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Application of the SWAT model to an AMD-affected river (Meca River, SW Spain). Estimation of transported pollutant load

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SUMMARY

The Meca River is highly contaminated by acid mine drainage coming from the Tharsis mining district, belonging to the Iberian Pyrite Belt. This river is regulated by the Sancho reservoir (58 hm^3), with a pH close to 4.2. In this work, the load transported by the Meca River to the Sancho reservoir has been assessed. Due to the lack of streamflow data, the hydrological behaviour of the Meca River basin has been simulated using the SWAT model. The model has been calibrated against registered daily inflows of the Sancho reservoir (1982–2000), excluding the hydrological years 2000/2001 and 2001/2002 that were kept for the validation. The results were satisfactory; the evaluation coefficients for monthly calibration were: $r = 0.85$ (Pearson's correlation coefficient), NSE = 0.83 (Nash–Sutcliffe coefficient) and DV = 1.08 (runoff volume deviation). The main uncertainty was the calibration during low water because of the poor accuracy in the measurement of the inputs to the reservoir in these conditions. Discharge and dissolved concentration relationships for different elements were obtained from hydrochemical samplings, which allowed us to estimate the element pollutant load transported to the reservoir: 418 ton/year of Al, 8024 ton/year of SO_4, 121 ton/year of Zn, etc. Based on these loads, concentrations in the reservoir were calculated for some elements. Apart from Mn and Sr, good adjustment between calculated and measured values was observed (±20% for Ca, Co, Li, Mg, Na, Ni, Zn and SO_4).

Capsule: Hydrological model combined with water quality data show how pollution by AMD can generate huge loads of contaminants acidifying streams and reservoirs.

Introduction

The Odiel River drains materials from the Iberian Pyrite Belt, which has important massive sulfide deposits, with original reserves of 1700 million tons (Sáez et al., 1999). Mining activity at the IPB is around 5000 years old, although large-scale exploitation did not begin until the second half of the 19th century (Leblanc et al., 2000; Nocete et al., 2005). The legacy of this intense mining activity is kilometers of dug galleries, open mines, mine dumps, tailing dams, smelting wastes, etc. Pyrite (and associated sulphides) oxidation occurs in these materials, generating an acidic leachate with large amounts of sulphates and toxic metals, a process which is known as acid mine drainage (AMD).

As a result, the Odiel River basin (Fig. 1) is highly contaminated by AMD (Sánchez España et al., 2005; Cánovas et al., 2007; Sarmiento et al., 2008). Although mining activity is nowadays very scarce, the Odiel River still carries large amounts of contaminants (Olías et al., 2006) due to the longevity nature of AMD contamination processes (Younger, 1997).

The Meca River, a tributary on the right margin of the Odiel River, is contaminated by AMD coming mainly from Tharsis mines, located to the north of the basin, and shows pH values close to 3.5 most part of the year. This river is regulated by the Sancho reservoir (with a storage capacity of 58 hm^3), one of the most important in the province of Huelva (SW Spain) which, due to AMD discharge, shows a pH around 4.2. The reservoir water is mainly for industrial use, although it must be treated before use.

There are numerous examples of lakes and open mines acidified by acid mine drainage. However, as far as we know, there are not many cases worldwide of large reservoirs acidified by AMD:

- The acid mine waters from Iron Mountain (California, USA) flow through Spring Creek Reservoir (capacity of 7.2 hm^3) and into Keswick Reservoir (29.3 hm^3) on the Sacramento River. Iron Mountain was once the largest producer of Cu in

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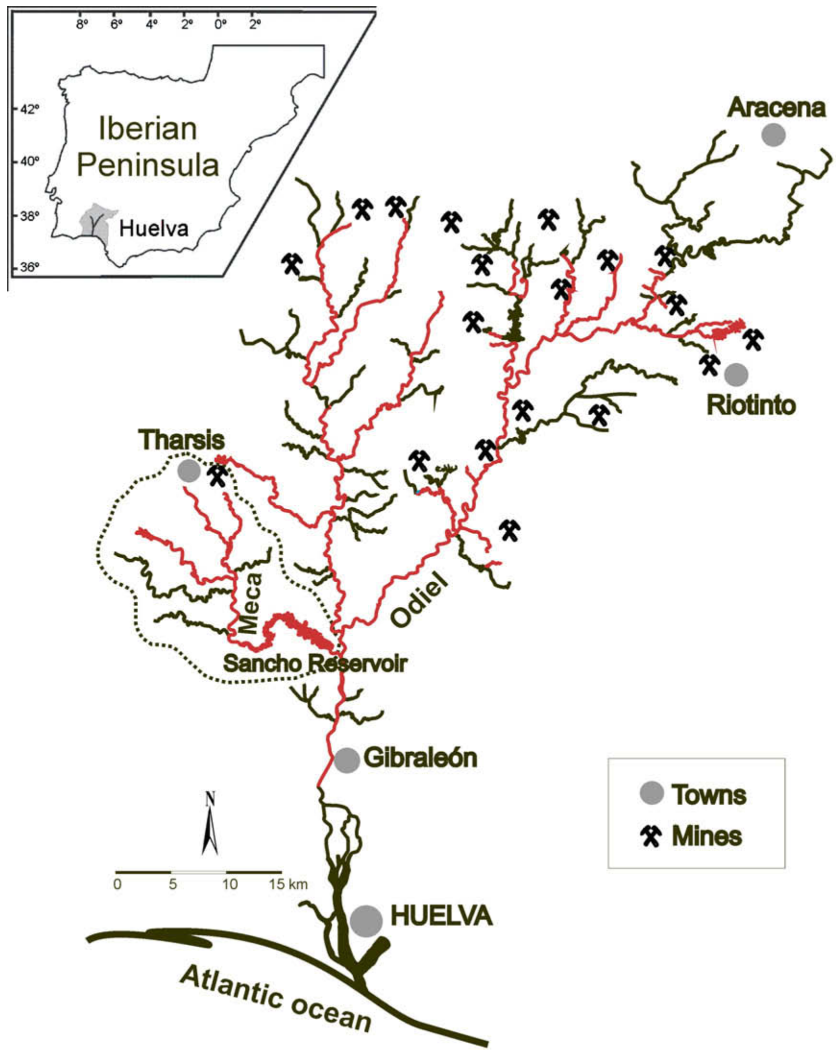

