

Supplementary Material S1. Extended case study information, selection and pictures of the sampling locations, field protocols and summary of laboratory analyses

A.- Extended case study information

A.1 The Mashcon watershed ecosystem

In average, the catchment has a cold and humid climate, but temperature and precipitation vary with elevation. Minimum and maximum temperatures, around 5 and 20 °C respectively, can be constant throughout the year. The annual precipitation ranges between 400 and 1200 mm depending on the elevation, with a marked dry season from May to September (GR de Cajamarca, 2012; INRENA, 2007). Two Andean ecosystems can be differentiated in the catchment, namely Quechua, and Jalca (which is a transition between the northern Paramo and the southern Puna, being also mountainous Andean ecosystems) (Vidal, 2014). Quechua refers to locations between 2300 and 3500 m.a.s.l., and is characterised by a combination of evergreen shrubs, arboreal and perennial herbaceous vegetation. Due to its temperate climate, human activities proliferate more than in the higher Jalca. Part of the Quechua is thus transformed into cultivated land and pastures. The Jalca, situated from 3500 to 4000 m.a.s.l., is dominated by herbaceous vegetation and hosts less terrestrial macro-fauna (INRENA, 2007).

The catchment's headwaters are formed in the hydrological centre Cajamarca-Hualgayoc, where major gold and copper deposits exist (Bissig et al., 2015). At the highest point of the basin, where the main tributary Rio Grande is recharged mainly with an artificial pumping system, groundwater is withdrawn for large-scale mining operations (Vela-Almeida et al., 2016). Below 3800 m of altitude, irrigation sprinklers and channels are used by farmers dedicated to cattle raising. Fresh milk sales are the most important source of revenue for farmers in Cajamarca province (Bernet et al., 2002). At 2838 m.a.s.l., the Rio Grande is deviated to a treatment plant for supplying water to 78000 people (SEDACAJ, 2017), roughly 70% of Cajamarca city inhabitants. In the lowest part of the catchment, where urbanisation starts to increase, the tributary Rio Porcón joins the Rio Grande to form the main river of Cajamarca city, Rio Mashcón (INRENA, 2007). Cajamarca city is the most densely populated area in the Mashcón catchment (INEI, 2009; UN, 2009). The most significant land change in the Jalca part is caused by the presence of MYSRL in an area of 155 km². The sheer size of MYSRL suggests that mining pollution could potentially enter other watersheds as well: Chonta at the Atlantic slope, and Rejo and Honda at the Pacific slope (Vela-Almeida et al., 2016).

The artificial recharge of the main river was deemed as a temporary solution to the lowering groundwater table marring minimum flow conditions. However a maintenance function is severely at risk, since natural flow conditions no longer exist and wetted perimeters deviate from a baseline needed to provide freshwater functions (Arroita et al., 2015; Hayes et al., 2018).

A.2 The rise of cattle farming in Cajamarca

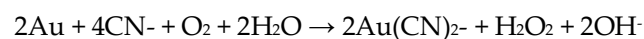
Before the settlement of MYSR, in 1974 the Nestlé company installed a milk condensation plant in Cajamarca, ensuring the purchase of milk production from Cajamarca province and surroundings. Massive imports of wheat and corn marred agricultural profits in the paramo since the 50's, thus milk industrialisation induced landowners to sell dry hillsides to invest in irrigation and dairy cattle in the

