

Wildfire Effects on a Watercourse Affected by Acid Mine Drainage (Odiel River, SW Spain)

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Abstract

Unlike in common hydrological years, when a sharp increase in dissolved concentrations and decrease in pH values is observed after the first autumn rainfalls, a different response is observed during the rainy events recorded after the occurrence of a wildfire. Decreases in most major elements, electrical conductivity (EC) and slight increases in pH were observed. Wildfire-ashes flushed during these events may have supplied sufficient alkalinity to attenuate the acidity, neutralizing the washout of the dominant efflorescent salts and the associated increase of AMD-elements concentrations in the river during the first rains of autumn in the Odiel watercourse.

Keywords: Ashes, Net Acidity, Efflorescent Salts, Washout, Seasonal Variations

Introduction

The Odiel and Tinto watersheds in the Huelva province (SW Spain), two world case scenarios of deeply polluted watercourses by acid mine drainage (AMD), present low pH values and extreme concentrations of dissolved contaminants, mostly metal(oid)s and sulfate, due to the contribution of diverse acidic leachates from historical massive sulfide mining sites of the Iberian Pyrite Belt (IPB) (Cánovas *et al.*, 2021). Their current water quality is of major concern given the limited water resources available in the study area, located in a Mediterranean semi-arid region, and the severe contamination that the pollutant load carries on to the Ría de Huelva estuary, part of which is a declared protected natural environment, eventually reaching the Atlantic Ocean (Nieto *et al.*, 2013).

Hydrochemical conditions of both basins are strongly dependent on several geochemical processes such as washout of efflorescent soluble salts, the transport of sulfide oxidation products from mine sites, mineral precipitation/dissolution with sorption/desorption processes or dilution by runoff (Cánovas *et al.*, 2017). These processes in semi-arid climates are mainly controlled by hydrological seasonal variations. The warm-dry season is characterized by an

intense precipitation of evaporitic salts which serve as a temporary storage of metal(loid)s and sulfate. With the beginning of the rainy season, the flushing of these soluble salts (and also sulfide oxidation products), stored along riverbeds and mine sites, releases an extreme load of acidity, thus registering annual maximum concentrations of dissolved elements and drastic pH drops in AMD-affected watercourses. Thereupon, decreases in concentrations are observed due to dilution processes, when no salts remaining in riverbanks are left to be washout, and pH generally increases (Cánovas *et al.*, 2008). Additionally, there are other factors that may play a key role in the AMD hydrochemistry (e.g. the settlement of treatment plants, adits sealing and tailings restoration, mine spills and/or factors related to climate change).

Climate models predict a magnification of wildfire events in Mediterranean regions. Wildfires can induce changes in soil physico-chemical properties, increases in runoff and erosion rates, and modify inputs of sediments, nutrients and other water constituents (Smith *et al.*, 2011). The mineralogy of the wildfire-ashes generated in Mediterranean climates is highly alkaline (greatly soluble and reactive in water) with inert amorphous silica (Ulery *et al.*, 1993; Pereira *et al.*, 2012). In fact, biomass

ashes have been used as reagent for acidic leachates treatment (Bogush *et al.*, 2020; Millán-Becerro *et al.*, 2021). Accordingly, a sampling campaign was undertaken to evaluate the fire consequences in the Odiel River hydrochemistry, after the first rainfalls of autumn. This is believed to be the first time that the direct consequences of a wildfire on an AMD-affected watercourse have been studied.

Methods

A sampling point located in the Odiel River middle basin was selected given its severe affection by the fire. The sampling campaign began after the cease of the wildfire, coinciding with the first rainfall after the dry season. This location is crucial in the Odiel River because it receives the acidic leachates from the Riotinto Mining District throughout the Agrio Creek, the main pollutant contributor to the Odiel watershed (Galván *et al.*, 2016).

Different physicochemical parameters such as pH, electrical conductivity (EC) and redox potential (ORP) were measured

in the field with a previously calibrated multi-parameter portable equipment. Water samples were filtered (Millipore 0.22 μm filters) and acidified to $\text{pH} < 1$ with suprapur HNO_3 (2%) immediately after sampling, for a total of 22 samples. Major elements were analyzed with ICP-OES, although only Fe, Al, SO_4 , K, Ca and Mg concentrations are shown in this study. Net acidity was calculated using the modified method of Kirby and Cravotta (2005). Flow data were obtained from the Sotiel Coronada gauging station, located downstream of the sampling point (23 km), and correlated with precipitation data from a pluviometric station located around 7 km from the sampling point.

Results

Contrasting the usual AMD behavior during the previous hydrological years, when a sharp rise in dissolved elements concentrations and lower pH values are observed after the warm-dry period coinciding with the first rainfalls of autumn, a different response was recorded during the post-fire rain events.