Fig. 1. Location of the Odiel River, Meca River basin and main mine sites (in red: AMD contaminated streams). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

California and is the largest source of surface water pollution in the United States and the most corrosive water in the world (Nordstrom et al., 2000). Prior to Superfund remediation efforts, more than 2500 tons of pyrite weathered every year and about 300 tons of dissolved Cu, Zn and Cd drained annually into the Sacramento River via Spring Creek (Nordstrom et al., 1999). The pH of Spring Creek Reservoir was about 2.5 during low flow and sometimes more than 5 during high flows (Nordstrom et al., 1999). At present the situation is much better thanks to remediation measures that retain 95% of Cu, Cd and Zn (EPA, 2006).

- The Dillon reservoir is located in the southern part of Summit County near the town of Dillon (Colorado, USA). Its total storage capacity is 310 hm^3. The Breckenridge mining district is located within the Dillon reservoir basin and contains a large number of abandoned mines (Apodaca et al., 2000). The Snake River, Blue River, and Tenmile Creek transport dissolved and suspended toxic elements (Fe, Al, As, Cd, Cu, Pb and Zn) to the reservoir. The pH in the reservoir is circumneutral and the bottom sediments are accumulating trace elements. Concentrations of trace elements in the water column are not high, i.e. approximately 25 μg/L of Zn and 1.5 μg/L of Ni (Munk and Faure, 2004).
- The Ocoee No. 3 reservoir in the Ducktown Mining District (Tennessee, USA) with a capacity of 5.2 $hm^{3.}$ Former mining activities lasting 140 years in the Ducktown Mining District has contaminated the streams draining the district. North Potato Creek (pH 3.7) and its major tributary, Burra Burra Creek (pH 3.4), are two of the most heavily affected (Lee and Faure, 2007). In the reservoir the dissolved concentrations of trace metals are, i.e. 460–1700 μg/L of Fe, 0.038–0.390 mg/L of Mn, 0.020–0.420 mg/L of Zn, etc. (SAIC, 2003).
- Igarashi and Oyama (1999) described a reservoir, located in central Japan, constructed for electricity generation with a capacity of 1 hm^3 approximately. Rocks excavated from a rhyolitic formation were dumped in the center of the reservoir. Due to the oxidation of pyrite contained in these rocks, the water reservoir undergoes acidification, the water pH of the reservoir was reduced to approximately 4.5 and soluble Al ranged from 1 to 2 mg/L.

Compared to these examples, and given the large volume of stored water, the Sancho reservoir is an extreme case of AMD pollution.

In this region there are few stream-gauge stations and often they show malfunctioning with long periods without data. The main objective of this work is the application of a hydrological model in order to generate streamflow data which will allow us to determine the element load carried by the Meca River into the Sancho reservoir.

To obtain streamflow data the program SWAT will be used. Applications of SWAT in humid regions are numerous (i.e., Srinivasan et al., 1993; Srinivasan and Arnold, 1994; Cho et al.,1995; Arnold et al., 1999; Santhi et al., 2001). However, examples in drier environments, as the Meca River, are still relatively limited (Conan et al., 2003; Bouraoui et al., 2005; Ouessar et al., 2008). As far as we know, other hydrological models have not been applied in the Odiel River basin.

Two new reservoirs are planned in the Odiel River within the National Hydrologic Plan, Alcolea (300 hm^3) and Coronada (800 hm^3) mainly destined to the irrigation. There are doubts about the water quality of these reservoirs because they will receive acid mine water, the methodology presented here can be of interest for these new dams.

The Meca River basin

The Iberian Pyrite Belt, a first-order metallogenic province for its large massive sulfide reservoirs, has its central and largest domain within the South-Portuguese Zone. The materials on which the Odiel River basin is located belong to the South-Portuguese Zone, which includes 3 units of different lithological characteristics (Sáez et al., 1996). The lower unit or Phyllitic–quartzitic (PQ) group, over which the Vulcanosedimentary Complex (CVS) is located – the massive sulfide deposits and mineralization are associated to this complex – and finally the series ends up with the unit of synorogenic sediments (Culm Group). The Meca River network flows mostly across the IPB materials, with slates as the prevailing lithological formation.

The Meca River basin has an area of 315 km^2 and an average height of 149 m. There are no steep slopes and maximum height is 394 m (Fig. 2). The climate is of a Mediterranean type, with yearly mean rainfall of 632 mm, although it shows high intra- and interannual variability. The mean temperature is 19 °C.

The most important vegetal species, given its extension, is *Eucaliptus* coming from reforestation. Next, in order of importance, are grassland and scrubland. The soils in this area are generally weakly developed, according to the Soil Taxonomy classification, inceptisols prevail.

The Meca River is deeply contaminated by AMD coming from the Tharsis mining district. Close to the mining areas, values of pH ~ 2.6 and concentrations of ~1 g/L Al, 2 g/L Fe, 412 mg/L Zn, 167 mg/L Cu, 3.6 mg/L As, etc. are found (Sarmiento, 2008; Sarmiento et al., 2009b).

