-runoff relationship can now be obtained for every station.

In respect of collecting samples of the runoff water, two automatic samplers (American Sigma 900) were also installed alternatively on the stations. These samplers can be set on different configuration for the bottles inside up to 24 separate samples. They have its own pumping system and can be triggered by an external signal from the level transmitters.

3 Hydraulic-hydrologic characterization

The hydraulic characterization of the system was done on behalf of knowing its rainfall-runoff relationship. This is a key part of the present study, and also for the analysis done during the measuring campaign, as the pollutants and other parameters were registered from the runoff water values. The measurements stood for a period which was considered long enough, including both dry and wet seasons.

Historical rainfall data for the area were available from the weather station at the airport at Vigo Peinador, which is next to the mines. Maximum values in 24 hours from 1982 to 1993 can be obtained. If we compare these values with those registered by the ARG100 rain gauge, the results can be shown on table 1.

Table 1. Historical and measured data for rainfall (millimetres)

	jan	feb	mar	apr	may	jun	jul	agu	sep	oct	nov	dec	tot
Peinador mean	196	198	104	167	127	76	45	46	100	193	257	223	1727
Peinador stdev	154	102	79	92	94	31	42	41	67	109	113	125	349
Porriño measures	463	167	766	95	118	137	54	71	28	n.d.	n.d.	340	2239

The analysed period is clearly an extremely rainy one, with a cumulate value for rainfall of 2239 millimetres in 10 months, which is really higher than the average. Pollutants conveyed by runoff were measured in both heavy continuous rainfall periods and in single storm events were separated from each other in time, collecting an accumulated high amount of particulate solids and other.

For the measuring of the flowrate at the selected location, five stations with a small cubicle were built. Between their legs, a V-notch weir was placed to be used with a level transmitter. Regular maintenance works were performed in order to keep the upstream part of it free of sedimentation.

The morphology of the basins, with very different degrees of impermeability, makes them have a dissimilar behaviour. In particular, station 5, collecting the flow from a basin with some vegetal cover, has a certain amount of subsurface waters, while in other areas there only runoff in rain time.

The first important information about the basin is their unit volume, that is, the runoff flowrate per millimetre of rainfall. These data is basic information about the size of the tributary basins and is a key parameter for the design of equipment.

The total volumes, unit volumes, maximum flowrates and mean flowrates for each sub-basin are in table 2.

Table 2. Volumes and flowrates for all sub-basins

Basin	Total volume (m^3)	Unit volume (m^3/mm)	Max flowrate (l/s)	Mean flowrate (l/s)
1	297.472	250.36	358.28	14.89
2	83.073	83.26	95.03	5.87
3	69.556	175.65	101.14	3.03
4	26.309	66.44	95.76	1.18
5	2.262.578	1335.01	691.75	98.43

Basin 5 has the highest flowrate levels. This fact is very important as basin 5 has some vegetal cover as said, and then it has some delayed runoff and lower values of pollution. Otherwise, station 3 has a very low mean flowrate, but it can increase to extreme values in storm time. These differences are shown on figure 3.

It can be noticed in the figure that basin 3 has nearly null storage capacity (as well as basin 4), and otherwise the behaviour of basin 5 is definitely conditioned by its vegetal cover. Hydraulic characterization of the basins will then follow separate ways for both stations 3 and 4 and for station 5. This divergence will also stand for pollution characterization, whether for random samples, or for storm event samples.

