

Article

Acidification Assessment after Peat Bog Drainage in the Catalan Pyrenees (NE Iberia)

Alba Catalán, Montserrat Antúnez and Rosa M. Poch * 

Department of Environment and Soil Sciences, University of Lleida, 25003 Lleida, Spain; alcame31@gmail.com (A.C.); montserrat.antunez@udl.cat (M.A.)

* Correspondence: rosa.poch@macs.udl.cat; Tel.: +34-973-702621

Received: 25 June 2019; Accepted: 16 September 2019; Published: 18 September 2019



Abstract: The Pyrenean range (NE Iberian Peninsula) has some favourable lithological and climatic conditions (iron-rich parent materials and udic moisture regimes) for the formation of acid sulfate soils (ASS) that have not been reported on from the region until now. The analyses of a drained peat bog near València d'Àneu revealed a pH (1:2.5) of 3.7. We hypothesize that it contained sulfidic materials that were oxidized during drainage, which could have caused its acidification. The main goal of this study is to understand the characteristics and the potential acidity of these organic soils and the consequences that this could generate in the current environment. In order to do so, several profiles were described and sampled in the field for chemical and micromorphological analyses. The results show that the oxidation of the newly formed pyrite in the soil or pyrite contained in the Cambro–Ordovician parent material was responsible for the low pH and high electrical conductivity (EC). The soils still contain sulfidic materials at present, which could be oxidized in the future, with the consequent risk for water quality. The results will be useful to evaluate the risk of other peats in the Pyrenees becoming acid sulfate soils if drained.

Keywords: acid sulfate soils; acidity potential; gypsum; pyrite; Catalan Pyrenees

1. Introduction

Acid sulfate soils (ASS) are soils or sediments with a very low pH due to the oxidation of iron sulfides (termed “actual ASS”), and/or soils containing iron sulfides or other sulfidic materials that have not been exposed to air and oxidised (“potential ASS”) [1–5]. Actual and potential ASS are often found in the same soil profile [6].

Acid sulfate soils worldwide occupy an area of at least 17 million ha [7]. They are mostly located in tropical coastlands but they are also found in higher latitudes, as in several countries in Central and North Europe [8]. While they are generally associated with coastal areas, inland ASS are also profusely reported, mainly in Australia, in Fe-rich areas subjected to waterlogging [8,9].

In the Iberian Peninsula, sulfaquents have been reported in the north, where they occupy an area of only 53.6 km² [10]. They contain sulfidic materials at a given depth and are permanently saturated with brackish water [11]. They are found in coastal marshes and depressions associated with hydraquents and salids. Sulfaquents also appear in the Ebro Delta and in other Mediterranean coastal areas [12]. When drained or exposed to aerobic conditions, the sulfidic materials oxidize and the soils become extremely acidic (pH < 3.0) since the buffering capacity is too low to neutralize the sulfuric acid formed (e.g., as in the Tinto and Odiel rivers, in the Province of Huelva) [11].

The occurrence of peatlands in the Pyrenees range is widely recognized and some of them have been profusely studied, mostly as a tool to study landscape evolution during the Quaternary [13,14]. On the contrary, no data exist about the possible risks associated with their management.

The Pyrenean range (NE Spain) has some favourable lithological and climatic conditions (iron-rich parent materials and udic moisture regimes) for the formation of acid sulfate soils. In spite of that, they have never been reported until now, probably due to the lack of adequate geomorphic locations with strong reducing conditions. In this context, the earthworks associated with the construction of the C-28 road near València d'Àneu totally modified the morphology of a 2.8 ha old peat bog, partly drained at present, on the right bank of the Bonaigua River, at an altitude of 1500 m above sea level. The peat bog is composed of two clearly differentiated sedimentary units: The upper unit, mainly organic, and the lower unit, containing granite with gravels and some boulders in the transition between the two units [15]. In the shallowest part, a peaty horizon is described in which secondary roots abound and at a greater depth (146 to 150 cm) a silty clay phase of a few centimeters thick is present where the peat practically disappears. From the surface to 2 m deep, stems, tubular roots and plant remains, mainly wood, are present. In this spot, a soil monolith was extracted as part of the Pyrenean Soil Museum Project of the Institut Cartogràfic i Geològic de Catalunya (ICGC). Baltiérrez [16] described the monolith's profile as having the following sequence: A-H1-H2-H3-2Bg-H4-3Bg-H5 and classified it as Fluvaquentic Haplofibrists [17] or Fibric Histosol [18].