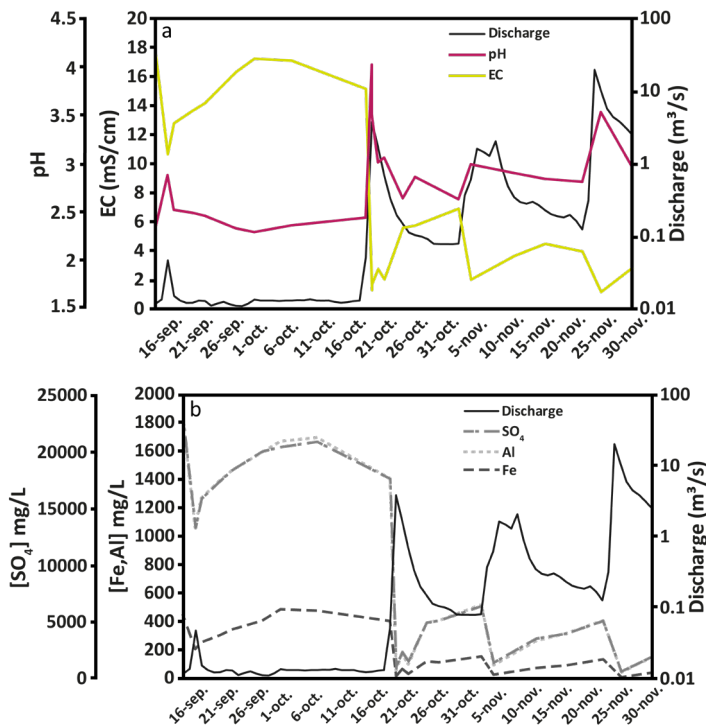


Figure 1 a. Temporal evolution of main physicochemical parameters and riverflow during the sampling period b. Concentration evolution of dissolved Fe, Al and SO_4 throughout the campaign.

All major elements underwent a drastic fall in concentration in the sampling point. Thus, during the first rainy event, the EC suffered a substantial drop, caused by a decrease in the concentration of most dissolved elements (Fe: from 443 to 205 mg/L; Al: from 1805 to 1059 mg/L; sulfate: from 22.8 to 13.3 g/L), coinciding with a slight increase in pH (fig. 1), contrary to the expected hydrochemistry changes in these waters during the fall season. Net acidity lessens from an initial value of 12 to 7 g/L of CaCO₃ equivalent. It is rather significant since the registered streamflow increment during the first rains may be not sufficient to provoke this response by dilution processes. This could be due to the dissolution of ashes accumulated after the fire. Wildfire-ashes flushed during these events possess high alkalinity (Ulery *et al.*, 1993; Pereira *et al.*, 2012), and may have attenuated the acidity carried by the Odiel River, neutralizing the dominant effect of evaporitic salts washout and causing the precipitation of pollutant elements during the first autumn rains. This neutralization capacity of biomass ashes has been widely reported (e.g., Bogush *et al.*, 2020). In the following days, a recovery towards the original conditions is observed.

The second rainy event caused a major riverflow rise more than the previous one. Hydrochemical conditions showed a further decline in dissolved elements concentrations, reaching a net acidity of 0.36 g/L of CaCO₃ eq. and a reduction of more than 90 % for the major elements. EC declined from 15 to 1 mS/cm and pH values increased up to 4

(fig. 1). In this event, the washout of salts and probably ashes must have been negligible, since most of it would have been dissolved during the first rains, dominating in this case a strong dilution process. Finally, the last two events were controlled by run-off dilution processes.

Discussion

In an effort to determine the influence of ashes dissolution on the water hydrochemistry, some geochemical tracers were considered. Additionally, Fe/SO₄ and Ca/Mg ratios were calculated to infer the geochemical processes dominating during the sampling period.

Potassium (K) is a main inorganic compound of wild-fire ashes forming base mineral phases which are easily soluble in water (Ulery *et al.*, 1993; Pereira *et al.*, 2012). Given its high content in ashes, K was considered as a geochemical tracer, along with S, common in AMD-affected watercourses (fig. 2) but not present in ashes. "Pre-rain" samples show the river conditions after the fire but before the beginning of the rains (the Odiel River is homogenized with the Agrio Creek discharge hydrochemistry during the summer); "1st Rain" and "2nd Rain" samples represent the evolution after the first and second rainfall events associated with a slight and a great increase in streamflow, respectively.