The Sancho reservoir has a capacity of 58 hm^3 and, when totally filled, a maximum depth of 33 m and a surface area of 4.27 km^2. The pH is approximately constant through the year, close to 4.2, with high concentrations of toxic elements such as Al (3 mg/L) and Zn (1.7 mg/L). The reservoir behaves like a holomictic and monomictic lake, having a summer thermal stratification which disappears during winter. In summer, the formation of a thin anoxic bottom layer (thickness lesser than 0.5 m) is observed, which is removed by winter homogenization. In the bottom sediments, elevated concentrations of toxic elements are found (Sarmiento et al., 2009a).

Methodology

To determine the load transported by the Meca River, time-continuous data on flow and water quality at some points of the basin are needed. There are no stream-gauge stations at the Meca River basin. The only available data on flow are daily inflows from the Meca River to the Sancho reservoir, for the period 1982–2002. These data are calculated by differences between variations in stored volume in the reservoir and outputs (evaporation, releases and derivations). As a result, the SWAT hydrological model has been chosen, that will be calibrated and validated with data on inflow to the Sancho reservoir.

Principles of the SWAT model

SWAT – Soil and Water Assessment Tool – is a semi distributed hydrological model with ArcView GIS 3.2 interface called AVSWAT, which delimits the river watershed and network using the Digital Elevation Model (DEM) and calculates the daily water balance based on soil type, slope, land use and weather data.

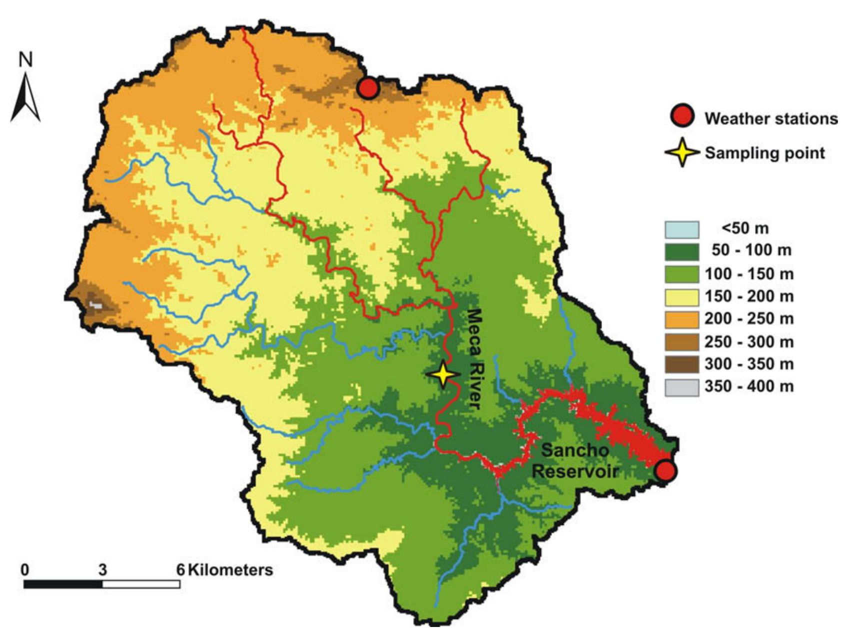

Fig. 2. Digital Terrain Model of the Meca River watershed, indicating location of sampling point at the Meca River (in red: AMD-contaminated streams). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The model is based on the water balance general equation:

$$SW_t = SW_0 + \sum_{i=1}^{t}(R_{day} - Q_{surf} - E_a - W_{seep} - Q_{gw})$$

where SW_t is the final soil water content, SW_0 is the initial soil water content, t is the time, R_{day} is the rainfall, Q_{surf} is the surface runoff, E_a is the amount of evapotranspiration, W_{seep} is the amount of water entering in the vadose zone from the soil profile, and Q_{gw} is the amount of water returning to the rivers as base flow.

To calculate the surface runoff, the SCS curve number procedure was used. This method calculates the surface runoff based on soil type, slope, initial soil moisture state, land use, and management practices (Arnold et al., 1995).

The model represents spatial variability in the watershed by discretizing it into smaller units in two steps. First, the division into subbasins is made and the water network is calculated. Second, each subbasin is divided into several Hydrologic Response Units (HRUs) with homogeneous characteristics of use, coverage and soil type. The HRUs represent percentages of the subbasin area and are not identified spatially in the simulation (Gassman et al., 2007). The estimation of each subbasin runoff is made by simply adding those of the HRU that make up the subbasin, and is routed into the associated channel up to its mouth along the drainage network. The propagation method used was the variable storage routing method (Williams, 1969).

The Hargreaves method was used to calculate potential evapotranspiration. This method only needs daily values for minimum and maximum temperatures and geographical location (Neitsch et al., 2002).

The portion of rainfall that does not turn into surface runoff is divided by percolation and evaporation. The water that percolates into the ground can go back to surface streams either by lateral flow through soil profile or as base flow coming from the aquifer. SWAT divides the groundwater system into two aquifers, one unconfined (which contributes to surface water flow) and a deep, confined aquifer where infiltrated water does not return to the system.

Water quality data and analytical techniques

The analytical data for the present study correspond to the samplings performed at: (1) a point of the Meca River (Fig. 2), upstream the Sancho reservoir, (2) at the Sancho reservoir and (3) at small AMD-unaffected reservoirs in the Odiel watershed. Sample collection was performed from hydrological years 2003/04–2005/06.

Electrical conductivity, pH and redox potential were measured *in situ*. All samples were collected in pre-cleaned polypropylene bottles, which were rinsed thoroughly with HNO_3 solution (10%) and deionized water before use for cations and only deionized water for anions. Water samples were filtered immediately after collection through 0.22 μm Millipore filters fitted on Sartorius polycarbonate filter holders. Samples for major cations and metal analysis were acidified in the field to pH < 2 with HNO_3 (2%) Merk Suprapur. Then, they were stored in the dark at 4 °C in polyethylene bottles until analysis. Samples collected for SO_4^{2-} determinations were filtered but not acidified.