lower valleys. Later, dairy cattle gradually extended from the valley to the upper paramo, replacing sheep farming considerably. Hillsides with irrigation also shifted the crops to forage, since the latter is more drought, freeze and plague-resistant. Hence the biweekly income was guaranteed. With the agrarian reform of the 70's, new landowners reallocated lands and cattle to smaller farmsteads, thereby losing entrepreneurship and genetic quality of dairy cattle. Trends towards individualization and inheritance of lands made of rural economy a "shelter" occupation. In the 80's, terrorist's operations (MRTA and Sendero Luminoso) induced migration from rural to urban areas. In the 90's milk production is recovered with the inclusion of new provinces raising cattle, leading to larger production, but keeping specific productivity low. Artisanal production of dairy products flourished, as well as cheese shops. The introduction of another milk firm in Cajamarca, Grupo Gloria S.A., in 1999 produced an imbalance between milk and cheese markets, increasing milk price in 20%. Once Gloria reached its objective of collecting 80 m³ of milk per day, prices went back to normal. The establishment of MYSRL operations (1993) developed under the premise of reaching a link with local economy and a positive impact on it. By 2003, a total of 8000 Yanacocha's employees consisted of 50% Cajamarquinos. Likewise, 500 local providers benefitted from the mine-generated demand. In parallel, Cajamarca's population increased abruptly, and lands were purchased at high prices by senior mine workers. Cattle ranchers seized this opportunity and soon the country side was invaded by buildings of noble material. Besides the reduction of land area for cattle, the dairy cattle sector is now affected by the low availability of water for forage production, and farmers claim environmental contamination is marring animal development and product quality (Escurra, 2001).

A.3 Minera Yanacocha S.R.L. (MYSRL)

Gold Mining Technology

MYSRL is located on the Yanacocha Mountain, at headwaters of four important sub-catchments: *Chonta*, *Mashcón*, *Rejo* and *Honda* (Vela-Almeida et al., 2016). The four main phases for gold production are: extraction and transport of ore-rich material to leaching heap, leaching, recuperation and refining. During the first phase, explosives are placed in drilled holes to fragment the rock, which is then transported on trucks to the pit to leaching pads. At these pads, the gold-containing minerals are deposited and subsequently dripped with a sodium cyanide (NaCN) solution to recover the gold and silver mercury complexes as follows (Matlock et al., 2002):



To prevent the formation of toxic cyanide gases, lime is sprayed on top of the solution to maintain a sufficiently high pH. The enriched solution is collected in pipes and conveyed to a large basin. During the recuperation stage, the solution first flows through one or more activated carbon columns to concentrate it, and then it flows to the Merrill-Crowe gold recovery process. The purpose of this process is to convert the gold and silver to a solid state. To do this, a rich zinc powder solution is added which precipitates the gold and silver. The precipitate is then filtered from the solution and sent to the refinery, while the poor solution is sent back to the leaching pad for reuse. In the refining process, the precipitate from the Merrill-Crowe process is converted to the final product: doré bars, containing a mixture of gold and silver. This is done by first drying the precipitate at high temperatures (650°C), to recover the water and mercury contained in it, and then sending it to electric smelting furnaces (1300°C) where gold and silver are separated from the other metals (Lombardi, 2007).

Environmental impacts

The main metals extracted in the Yanacocha mine are gold and silver. The current operations consist of 13 open pits whereof 7 in activity, 9 rock residue heaps and 4 cyanide leaching piles that cover

an area of 37 km³. In 2015, 26.02 tons of gold and 12.76 of silver were produced. MYSRL has the permission to withdraw groundwater from the open pits at a rate of 570 L/s, or 17.976 Mm³ a year, securing the working environment by drying the pits (MYSRL, 2011). Consequently, the phreatic level has fallen 100 m in some areas. Treated waste water is discharged in brooks (Table B.1). The 14 authorized discharge points are shown in Figure 1B in the main manuscript.

Table S1. Discharge water volumes of MYSRL, authorised by the National Water Authority.