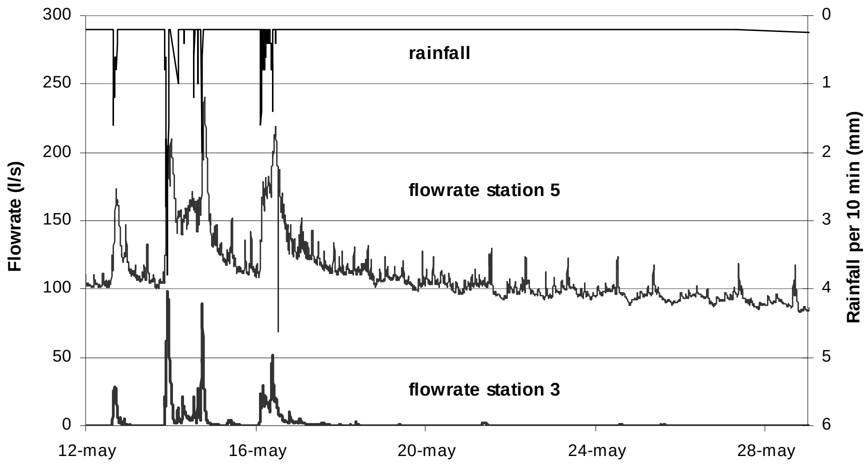

Fig. 2. Rainfall-runoff measures for stations 3 and 5

4. Characterization of pollution.

Two different strategies were then established to analyse the pollution. On one hand, random samples were collected in every station, in such a large number to be considered representative of the main behaviour. One the other hand, in those stations having higher levels of pollution, discrete samples were collected by the Sigma automatic samplers following some threshold of flowrate increase, due to stormwater or an incidental spill. This was studied to find out if there are higher degrees of pollutants mobilized by runoff in the first stages of these episodes, and the final runoff water do not have substantial levels of pollution. In short, if there is some flushing of the basins.

Knowing the time evolution of pollution during a storm event hints discrete sampling. Automatic samplers permit this kind of analysis. They can be triggered by an alarm from the level transmitters, following a previously defined threshold of water level. From this time, they start collecting samples at fixed time intervals up to 24 bottles. The time interval was chosen to be 5 minutes between the first 12 samples, and 15 minutes for the last ones, and then trace the event during four hours.

Both random and discrete samples were studied in many parameters, including pH, conductivity, turbidity, nitrates, nitrites, ammonia nitrogen, DO, COD, carbon (TC, TIC and TOC), solids (TS, TDS, TSS, total volatile solids TVS, total fixed solids TFS, fixed dissolved solids FDS, volatile dissolved solids VDS, fixed suspension solids FSS, and volatile suspension solids VSS) and metallic elements (Al, Fe, Cr, Mn, Ni, Cu, Zn, As, Cd, Hg and Pb). The very first were analysed for the complete set, checking the presence of nitrogen as a tracer of wastewater flow. The solids characterization was very complete on behalf of tracing organic particulates to justify a part of the COD. Once determined that the organic part of the pollutants was quite small, the analysis were focused on tracing solids. For every sample (55 random, 192 storm event discrete) pH, turbidity, conductivity, COD, ammonia nitrogen, TS, TSS and TDS were analysed. All values permit a high degree of knowledge on the pollutants conveyed, in terms of concentration and total mass.

The conveying of pollutants was studied with the help of a specific methodology based on five tools: instantaneous concentration, event mean concentration, mass of pollutants crossing the control section, normalized cumulative mass graphics and statistical analysis (accumulated probability). Three of them are now described.

- Event Mean Concentration (EMC)

As the event variability is very high, some authors suggest working with flowrate weighted averages

$$EMC = \frac{total\_runoff\_mass}{total\_runoff\_volume} = \frac{\sum Q_i \cdot C_i}{\sum Q_i} \qquad (4.1)$$

Q_i for instant flowrate, C_i for instant concentration

- Mass balance

From the flowrate and the concentration measured in fixed interval samples, an estimation of the cumulated mass can be calculated for the different pollutants, and then the specific load for each basin. With these values a time evolution graph (pollutograph) of the concentration can also be drawn.