Concentrations of dissolved Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Si, Sn and Zn were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES Jobin–Yvon Ultima2). Multielemental standards solutions prepared from single certified standards supplied by SCP SCIENCE were used for calibration. They were run at the beginning and at the end of each analytical series. Certified Reference Material SRM-1640 NIST fresh-water-type and inter-laboratory standard IRNM-N3 waste-water test material (European Commission Institute for Reference Materials and Measurements) were also analyzed. Detection limits were calculated by average and standard deviations from ten blanks. Detection limits were less than 200 μg/L for Al, Fe, Mn, Mg and Ca, less than 50 μg/L for Zn, 5 μg/L for Cu, 2 μg/L for As and 1 μg/L for the rest of the elements. SO_4^{2-} was determined by Ion Chromatography using a Dionex DX-120 fitted with an AS 9-HC of 4 × 250 mm column and a 4 mm ASRS-ULTRA suppressing membrane, detection limit was 0.5 mg/L.

Calculation of the element load

When strongly correlated and reproducible, concentration versus discharge plots can be used to predict stream hydrochemistry from streamflow. A high discharge resulting from rainfall normally dilutes dissolved elements (p. 300, Langmuir, 1997). The ratio between flow and element concentration is often stated using the equation (Appelo and Postma, 1999; Igarashi et al., 2003):

$$C = \alpha Q^{\beta}$$

where C is the element concentration in mg/L, Q is the flow in L/s, and α and β are constants which vary depending on the element concentration in base flow and overland flow. Usually, concentration in the overland flow is lesser and β has a negative value.

Using this formula and the flow data, the concentration for the days in which no sampling was performed, and therefore, an accurate estimation of the load transported by the river can be obtained (Olías et al., 2006). These relationships were obtained, with discharge data from SWAT and concentrations measured in samples, to estimate the load transported by the Meca River.

SWAT model input data

The topography was obtained based on the Digital Elevation Model (DEM) of the Andalusian Regional Government with an accuracy of 10 × 10 m. Based on the DEM, the program draws the slope map, delimits the watershed and defines the water network (Fig. 2).

The subbasins are defined by entering a threshold area value. This value controls the detail of the drainage network and the size and number of subbasins. An outlet (the point which defines the creation of a subbasin) has been included at the quality control point of the Meca River (Fig. 2), so that streamflow data will be obtained at this location. With a threshold area of 3000 ha, six subbasins were obtained.

For the land use map, the initial data were those available at the Andalusian Department of Environment, coming from the photo interpretation of a 1999 flight. The land uses have been related to those included in the SWAT database. As cited before, the main land uses are plantations of *Eucaliptus globulus* (25% of the surface), grassland (21%) and scrubland (13%).

Soil data were obtained from a thorough initial reconnaissance of the area (Domingo Santos, 2002; Fernández de Villarán, 2006). Although 35 soil units were distinguished in the basin, those with surface area under 2% have been grouped to others of similar characteristics. As a result 12 soil types were obtained, their main characteristics are shown in Table 1. The available water capacity was calculated using the formula by Saxton et al. (1986).

Once land use and soil type were entered, the second level of subdivision into HRUs was carried out. To determine the number of HRUs by subbasins, a 7% threshold for land use and a 2% threshold for soil type were used (land use or type under these values were eliminated and reapportioned proportionally among the rest, so that 100% of the surface is simulated). The final number of HRU's was 143.

Table 1
Main characteristics of considered soil types (AWC: available water capacity, SHC: saturated hydraulic conductivity).

Soil code	1	2	3	4	5	6	7	8	9	10	11	12
Basin surface (%)	3.71	3.70	4.34	29.43	28.22	2.71	4.65	4.0	2.0	9.38	3.11	3.65
Depth (cm)	124	90	48	34	58	55	91	85	113	60	89	95
AWC (mm H_2O/mm soil)	0.09	0.14	0.14	0.14	0.15	0.15	0.15	0.13	0.16	0.15	0.11	0.10
Rock fragment (% weight)	0.6	43.0	43.7	39.0	39.3	35.6	36.8	37.8	19.3	36.1	23.4	4.1
Clay (% fine fraction)	15.3	21.5	23.6	18.4	26.8	16.9	25.1	29.0	45.6	29.7	20.9	12.9
Silt (% fine fraction)	13.1	42.9	41.7	40.2	41.3	48.3	45.2	30.3	39.9	40.4	22.0	20.1
Sand (% fine fraction)	71.7	35.5	34.7	41.4	31.9	34.8	29.7	40.7	14.5	29.9	57.0	67.0
Organic content (% weight)	1.74	1.57	3.18	1.70	2.41	1.99	1.60	2.23	0.77	2.70	2.43	1.83
SHC at 100 cm (cm/h)	18.6	2.88	1.43	1.64	1.53	1.82	1.17	1.88	0.22	2.16	8.49	3.87
SHC at 50 cm (cm/h)	2.78	0.73	1.05	1.26	0.45	1.00	0.57	0.06	0.04	0.56	0.85	5.88
Bulk density (g/cm^3)	1.51	1.33	1.25	1.33	1.32	1.25	1.29	1.40	1.32	1.30	1.45	–
Soil hydrologic group	B	C	B	B	C	C	C	D	D	C	C	B

Weather data (daily data of rainfall and maximum and minimum temperatures) were obtained at two weather stations (Fig. 2). The series of daily data underwent quality control. Incoherent data were corrected and periods without data were replaced with interpolated values from regression with nearby gages, to have homogeneous and complete series available.