Origin of water to discharge	Name discharge point	Receptor water body	Annual discharge volume (Mm ³)	Yearly average flow (l.s ⁻¹)
Western zone of operation	DPC-1	Pampa Larga	1.265	40.11
	DPC-3	Callejón	15.000	475.64
	DPC-4	Encajon	7.000	221.96
	DPC-5	San José	1.581	50.13
	DPC-6	Shilamayo	21.597	684.81
	DPCLSJ2	San José	1.107	35.09
Eastern zone of operation	DPC8	Ocucha Machay	5.000	158.55
	DPC9	Amacocha Pachanes	8.000	253.67
	DPC10	Chaquicocha	10.000	317.09
	DPC11	La Shacsha	2.000	63.42
	DPC12	Colorado	2.000	63.42
	VERT.RSJ	San José	15.000	475.64
Treated domestic waste waters	STPCHL	Cushurubamba	0.003	0.09
	PVQSH	Shoclla	0.123	3.89

In total, the National Water Authority (ANA) authorised MYSRL to discharge 89.675 Mm³ a year. From this, 22 Mm³ can be discharged in brooks of the Mashcón catchment. The *Río Grande*, that was once formed by the confluence of the *Callejón* and *Encajon* brooks, now originates from an artificial process by a cluster of pipes installed by MYSRL for discharging water. The actual water use is estimated by MYSRL as the difference between withdrawal and discharge, which was approximately 4.1 Mm³ for the year 2012. MYSRL claims that most of the withdrawn water is returned to its original catchment. Notably, the extracted groundwater is also discharged as surface water. Complaints about the high sediment load due to discharged water induced MYSRL to build two dams for sediments retention. One, built in 2004, is located in the *Río Grande*, and the other, built in 2002, is in the *Río Rejo*. These dams are also used to release additional water (around 50-80 l.s⁻¹) during the dry season. After complaints about downstream water shortage, MYSRL agreed to maintain a minimal discharge of 500 l.s⁻¹. Other measures taken by MYSRL against water shortage are the building of family reservoirs and the San José reservoir, which discharges water in several irrigation channels since 2007 (MYSRL, 2011).

B.- Selection of monitoring locations

The sampling locations were selected according to the absence or presence of different impact factors (i.e. from general ecological knowledge and visits to the field). The differentiation of sampling subsystems (see Table 1 in main manuscript) is based on the most comprehensive study of terrestrial ecoregions in Peru by Britto (Britto, 2017), which was initially postulated in the thesis of the Peruvian scientist M. Pulgar Vidal (Vidal, 2014).

Sampling locations identified as 12, 14, 15, 17, 18, 19, 20, 30 and 34 were chosen as potential reference sites because they had naturally looking banks, substrate and vegetation, they didn't originate from the mining area and the main land use was pasture, with no agriculture (except for location 15), no rural housing (except for location 18) and no inflow of wastewater or other artificial streams. To show the impact of pollution from the city, locations 1 and 2 and 37 to 40 were chosen. These points are

the most downstream points and are located in the outskirts of Cajamarca city. There were visible impacts from household sewage, stone factories near the river, a small dam and open littering, among others. Some midstream points (e.g. points 16 and 21) were chosen to show the impact of agriculture and the use of irrigation canals. Sampling locations more upstream (i.e. 23, 25 and 26 to 29), so closest to the mine, were chosen to assess direct impacts coming from mining activities. According to Vela-Almeida et al. (2016) the *Callejón* and *Encajón* tributaries (i.e. highest-altitude tributaries of the *Río Grande*) were the most impacted by the mine, receiving discharges from a reservoir fed with treated mine and groundwater.

The samples were divided into two sets of groups. Firstly, the samples were divided into three groups according to the stream in which they were taken: (i) Main water course: (*Río Grande* + *Río Mashcón*), (ii) *Río Porcón* and (iii) Tributaries (Supplementary materia S3 – Table S3.A). Secondly, the sampling points were also grouped according to the possible impact. The points closest to the mine, so the most upstream points, were grouped as ‘mine’, the most downstream points were grouped as ‘city’, samples taken in the *Porcón* were grouped as ‘porcon’ and, lastly, points taken between the mine group and city group where the main land use was agriculture (grassland) were grouped as ‘midstream’ (Figure 3.2). Furthermore, location number 3 was discarded in the end due to the high chances of redundancy with its two most proximal locations, hence saving monitoring efforts for other more relevant locations.