- Normalized cumulative mass

Normalized cumulative mass graphs permit to determinate if first flush phenomena is happening on the basin or not. Thornton et Saul (1996), as well as Person (1986) define the first flush phenomena as a rainfall-runoff event in which the first stages carry significant higher values of pollution than the final phase. Some factors affecting first flush (Gupta et al, 1996) are the instant of the day, condition and persistence of dry time, amount and singularities of the pollutants, kind of rainfall, drainage characteristics, size and shape of basins, cumulated sediments.

The method to estimate the first flush is to plot normalized cumulative mass emission against normalized cumulative volume (Griffin, 1980). If the plot follows the 45 degrees straight line, there is no first flush. As far as the plot is separated from this bisecting line, the higher degree of first flush occurs. This tracking tool is a key to define the management strategies to control and treat the spills.

5. Analysis and interpretation of results

Here we present the most important results for the present study, for random and event samples. Random samples were collected in different seasons at the five control station to know the pollutant evolution in both wet and dry time. If we focus on stations 3, 4 and 5, the results can be shown in table 3.

Table 3. Analysis results for random samples

	STATION 3			STATION 4			STATION 5		
	min	avg	max	min	avg	max	min	avg	max
pH	7.80	8.92	9.98	6.34	7.47	11.31	2.65	5.95	7.07
Turbidity (NTU)	55	920	4090	158	1252	5300	20	182	775
Conduc (uS/cm)	133	506	2610	50	260	1458	63	184	1164
NO_2-N (mg/L)	0.01	0.04	0.10	0.00	0.01	0.05	0.00	0.01	0.02
NO_3-N (mg/L)	1.00	2.32	4.20	1.50	1.86	2.30	1.00	1.40	2.00
NH_4-N (mg/L)	0.03	0.09	0.27	0.04	0.44	4.24	0.03	0.18	0.87
COB (mgO_2/L)	19.0	107.7	272.0	10.0	45.2	154.0	0.0	16.2	53.0
Solids									
TS (mg/L)	218	4116	15106	254	2267	6456	70	243	964
TDS(mg/L)	96	230	620	58	229	736	28	125	610
TSS(mg/L)	34	3887	14486	122	2038	5981	0	117	354
TVS(mg/L)	38	127	348	34	50	72	10	83	406
TFS(mg/L)	150	3348	11118	220	1041	2342	54	120	260
FDS(mg/L)	96	131	152	52	202	724	40	84	222
VDS(mg/L)	2	40	71	2	18	34	0	104	558
FSS(mg/L)	40	3217	10968	106	839	1618	0	114	426
VSS(mg/L)	0	87	292	0	32	60	0	27	132
SSed(ml/L)	1	25	96	0	4	26	31	31	31
Carbon									
TC (mg / L)	9.70	9.70	9.70	3.07	3.07	3.07	2.45	3.40	5.30
TIC (mg / L)	8.17	8.17	8.17	2.22	2.22	2.22	0.61	1.32	1.67
TOC (mg / L)	1.53	1.53	1.53	0.86	0.86	0.86	0.78	2.09	4.70
Element									
Al (mg/L)	29.59	39.65	49.71	17.85	26.28	34.72	2.52	9.31	16.32
Fe (mg/L)	37.78	74.23	110.69	26.27	39.95	53.64	2.23	35.04	94.09

Cr (µg / L)	15.79	28.56	41.34	15.81	19.65	23.49			
Mn (µg / L)	585.1	1031.7	1478.3	372.6	533.5	694.4	65.7	359.9	840.0
Ni (µg / L)	24.70	25.90	27.10	16.22	25.70	35.17	12.15	18.41	30.00
Cu (µg / L)	35.50	39.27	43.04	10.16	16.36	22.55	2.94	25.32	60.00
Zn (µg / L)	166.9	378.3	589.8	128.4	186.1	243.8	23.3	246.0	670.0
As (µg / L)	10.21	17.47	24.73	7.18	8.96	10.74	1.60	3.97	7.00
Cd (µg / L)	0.27	0.31	0.35	0.00	0.00	0.00	0.00	0.00	0.00
Hg (µg / L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb (µg / L)	41.84	55.10	68.36	24.09	33.26	42.42	3.37	14.73	29.00