Results and discussion

Model calibration and validation

For the model calibration, the flow series was compared with daily data of the inflows to the Sancho reservoir for the hydrologic years 1982/1983–1999/2000. The application of the model in the first simulations showed highly significant differences between estimated and observed flows, mainly because the groundwater default values established by the model do not reflect the watershed reality.

A sensitivity analysis was performed to detect the most influential variables in the calibration process (Neitsch et al., 2002). The groundwater adjusted variables were: baseflow recession coefficient (ALPHA_BF), groundwater 'revap' coefficient (GW_REVAP), and groundwater delay time (GW_DELAY). It was also necessary to calibrate the surface runoff generated. For this purpose, the SCS curve number (CN2), the soil evaporation compensation factor (ESCO), and the available water capacity were modified (SOL_AWC) (Neitsch et al., 2002).

Although there are no relevant aquifers in this area, the fracturation of slates near the surface acts as a minor shallow aquifer that must be considered in the simulation. The baseflow recession coefficient (ALPHA_BF) is a direct index of groundwater flow response to changes in recharge. Values vary from 0.1 to 0.3 for land with slow response to recharge to 0.9–1.0 for those with a rapid response. The final value was established in 1.0 due to the rapid response of the basin (Table 2).

The groundwater 'revap' coefficient (GW_REVAP) regulates the movement of water from the shallow aquifer to overlying unsaturated zone (in dry periods, water in the capillary fringe will evaporate and diffuse upward). The water also can be removed from the aquifer by deep-rooted plants. The value for GW_REVAP should be between 0.02 and 0.20 (Neitsch et al., 2002); values close to 0 indicate no upward water flux, when approaches 1 the rate of transfer from the shallow aquifer to the root zone approaches the rate of potential evapotranspiration. The initial value 0.02 was changed to the maximum (0.2) because of the existence of important eucalyptus plantations.

Table 2
Initial and final values for the calibrated variables.

	Initial value	Final value
ALPHA_BF	0.048	1
GW_REVAP	0.02	0.2
GW_DELAY	31	1
CN2	CN2	CN2–2
ESCO	0	0.01
SOL_AWC	AWC	AWC + 0.04

The groundwater delay (GW_DELAY) is the lag between the time that water exits the soil profile and enters the shallow aquifer. It will depend on the depth to the water table and the hydraulic properties of the geologic formations in the vadose and groundwater zones. The initial value was 31 days and finally was established in only 1 day.

The SCS curve number (CN2) is a function of the soil's permeability, land use and antecedent soil water conditions. The ESCO coefficient allows the user to modify the depth distribution used to meet the soil evaporative demand to account for the effect of capillary action. ESCO must be between 0.01 and 1.0. As the value for ESCO is reduced, the model is able to extract more of the evaporative demand from lower levels. SOL_AWC is the plant available water (is calculated by subtracting the fraction of water present at permanent wilting point from that present at field capacity).

As the runoff obtained in the first simulations was still high, and following the SWAT's manual recommendations (Neitsch et al., 2002), the initial values of CN2 were reduced in 2 units, the soil evaporation compensation factor (ESCO) was established at 0.01 and soil available water capacity (SOL_AWC) was increased in 0.04 units for all the soil types (Table 2).

Added to the difficulty of the model calibration was another disadvantage caused by the inaccuracy in the measurement of daily input to the Sancho reservoir under low water conditions. Daily inflows are calculated by differences between variations in stored volume and recorded outputs (releases, derivations and evaporation). When inputs are low in relation to stored volume variations, small inaccuracies in the measurement of reservoir water level (e.g. by wind action) imply a significant error in the calculation of input and even negative input flows are obtained. Most of the flow data during low water season had to be rejected for this reason, which makes it impossible to calibrate the model for low water.

The model was manually calibrated by optimizing Pearson's correlation coefficient (r), Nash–Sutcliffe's efficiency (NSE) parameter (Nash and Sutcliffe, 1970), root mean square error (RMS; Hogue et al., 2006), and runoff volume deviation (DV; Boyle et al., 2000).

The results of the statistical indices for the calibration period are shown in Table 3. The value for Pearson's correlation coefficient (r) on a monthly basis is 0.85, showing a good adjustment between simulated and observed values. On a daily basis, the correlation coefficient drops to 0.78. Monthly NSE is 0.83; values over 0.75

Table 3
Statistical indexes for the calibration and validation period.

	Calibration		Validation	
	Daily	Monthly	Daily	Monthly
r	0.78	0.85	0.83	0.95
NSE	0.52	0.83	0.36	0.7
RMS (m^3/s)	11.75	72.46	5.91	29.54
DV	1.08	1.11	1.48	1.61

are considered as 'very good' (Moriasi et al., 2007). The runoff volume deviation (DV) between simulated and observed flows for the whole period shows that contribution is 8% overestimated using the model, also 'very good' according to Moriasi et al. (2007).

Fig. 3 shows the monthly evolution of the model simulated results along with the data observed at Sancho reservoir. Visually, a good adjustment is observed, although there are some significant differences in some summers (1987 and 1998). It has been checked that there is no trend among the differences between the observed and simulated values.

Once the model was calibrated, the following step was its validation with the daily input data to the Sancho reservoir for the hydrologic years 2000/2001–2001/2002. In Fig. 4 a good adjustment can be observed, although there are no observed data under 0.1 m^3/s due to the inaccuracy in the measurement of the input flows to the reservoir. Pearson's correlation coefficient values and RMS improve with respect to the calibration period (Table 3). On the contrary, NSE values decrease and on the monthly basis would be considered as 'good' by Moriasi et al. (2007). There is an important increase in runoff volume deviation that would be 'unsatisfactory' according to Moriasi et al. (2007). These deviations are mainly due to the year 2001/2002 (DV of 1.60) and are explained by very high precipitations in the rainfall gauge of the Sancho reservoir that were not registered in the other gauge in the basin (Fig. 2) and its surroundings. Probably, there was a mistake in this period or the intense precipitations affected to a small zone and the model use this value in a wider surface of the basin. Intense, localized rainfalls are common in the zone and more gauges would be suitable to avoid this kind of problems.