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B.1 Pictures of the sampling locations.

Location number 3 is not shown because it was decided in the end to discard it due to potential redundancy with adjacent sampling sites. Location 22 was divided in two sites due to the presence of an irrigation outflow: site 22.1 and site 22.2 (Figures B.21 and B.22).



Figure B.1: Location 1 (upstream)



Figure B.2: Location 2 (downstream)



Figure B.3: Location 4 (downstream)



Figure B.4: Location 5 (downstream)



Figure B.5: Location 6 (downstream)



Figure B.6: Location 7 (downstream)



Figure B.7: Location 8 (upstream)



Figure B.8: Location 9 (downstream)



Figure B.9: Location 10 (upstream)



Figure B.10: Location 11 (downstream)



Figure B.11: Location 12 (downstream)



Figure B.12: Location 13 (upstream)



Figure B.13: Location 14 (upstream)



Figure B.14: Location 15 (upstream)



Figure B.15: Location 16 (downstream)

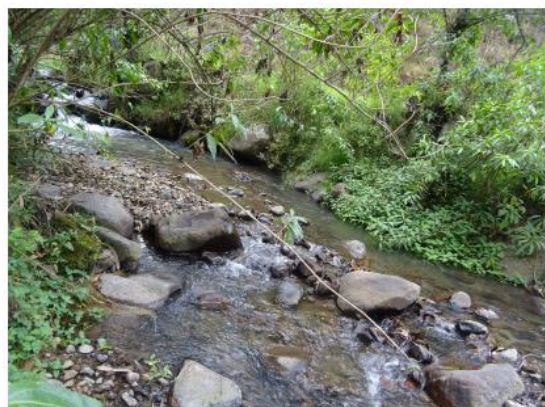


Figure B.16: Location 17 (upstream)



Figure B.17: Location 18 (upstream)



Figure B.18: Location 19 (downstream)



Figure B.19: Location 20 (upstream)



Figure B.20: Location 21 (downstream)



Figure B.21: Location 22.1 (upstream)



Figure B.22: Location 22.2 (upstream)



Figure B.23: Location 23 (upstream)

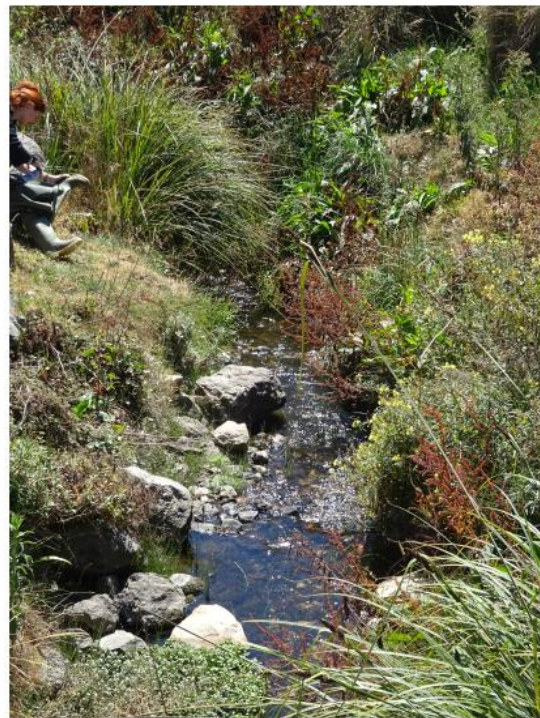


Figure B.24: Location 24 (downstream)



Figure B.25: Location 25 (downstream)



Figure B.26: Location 26 (upstream)



Figure B.27: Location 27 (upstream)



Figure B.28: Location 28 (downstream)



Figure B.29: Location 29 (downstream)



Figure B.30: Location 30 (downstream)



Figure B.31: Location 31 (upstream)



Figure B.32: Location 32 (downstream)



Figure B.33: Location 33 (upstream)



Figure B.34: Location 34 (upstream)



Figure B.35: Location 35 (upstream)



Figure B.36: Location 36 (upstream)



Figure B.37: Location 37 (downstream)



Figure B.38: Location 38 (downstream)



Figure B.39: Location 39 (downstream)



Figure B.40: Location 40 (downstream)

C. Field Protocols for hydromorphology and landuse

Table C1. Field protocol for landuse and hydromorphology characterisation.