The preliminary analyses revealed a high electrical conductivity (EC) in the first organic horizons reaching levels of 9.23 dS/m at 25 °C and an actual or effective acidity around pH 3.7 (1:2.5 soil:water) and around pH 2.5 (1:5 soil:water). We hypothesize that the old peat bog contained sulfidic materials that were oxidized during the drainage, which could have caused a decrease in pH in organic soils.

Acid sulfate soils are hazardous to natural and managed ecosystems [19]. In particular, potential ASS, when drained, can be responsible for fresh water acidification, which in mountain environments such as the Pyrenees could severely affect aquatic and soil ecosystems. Management techniques to minimize these hazards rely on the correct identification and classification of ASS materials [20].

The aim of this study is the characterization of partly drained peat bog soil in the Catalan Pyrenees in order to determine the origin of the acidity, salinity and net acidity. The results will be useful to locate other spots with acidification risk and eventually to add it to the geological risk programme of the ICGC.

2. Materials and Methods

2.1. Site Description

The study area is located in the Catalan Pyrenees (NE Iberian Peninsula). The characterized peatland is located 63 km from the C-28 road, between Prats de la Vila and Campolado, near València d'Àneu (Figure 1). The altitude is 1150 m asl and it has an extension of around 2.8 ha.

The area has a western Mediterranean climate with an oceanic influence and an average annual precipitation of 1181 mm, which is concentrated in autumn, winter and spring. The average annual temperature is 3 °C, which varies from −4.8 to −1.9 °C during the winter and from 9.2 to 11.6 °C in the summer, for the period 2001–2017. The soil moisture and temperature regimes are udic and frigid, respectively [21].

Geologically, the peat bog of València d'Àneu is located in the Pyrenean Axial Zone, where the substratum is formed by Paleozoic rocks of ages between the Cambro-Ordovician and Upper Ordovician and the overlying Holocene deposits [22]:

- Cambro-Ordovician sedimentary materials: Rhythmic alternation of quartzitic sandstones with feldspars and slaty lutitic layers, with thicknesses ranging from a few centimeters to few decimeters. They form a thick and monotonous series, with some intercalations of black shades or very dark gray with iron sulfides, which give reddish colours when altered.
- Sedimentary materials: Formed by carbonaceous black shales, very rich in organic remains and sulfides. They are characterized by being relatively soft, and have grayish or whitish colours due to their superficial alteration. They are interpreted as marine sediments, deposited in low

oxygenated environments that favor the accumulation of organic matter and the precipitation of sulfides.

Finally, Losantos [22] described that the materials found in the peat bog of València d'Àneu possibly accumulated in a glacial excavation pit: Its filling would be formed by a lower section of glacial deposits (conglomerates of granitic blocks), with gravels and boulders in the upper part that would indicate the circulation of surface water on top of the peat, formed with abundant plant remains.

The vegetation that surrounds the peat bog is represented by some deciduous oaks (*Quercus* sp.) that are combined with hazel trees (*Corylus* sp.), birches (*Betula* sp.) and pines (*Pinus* sp.), and, in many cases, they occupy abandoned fields [16]. The land use of peat bog is mainly forestry, but the central zone is used for cattle grazing.