Water quality data

A summary of the results obtained from the sampling point at the Meca River (Fig. 2), Sancho reservoir, and other reservoirs not affected by AMD in the Odiel watershed is shown in Table 4. Concentration of Sb, Se and Sn are not shown because they are normally below the detection limits.

Both the Sancho reservoir and the Meca River have acidic waters, high electrical conductivity and heavy metal and metalloid concentration. Concentrations are generally lower in the reservoir due to the dilution effect occurring during floods (Cánovas et al., 2008). Standard deviation values are remarkably lower in the Sancho reservoir, since variations are softened by the large volume of stored water.

The waters of the reservoirs that do not receive acidic leachates show a pH value around neutral and low mineralization (mean electrical conductivity of 157 µS/cm). They are bicarbonate waters with low sulphate content (just 19.5 mg/L). Al, Co, Cu, Mn, Ni, Zn and SO_4 concentrations are much lower than in the Sancho reservoir.

Element load to the Sancho reservoir

Thanks to the flow data obtained from the SWAT hydrologic model and the water quality data, relationships between flow and concentration of the different elements studied can be established.

Only those relations with determination coefficient (R^2) higher than 0.8 were used for calculating the loads according with the methodology exposed in epigraph 3.3. Some examples of concentration/flow ratios can be observed in Fig. 5 and the results are shown in Table 5. There are some elements for which no good con-

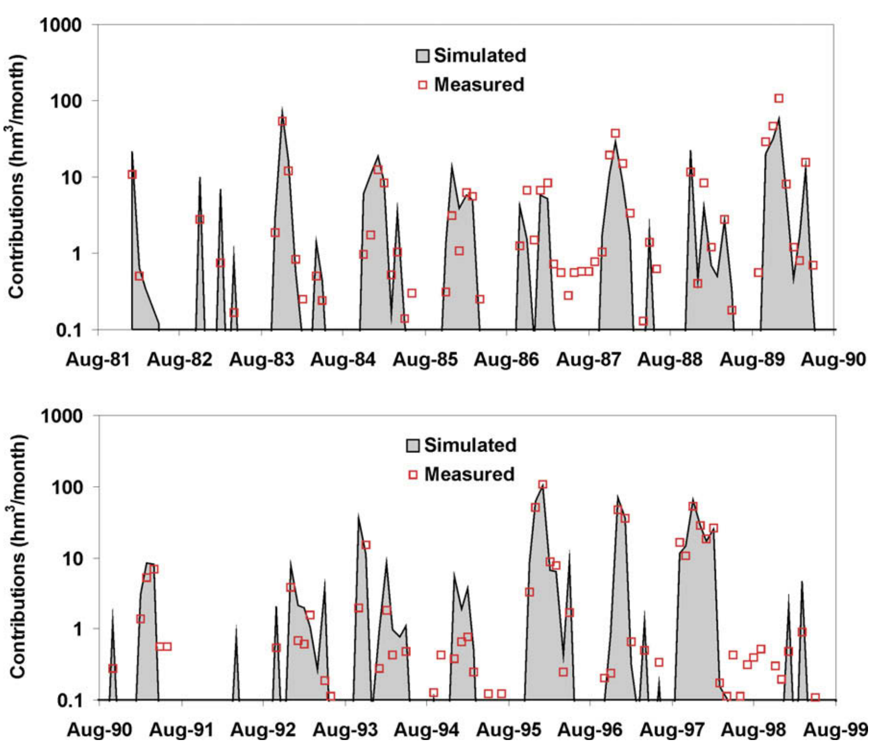

Fig. 3. Monthly evolution of simulated and observed contributions for the calibration period.

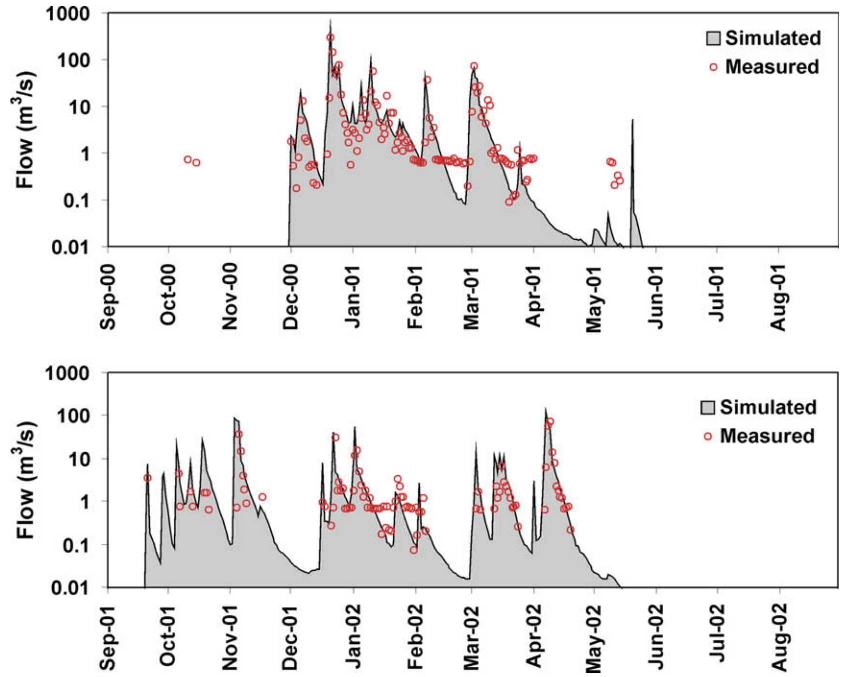

Fig. 4. Daily evolution of simulated and observed stream flow for the validation period.