Variables	Key	Meaning
Shading:		
	0	No shading
	1	partly shaded, limited stretch <33%
	2	partly shaded, longer stretch 33-90%
	3	partly shaded, whole stretch >90%
	4	completely shaded, limited stretch >33%
	5	completely shaded, longer stretch 33-90%
	6	completely shaded, whole stretch >90%
Presence of macrophytes		
	0	No macrophyte
	1	Interrupted
	2	Contiguous
% of bed covered by macrophytes		
	0	Invisible or no macrophyte
	1	Rare = 1-5%
	2	Occasional = 5-25%
	3	Frequent = 25-50%
	4	Common = 50-75%
	5	Abundant = 75-100%
Landuse:		
1: Natural herbaceous vegetation	NV	
2: Grasslands	GL	
3: Bushes/ Trees groups	BT	
4: Residential Area	RA	Landuse is considered as residential area
5: Urban Area	UA	(RA) if less than 50% is urbanised area.
*The dominant agricultural activity is ryegrass production for cow farming (i.e. grasslands).		
Valley form:		
	1	Canyon
	2	V-shaped valley
	3	Trough
	4	Meander valley
	5	U-shaped valley
	6	Plain floodplain
Channel form		
	1	Meandering
	2	Braided
	3	Anabranching
	4	Sinuate
	5	Constrained (natural)
	6	Constrained (artificial)

(continuation of Table C1)

Variables	Key	Meaning	Others
Variation in flow	0	absent	Bank shape:
	1	at human constructions	1 - concave
	2	low	2 - convex
	3	moderate	3 - stepped
	4	high	4 - wide lower bench
Sludge layer			5 - undercut
	0	absent	Bed compaction
	1	<5cm	1 - tightly packed
	2	5 - 20 cm	2 - packed, unarmoured
	3	> 20 cm	3 - moderate compaction
	blank	Invisible	4 - low compaction (1)
Dead wood			5 - low compaction (2)
	0	Absent	Sediment angularity:
	1	Limited	1 - very angular
	2	Abundant	2 - angular
Mineral substrates share:			3 - sub-angular
	0	0%	4 - rounded
	1	0-20%	5 - well rounded
	2	20-40%	
	3	40-60%	Bank slope
	4	60-80%	1 - 80-90 (degrees)
	5	>80%	2 - 60-80 (degrees)
Main sediment type:			3 - 30-60 (degrees)
	1	Boulder	4 - 10-30 (degrees)
	2	Cobble	5 - <10 (degrees)
	3	Gravel	
	4	Sand	Sediment matrix:
	5	Silt	1 - Bedrock
	6	Clay	2 - Open framework
Pool/Riffle Class			3 - Matrix filled contact
Class	1	Extensive sequence of pools and riffles	4 - Framework dilated
Class	2	High variety in pools and riffles	5 - matrix dominated
Class	3	Variety in pools and riffles, but locally	
Class	4	Pool-riffle pattern is poorly developed	
Class	5	Pool-riffle pattern is absent	
Class	6	Pattern absent due to structural changes	

D. Summary of laboratory analyses results

Table D1. Mean, standard deviation, minimum and maximum values for each physicochemical variable after pooling the full data set by stream type (Grande= main water course, including the Mashcón river).