Samples to characterize increasing flowrate events were collected also in both wet and dry time, at stations 3, 4 and 5, in interest of analysing the situation with or without a base flowrate and the evolution of the pollutants. A previous significant threshold was defined to be the start of the event, and it was chosen to be representative of some storm or incident spill. Samples from 11 events were analysed and some results for total masses, maximum and average (in the EMC sense) concentrations are shown in table 4. In some cases it was not possible to collect runoff water for the 24 bottles as the sediments blocked the peristaltic pump of the sampler.

Table 4. Analysis results for event samples at stations 3, 4 and 5

Station	3	3	3	4	4	5	5	5
Date	Feb 9	Mar 9	Aug 8	Jul 7	Jul 20	Mar 17	Mar 30	Sep 09
Total volume (m3)	405	500	125	13	27	2811	1833	127
Total masses								
TS (kg)	1797	2006	2951	292	1020	418	198	418
TDS (kg)	73	78	28	5	10	215	103	13
TSS (kg)	1724	1927	2923	287	1010	195	96	406
COD (kg)	56	48	154	1	8	45	15	18
Max conc.								
TS (mg/L)	16284	12092	52734	30086	55410	282	306	8204
TDS (mg/L)	282	205	482	404	434	129	116	150
TSS (mg/L)	16108	11904	52406	29682	55076	196	190	8054
COD (mg/L)	312	158	2600	102	560	105	16	281
EMC								
TS (mg/L)	4433	4010	23592	23309	37082	149	108	3296
TDS (mg/L)	181	156	226	387	356	76	56	103
TSS (mg/L)	4252	3854	23366	22922	36727	69	52	3202
COD (mg/L)	137	96	1230	49	297	16	8	140

Elements were analysed only for three events, and the results are presented on table 5, with the averages set again in the EMC sense.

Table 5. Element analysis

	Station 3, aug 15th			Station 4, sep 22th			Station 5, sep 28th		
	MAX	MIN	EMC	MAX	MIN	EMC	MAX	MIN	EMC
Al (mg/L)	1397	29	526	282	32	114	153	51	99
Fe (mg/L)	2678	51	999	514	38	186	302	71	138
Cr (µg / L)	1306	31	456	0	0	0	0	0	0
Mn (µg / L)	39109	824	14415	5398	416	1875	3670	1002	1942
Ni (µg / L)	1288	27	442	72	7	29	45	15	22
Cu (µg / L)	2589	81	822	186	23	61	130	58	82
Zn (µg / L)	28840	1045	13039	4093	221	1258	2225	775	999
As (µg / L)	631	17	237	63	21	37	34	0	24
Cd (µg / L)	15.42	1.74	6.77	0.00	0.00	0.00	4.16	0.00	0.69
Hg (µg / L)	5.25	3.25	4.20	3.66	3.66	3.66	4.37	0.00	0.73
Pb (µg / L)	3370	87	1188	345	31	129	222	109	146

The values for pH, COD, TSS, TDS of all events were studied using four probability functions (Weibull, lognormal, extreme value and logistic), and the one which represented better the behaviour was found to be the lognormal. Results can be seen on figure 4.