Geochemical data are available from an annual series of the Odiel River prior to the wildfire (2015-2016), represented by the Odiel before the Agrio River (main discharge

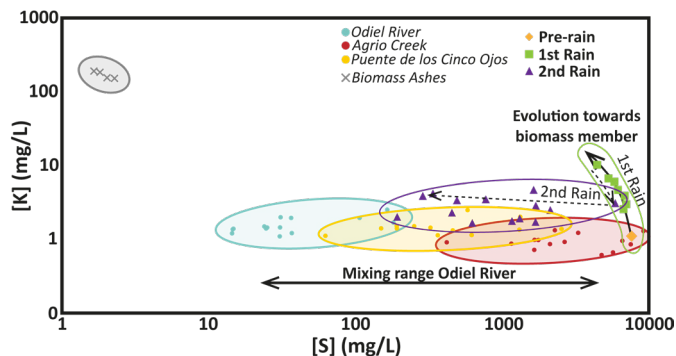


Figure 2 Potassium and sulfur concentrations in the Odiel River during the study period. Extreme end-members (biomass ashes and AMD-affected waters), are also represented to study their influence on the river hydrochemistry.

of the basin), the Agrio Creek itself and the Odiel at the Puente de los Cinco Ojos, coinciding with the sampling point of the study. This series shows the conditions of the Odiel during a hydrological year, showing a range of mixtures between the Agrio and the Odiel, resulting in the final mixture of Puente de los Cinco Ojos. On the other hand, biomass ash composition from regional vegetation as an analogous to wildfire-ashes is available. A first trend is observed within the first rains towards the biomass ash member (fig. 2). Given the high K content in fire ashes and this initial evolution, opposite to the normal trend towards the usual mixture member during the second rain (and other subsequent rain events recorded), it is suggested that ashes may have been entirely washed out during the first rains after the dry season. However, there is a slight deviation which could be interpreted as the remaining influence of ashes dissolution on the river hydrochemistry.

Element ratios (fig. 3) suggest an intense precipitation of Fe oxyhydroxysulfates during the study period. The Fe/SO_4 ratio decreases during the first rainy event evidencing a precipitation of these mineral phases instead of the common ratio increment as a result of efflorescent salts washout observed after the dry season. In this sense, the Fe-sulfate salts accumulated along riverbeds have high Fe/SO_4 ratios (iron content is greater than sulfate within evaporitic salts than in the river waters) so that its flushing may

cause a rise in the Fe/SO_4 ratio. Thus, the alkalinity provided by the ashes rises the pH and induces the precipitation of Fe mineral phases reducing the Fe/SO_4 ratio. In addition, it is expected that other elements co-precipitate and/or absorb with these mineral phases. The progressive increase of the ratio the following days may be due to transport of sulfide oxidation products from mine sites which may increase again the ratio in the river. During the second rainy event, the ratio drastically decreases as a result of a strong dilution process with pH increase leading to Fe precipitation (maybe coupled with the dissolution of remaining ashes from the first event). The decrease is followed by an increase that could be interpreted as effective evaporitic salts dissolution into the river water, coinciding with a slight EC increase (fig. 1).

Ca/Mg ratio increases during the two main rain events (fig. 3). Since evaporitic salts are richer in Mg than in Ca, their dissolution into the water would decrease the ratio. Therefore, these rises evidence the existence of Ca inputs, probably by the dissolution of deposited ashes, considering that Ca is also a major compound of biomass ashes in Mediterranean climates (Pereira *et al.*, 2012). Potassium concentration peaks coincide with the ratios (fig. 3) suggesting a clear ashes influence on the river hydrochemistry. Generally, these ratios support the neutralization of the efflorescent salts washout by ashes alkalinity.

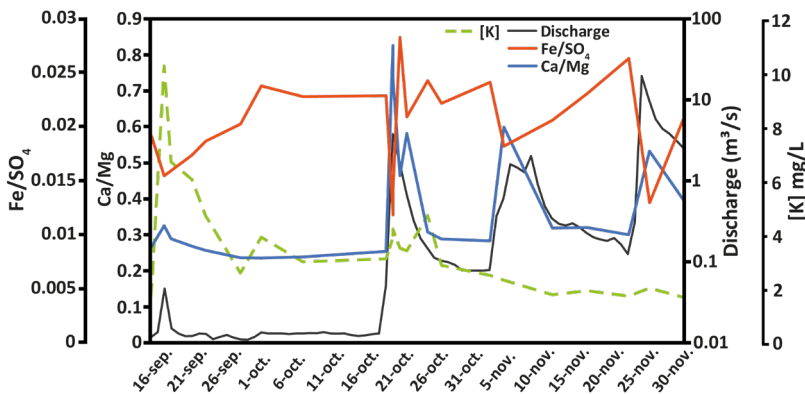


Figure 3 Fe/SO_4 and Ca/Mg ratios reflecting the geochemical processes occurring during the sampling period. Potassium concentration is also shown to assess the influence of the ashes.



Conclusions

Wildfire-ashes flushing during the first autumn rainfalls may have supplied sufficient alkalinity to attenuate the washout of AMD-evaporitic salts commonly observed in AMD-affected sites of semiarid climates and its implications (major pollution peaks of the year), preventing the usual increase in the Odiel River acidity. However, the acidity neutralization is temporary and punctual, with the river rapidly recovering to its original conditions after this quick dissolution and after the arrival of acidic leachates from mine sites. The results of this study shed light on the response of rivers to certain climate change effects, since climate models predict an increase in the number of wildfires, especially in Mediterranean climates.

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