Variable	Stream	Average	Stdev.	Min.	Max.	Variable	Stream	Average	Stdev.	Min.	Max.
NO ₂ -N (mgN/L)	Grande	0,0137	0,0257	0,0015	0,1100	Temperature (°C)	Grande	13.5	2.0	10.4	18.5
	Porcón	0,0034	0,0021	0,0015	0,0060		Porcón	14.0	1.2	12.3	14.8
	Tributaries	0,0306	0,0623	0,0015	0,1700		Tributaries	11.9	1.9	8.1	14.0
NO ₂ (mg/L)	Grande	0.046	0.087	0.005	0.370	EC (µS/cm)	Grande	495	126	411	933
	Porcón	0.012	0.006	0.005	0.019		Porcón	447	104	340	589
	Tributaries	0.101	0.207	0.005	0.570		Tributaries	315	224	78	743
NH ₄ -N (mgN/L)	Grande	0.796	2.393	0.015	9.210	pH	Grande	7.2	0.4	6.6	8.2
	Porcón	0.015	0.000	0.015	0.015		Porcón	7.4	0.2	7.2	7.6
	Tributaries	0.204	0.409	0.015	1.140		Tributaries	6.9	0.9	4.6	7.9
NH ₄ (mg/L)	Grande	1.03	3.09	0.02	11.90	DO (mg/L)	Grande	7.4	1.8	1.7	10.8
	Porcón	0.02	0.00	0.02	0.02		Porcón	7.8	0.2	7.6	8.1
	Tributaries	0.26	0.53	0.02	1.46		Tributaries	7.3	0.4	6.6	8.0
NO ₃ -N (mgN/L)	Grande	1.02	0.62	0.51	3.26	DO% (%)	Grande	100	25	22	153
	Porcón	0.26	0.07	0.23	0.37		Porcón	105	6	98	111
	Tributaries	2.22	3.57	0.23	9.88		Tributaries	100	3	94	103
NO ₃ (mg/L)	Grande	4.5	2.8	2.3	14.5	Turbidity (NTU)	Grande	21	76	0	366
	Porcón	1.2	0.3	1.0	1.6		Porcón	3	3	0	7
	Tributaries	9.8	15.8	1.0	43.7		Tributaries	3	4	0	11
Total N (mg/L)	Grande	2.3	3.0	1.0	12.7	Chla (µg/L)	Grande	3.9	5.7	0.2	22.6
	Porcón	1.0	0.0	1.0	1.0		Porcón	4.9	2.5	2.7	7.5
	Tributaries	2.9	3.9	1.0	11.4		Tributaries	4.0	3.3	0.2	10.8
PO ₄ -P (mgP/L)	Grande	0.21	0.48	0.05	2.10	COD (mg/L)	Grande	8	10	5	47
	Porcón	0.06	0.02	0.05	0.10		Porcón	10	5	6	16
	Tributaries	0.05	0.01	0.05	0.10		Tributaries	6	2	5	10
PO ₄ (mg/L)	Grande	0.65	1.46	0.15	6.43						
	Porcón	0.19	0.08	0.15	0.31						
	Tributaries	0.16	0.04	0.15	0.30						
Total P-P (mgP/L)	Grande	0,24	0,52	0,05	2,30						
	Porcón	0,08	0,04	0,05	0,13						
	Tributaries	0,06	0,01	0,05	0,10						
Total P (mg/L)	Grande	0.73	1.61	0.15	7.05						
	Porcón	0.23	0.11	0.15	0.40						
	Tributaries	0.17	0.04	0.15	0.30						
SO ₄ ²⁻ (mg/L)	Grande	166	25	130	215						
	Porcón	118	75	70	230						
	Tributaries	89	94	0	275						

- The quality control of physicochemical analyses included the use of disposable nitrile gloves and use of special sample containers materials depending on the type of analysis. Measurements' quality was regularly checked with standards of known concentrations, both for the laboratory kits as well as for the multiparameter probes used in the field.