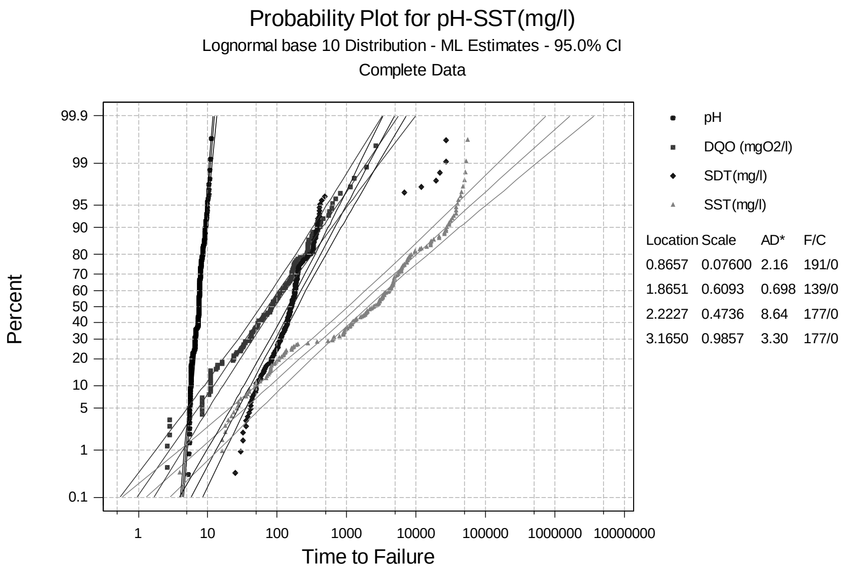

Fig. 3. Lognormal base10 analysis of the results for pH, COD, TDS, TSS

The normalized cumulative masses for COD, TDS and TSS measured at station 4, september 22th event, are plotted on figure 5, and they clearly show that there is no first flush phenomena in the runoff. Similar graphs were obtained for the remainder events.

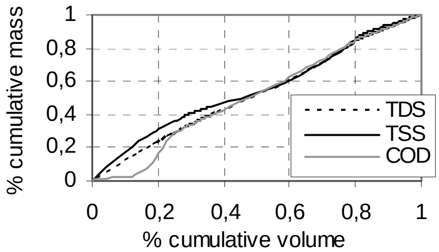

Fig. 4. Cumulative mass plot showing no first flush effect.

6. Conclusions

The Porriño quarries area has been studied in those aspects relative to the runoff, dividing it into 5 sub-basins, all them having a control station for flowrate measuring and pollution sampling. The methodology used to typify pollution has been demonstrated to be consistent, and has shown a high variability of the runoff pollutants during a storm event.

Sub-basin 5, is the most important in terms of flowrate, but not for pollution because of some vegetal cover. From highly degraded sub-basins 3 and 4, random samples had very high average values of Total Suspended Solids, up to 3800 mg/l, while sub-basin 5 reaches only 350 mg/l. Sub-basin 3 presents also substantial values for COD, with maximum concentrations up to 270 mg/l.

In the storm event samples, COD has evidenced to be an important problem, with Event Mean Concentration values from 100 to 500 mg/l. But again, the Total Suspended Solids are the most significant pollutants, with EMC values up to 37000 mg/l, representing a very high environmental impact on the aquatic systems unless control policies are developed. Measured values for flowrate, total masses and event mean concentration, as well as cumulative mass plots, permit the adequate dimension and management of solutions involving a treatment system.

Granulometry tests for the quarry explotation samples show a high degree of gradation, with 60% under 100 microns. Wastewater sediments also have 40% under 40 microns, remaining constant in the whole rainfall-runoff process. Laboratory analysis with samples of TSS ranging from 1400 and 35000 mg/L, showed that sedimentation ponds with retention times around three hours did not achieve water quality good enough for returning to the natural aquatic system. This led us to apply techniques to destabilize colloidal particles with a process of coagulation, flocculation and clarification through jar-tests, obtaining water good even for reuse. Optimal dose for the test of 35000 mg/L of coagulant and floculant were 588 gr/m^3 and 6 gr/m^3 respectively, with a residual turbidity of 2 NTU, similar to potabilized water. For the test of 1400 mg/L the values were 59 gr/m^3 and 6 gr/m^3, with a residual turbidity of 26 NTU. This suggests that with low sediment loads, mud or sediment feedback could help to the coagulation - flocculation process.

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