Table 4
Summary of the analytical results for the Meca River, Sancho reservoir, and AMD-unaffected reservoirs (n = number of samples; EC = electrical conductivity; SD = Standard deviation <l.d.: below detection limit).

		Meca River (n = 13)				Sancho reservoir (n = 8)				Unaffected reservoirs (n = 5)			
		Mean	SD	Min.	Max.	Mean	SD	Min.	Max.	Mean	SD	Min.	Max.
pH		3.55	0.62	2.81	4.43	4.24	0.22	3.94	4.68	7.2	0.5	6.6	7.72
EC	µS/cm	1434	650	706	2440	362	25	328	400	157	25	120	190
Al	mg/L	45.4	28	14.2	86.4	2.96	0.63	1.65	3.58	0.1	0.16	<l.d.	0.38
As	µg/L	10.7	–	10.7	10.7	5.51	0.39	5.23	5.78	5.1	1.91	3.01	7.85
Ca	mg/L	34.1	13.8	15.3	56.7	12.3	2.1	9.5	16	10.3	2.9	7.1	14.6
Cd	µg/L	35.5	28	4.5	79.2	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Co	µg/L	563	344	185	1044	72	18	58	114	<l.d.	<l.d.	<l.d.	<l.d.
Cr	µg/L	18	8.2	10.5	27.3	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Cu	mg/L	7.2	4.3	2.5	12.8	0.65	0.12	0.54	0.9	<l.d.	<l.d.	<l.d.	<l.d.
Fe	mg/L	12.3	6.6	1.9	20.2	0.39	0.41	0.15	0.86	0.37	0.26	0.18	0.55
K	mg/L	2.5	1	1.3	3.9	2.71	0.54	1.94	3.59	1.85	0.33	1.47	2.36
Li	µg/L	76.2	53.9	21	169.9	12.1	5.7	5.5	21.8	14.4	0.2	14.1	14.7
Mg	mg/L	67.9	32.8	27.2	111.3	13.5	3.1	11.1	20.6	7.6	1.6	6	10.2
Mn	mg/L	8.9	5.5	2.7	16.2	1.71	0.36	1.42	2.52	<l.d.	<l.d.	<l.d.	<l.d.
Na	mg/L	35.4	8.6	25.4	51.4	16.1	1.4	13.7	17.9	9.2	1.4	7.4	11.7
Ni	µg/L	252.2	161.5	61.9	458.8	30.7	11.9	19.4	55.8	5.5	0.2	5.3	5.6
Pb	µg/L	239.2	410.3	7	968.9	16.7	12.7	8.1	40.3	12.9	1.7	10.7	15.7
Si	mg/L	8.3	6.4	2.8	20.6	3.43	0.97	1.82	4.24	1.8	3.2	0.15	6.6
Sr	µg/L	118	54	52	196	65.1	27.4	43.7	126	44.2	3.3	39.3	48.6
Zn	mg/L	13.7	9.5	4.5	28.2	1.85	0.49	1.14	2.52	<l.d.	<l.d.	<l.d.	<l.d.
SO_4	mg/L	785	464	241	1399	121.2	31.4	78.4	185	19.5	6.5	13.9	32.1

centration/flow correlations were obtained (As = 0.37, Cr = 0.37, Cu = 0.7, Fe = 0.1, K = 0.74, Mo = 0.44 and Si = 0.76), and therefore it is not possible to calculate the load transported by the river for these elements. The low correlation value obtained for Fe is because its concentration is controlled by other processes besides dilution. Fe is the element that buffers the pH in the Meca river, so during floods tend to precipitate as Fe oxyhydroxysulphates. As and Cr are strongly sorbed/coprecipitated with these Fe minerals (Webster et al., 1998: Smith, 1999) and therefore also present low correlation values with streamflow.

The element load is calculated multiplying the daily calculated concentration by the flow. The yearly load is obtained by adding the daily loads. The Meca River at this point transports yearly 8024 tons of sulphates, 418 tons of Al, 121 of Zn, 81of Mn, etc. (Table 5).

The applied methodology can be checked dividing the annual mean load of each element by the mean water contribution for that period, so that its mean concentration would be obtained. If the elements behave in a conservative way, this value must be equal to the mean concentration in the reservoir.

Nevertheless, the discharge in the Meca River at the water quality sampling station are only 62.5% of the watershed contribution (this value is obtained comparing the discharge obtained from SWAT at this point and that of the whole basin). Downstream of this point, the Meca receives water from good quality tributaries (Fig. 2). To obtain the final water quality in the reservoir, these