Table D2. Variables and units measured with the YSI® multi-parameter probes

Variable	Units	Remarks
Temperature	°C	
Electric conductivity (EC)	µS/cm	Standardised to 25°C
pH	dimensionless	
Turbidity	NTU	
Chlorophyll-a (Chl-a)	µg/l and RFU	RFU= relative fluorescence units
Dissolved oxygen (DO)	mg/l	
Oxygen saturation (DO%)	%	Both local and adjusted to sea level.

Table D3. Variables and units analysed with the Hach-Lange ® cuvette test kits

Variable	Units	Detection range
Ammonium	mg/l	0.02-2.5
Nitrite	mg/l	0.005-0.1
Nitrate	mg/l	0.23-13.5
Total nitrogen	mg/l	1-60
Orto-phosphate	mg/l	1-16
Total phosphorus	mg/l	0.15-4.5
Sulphates (Hach® SulfaVer®4 kit)	mg/l	2-70
Chemical oxygen demand (COD)	mg/l	5-60

Table D4. Dissolved metals measurements ($\mu\text{g/l}$) in a Thermo Fisher Scientific® iCAP 6000 ICP-OES® ('inductively coupled plasma - optical emission spectrometry').

Subsystem	LOQ $\mu\text{g/L}$		Cd	Ba	Cu	Cr	Fe	Ni	Mn	Pb	Zn	As
	Sample	units	1.0	na	5.0	2.0	2.0	4.0	1.0	8.0	2.0	10
city	1	$\mu\text{g/L}$	0.1	67.8	2.2	1.6	44.8	0.7	108	-0.2	32.6	1.9
city	2	$\mu\text{g/L}$	0.0	53.2	2.2	1.3	10.7	0.4	102	-1.1	22.4	1.2
porcon	4	$\mu\text{g/L}$	0.0	106	2.1	1.9	222	0.5	255	-1.6	29.5	0.7
porcon	5	$\mu\text{g/L}$	0.0	44.5	2.1	0.8	133	1.1	359	-0.8	15.2	1.3
city	6	$\mu\text{g/L}$	-0.1	49.0	2.2	1.1	5.7	0.4	80.3	-0.4	16.4	1.0
city	7	$\mu\text{g/L}$	0.0	49.4	1.9	1.2	31.5	0.1	63.8	-0.4	16.5	1.3
midstream	8	$\mu\text{g/L}$	0.1	42.7	2.2	1.3	31.1	0.8	63.8	1.0	30.0	1.1
midstream	9	$\mu\text{g/L}$	0.0	42.1	1.8	1.1	25.5	0.5	59.4	-1.6	18.5	1.7
midstream	10	$\mu\text{g/L}$	0.0	42.0	1.9	1.1	23.6	0.4	53.2	-0.5	17.8	1.0
midstream	11	$\mu\text{g/L}$	0.0	41.7	1.9	1.1	23.7	1.2	52.5	-1.5	21.2	1.3
midstream	12	$\mu\text{g/L}$	0.1	33.5	1.9	1.2	16.0	0.6	37.0	-1.2	25.0	1.9
midstream	13	$\mu\text{g/L}$	0.0	33.9	2.1	1.3	14.0	0.2	36.6	1.3	20.8	2.1
midstream	14	$\mu\text{g/L}$	0.3	35.1	3.0	1.3	39.6	1.3	37.4	-1.1	430	1.4
midstream	15	$\mu\text{g/L}$	0.1	147	1.9	1.0	157	0.6	302	0.2	76.6	0.0
midstream	16	$\mu\text{g/L}$	0.2	31.1	2.1	1.0	12.6	0.3	31.3	-1.5	24.9	1.2
midstream	17	$\mu\text{g/L}$	-0.1	85.2	1.9	0.5	27.2	0.0	4.4	0.2	17.0	1.1
midstream	18	$\mu\text{g/L}$	0.0	84.4	1.7	0.7	19.3	0.2	3.6	-0.9	17.5	0.8
midstream	19	$\mu\text{g/L}$	-0.1	80.9	3.1	-0.3	54.4	0.3	6.8	-1.7	15.5	0.2
midstream	20	$\mu\text{g/L}$	-0.1	81.6	1.8	0.1	86.2	0.3	10.5	-1.7	16.0	0.7
midstream	21	$\mu\text{g/L}$	0.1	27.8	2.5	0.7	11.4	0.7	30.3	-0.3	27.4	1.2
mine	22.1	$\mu\text{g/L}$	0.1	59.8	2.7	1.0	21.4	0.1	59.2	0.0	38.4	0.1
mine	22.2	$\mu\text{g/L}$	0.1	59.6	1.6	0.1	27.8	0.4	28.6	-0.3	39.1	1.0
mine	23	$\mu\text{g/L}$	0.0	38.6	2.1	0.1	6.0	0.3	2.2	-1.1	17.6	0.5
mine	24	$\mu\text{g/L}$	0.1	63.8	3.2	1.6	34.9	0.6	64.3	0.4	75.1	1.3
mine	25	$\mu\text{g/L}$	0.0	39.8	1.9	0.7	386	0.4	132	-0.2	30.9	0.1
mine	26	$\mu\text{g/L}$	0.4	21.5	2.7	0.3	8.7	0.1	39.7	-0.2	29.7	3.0
mine	27	$\mu\text{g/L}$	0.3	21.2	2.7	0.8	8.3	0.9	38.4	0.1	27.5	3.2
mine	28	$\mu\text{g/L}$	0.3	21.1	2.8	0.2	9.0	0.6	36.4	-1.1	27.9	4.1
mine	29	$\mu\text{g/L}$	0.4	20.9	3.9	-0.3	9.8	0.7	35.6	0.4	28.6	3.6
mine	30	$\mu\text{g/L}$	0.1	43.3	1.3	-0.2	146	0.8	71.1	-0.8	37.0	1.1
mine	31	$\mu\text{g/L}$	0.4	24.0	2.4	-0.8	8.8	0.6	37.9	1.2	26.3	4.2
mine	32	$\mu\text{g/L}$	0.3	22.5	2.9	-1.0	16.3	0.7	37.9	1.2	26.3	3.3
mine	33	$\mu\text{g/L}$	0.4	25.2	3.8	-0.1	42.1	1.1	42.0	0.4	108	3.6
mine	34	$\mu\text{g/L}$	0.1	65.1	1.4	-0.7	165	1.6	121	-0.4	28.9	0.7
porcon	35	$\mu\text{g/L}$	0.1	50.9	1.5	0.1	141	0.4	238	2.4	21.7	0.7
porcon	36	$\mu\text{g/L}$	0.0	49.6	1.4	-1.0	87.9	0.3	226	-1.2	15.3	1.5
city	37	$\mu\text{g/L}$	0.1	51.4	18.2	-0.6	9.1	-0.2	103	-0.2	18.0	1.2
city	38	$\mu\text{g/L}$	0.0	48.7	1.8	-1.1	7.7	0.5	88.8	0.6	15.0	1.1
city	39	$\mu\text{g/L}$	0.1	85.2	1.4	-1.4	164	0.7	639	-0.2	16.1	3.7
city	40	$\mu\text{g/L}$	0.2	96.4	2.4	-1.1	339	1.2	473	0.2	21.3	4.4

- Quality control of metal analyses included the use of disposable nitrile gloves, syringes and filters for taking and handling samples, as well as the use of standard solutions for verifying that recovery percentages are near to a value of 100% for the analyte. Measurements for cobalt are not shown since 80% of the samples were below the limit of quantification (LOQ=2 $\mu\text{g/l}$). Whereas samples 22.1, 22.2, 24 and 34 showed values of 4.6, 2.6, 4.2, and 2.5 $\mu\text{g/l}$, respectively.