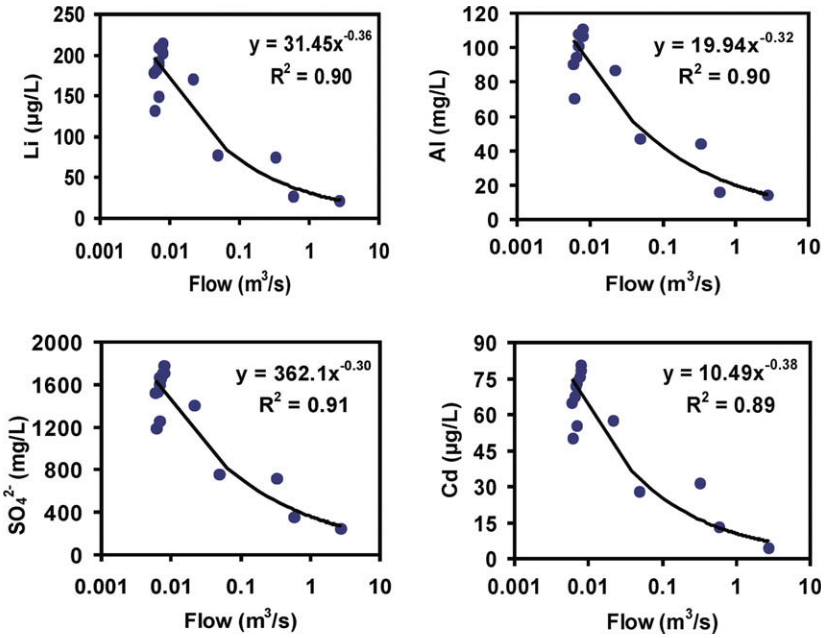

Fig. 5. Some examples of streamflow – element concentration relationships. Circles represent measured concentration and flow obtained from SWAT for the sampling day.

Table 5
Annual mean dissolved load transported by the Meca River at the sampling point (ton/year).

Al	Ca	Cd	Co	Li	Mg	Mn	Na	Ni	Pb	Sr	Zn	SO_4
418	561	0.2	6	0.6	918	81	798	2	0.3	2	121	8024

uncontaminated contributions must be taken into account. As a result, it was considered that the chemical composition of the water generated in these zones is the same as the water in the unaffected reservoirs of the watershed (Table 4). The final composition of the reservoir is calculated as a mixture of the concentration obtained at the Meca sampling point based on the annual load (62.5%) and the concentration of the unaffected reservoirs (37.5%).

The values thus obtained are compared with the real values analyzed in the Sancho reservoir (Table 6). A very good adjustment (20%) for Ca, Co, Li, Mg, Na, Ni, Zn and SO_4 is observed, as expected for elements which behave conservatively in low pH water (<4.5) from the basin (Olías et al., 2004; Cánovas et al., 2007; Sarmiento et al., 2009b).

Although Mn and Sr have also been reported to be conservative, their calculated concentrations in the reservoir are much lower than observed. There are some outcrops (4.8% of the basin surface) of Miocene bioclastic limestones in the southwestern part of the basin. However, if this was the source of these two elements, also a significant Ca supply should be expected. Another possible explanation would be hydrolysis in the reservoir acidic waters of silicate minerals transported in suspension during floods. This behaviour is also shown by other elements such as Si and K, abundant in silicates, although they are not shown in Table 6 because their relationships with streamflow present determination coefficients slightly lower than 0.80.

Table 6
Analyzed and calculated values at Sancho reservoir and difference (%) with respect to calculated values.

	Measured values	Calculated values	Difference (%)
Ca (mg/L)	12.3	10.8	13
Cd (µg/L)	<l.d	2.46	–
Co (µg/L)	72.0	78.0	−8
Li (µg/L)	12.1	13.1	−7
Mg (mg/L)	13.5	14.3	−5
Mn (mg/L)	1.71	1.01	69
Na (mg/L)	16.1	13.4	20
Ni (µg/L)	30.7	29.2	5
Sr (µg/L)	65.1	38.8	68
Zn (mg/L)	1.85	1.58	17
SO_4 (mg/L)	121.2	107.1	13

Relationships between streamflow and element concentrations can change through the year in the Odiel and Tinto Rivers (Olías et al., 2006). In autumn, the first rains produce the dissolution of the soluble salts deposited in summer by the intense evaporation along the river margins and in the mining zones. This process, called 'rinse out' or 'flush out', means an important contribution to the annual load transported by the Tinto River (Cánovas et al., 2008). In the current study none of the analyzed samples correspond to this period of high concentrations and thus the obtained loads could be underestimated. Nevertheless, the excellent agreement between calculated and measured concentrations in the reservoir seems to indicate that this process is not important in this case.

Conclusions

The SWAT model is a useful tool to reproduce flow historical records and simulate results whenever gauging data are unavailable. Its main disadvantages are the numerous input parameters, each of which affects other parts of the model, so that it is possible to obtain similar results with different combinations of parameters. As a result, calibration with real data at some points of the watershed, or in watersheds with similar characteristics, is fundamental to achieve reliable results.

To calibrate and validate the simulated results, daily inputs obtained at the Sancho reservoir, located at the end of the watershed, were used. The poor accuracy in the measurement of the inputs to the reservoir during low water made it impossible to calibrate the model under such circumstances. Very good adjustments were achieved during wet years, whereas the differences between simulated and observed flows in dry years were much higher. According to Moriasi et al. (2007), the adjustment obtained in the Meca watershed is 'very good' for the calibration period and decrease slightly during validation.

The ratio between element concentration and flow is a suitable method to obtain the element load, but is not applicable to elements (such as As, Fe or Cu) which do not show good ratios with flow and for which an alternative methodology should be proposed.

The results show that the Sancho reservoir receives a large amount of dissolved metals coming from the AMD generated at the mining facilities. The Meca River transports huge amounts of dissolved toxic elements, with Al (418 ton/year), Zn (121 ton/year), and Mn (81 ton/ year) as the most outstanding. The transported amount of Co, Ni and other toxic elements is much lower (<10 ton/ year).

For elements that can be considered as conservatives, the methodology used has been checked dividing these loads by the annual contribution and comparing it with the analyses of the Sancho reservoir. For this purpose it is necessary to weight the composition obtained at the sampling point with the inputs of good quality water coming from the AMD-unaffected streams in the watershed. The calculated and analyzed values for the reservoir water composition show a good adjustment (20%) for most of these elements (Ca, Co, Li, Mg, Na, Ni, Zn and SO_4).

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