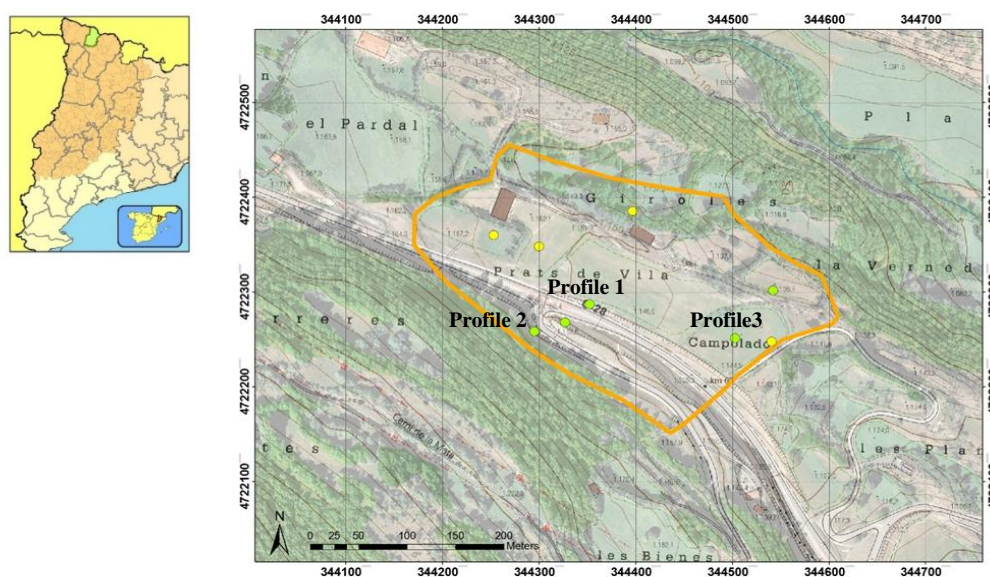


Figure 1. Location of the study site (València d'Àneu, Lleida). The characterized peatland is located 63 km from the C-28 road, between Prats de la Vila and Campolado. The yellow circles indicate the observations made in the field, while the green circles refer to the study pits.

2.2. Soil Sampling, Morphology and Micromorphology

Three profiles were described and classified in the study area following SINEDARES [23] and Soil Taxonomy [18]. For each profile, 0.5 kg of sample from each horizon was collected. Elements which could interfere with subsequent analyses such as shells, gravel, coal or others were discarded [24].

Furthermore, two undisturbed soil samples (corresponding to two subsurface organic horizons of profiles 1 and 2) were taken for micromorphological analysis following the specifications of Benyarku and Stoops [25]. The blocks were dried at room temperature and impregnated with polyester resin. One vertical thin section (50-mm wide, 130-mm long) was made from each block. Subsequently, they were studied using a polarizing microscope following the guidelines of Stoops [26]. The thin sections were used as a complement to the chemical methods; specifically, to determine the presence of diagnostic minerals such as pyrite, gypsum or jarosite indicating reduction or oxidation processes.

2.3. Laboratory Methods: Physical and Chemical Analysis

In the laboratory, part of each sample was air-dried in a fan-forced oven set at 80 to 85 °C for at least 48 h to minimize oxidation of pyrite [27,28]. All samples were sieved gently to 2 mm before being analyzed. Electrical conductivities (ECs) were determined with a glass electrode (CRISON GLP31) in a 1:5 soil/water suspension following the directions of Jayalath [28].

Organic carbon was measured using the Walkley–Black method, through an acid-dichromate digestion [29]. For those samples exceeding 8% of organic carbon, the ignition method was applied [30]. It consisted of combustion at 550 °C for 6 hours in a muffle furnace (HERON 12-PR).

Soil reaction or pH was determined with a pH meter (HACH, GLP 22) in 1:1 and 1:2.5 soil/water suspensions [25,29]. The potential acidity was also measured with a pH meter in a 1:2.5 soil/1N KCl solution [29]. Finally, the samples were treated with hydrogen peroxide (H₂O₂) using a 1:1 soil/30% hydrogen peroxide solution, to determine the pH after oxidation of sulfur ions [28].

Qualitative reaction to sulfur and chloride was determined with the reagents BaCl₂ and AgNO₃ at 10%, respectively. The reaction was positive when the extracts showed a white precipitate [29].

The SPOCAS (peroxide oxidation combined acidity and sulfur) method was applied to obtain the total potential acidity, which is determined as the sum of the soil's potential sulfidic acidity and the actual acidity on two sub-samples or trails (called acidity trail and sulfur trail), according to the following equation:

Net acidity = potential sulfidic acidity + actual acidity + retained acidity – measured acid neutralising capacity (ANC)/fineness factor

The Actual Acidity is a measure of current acidity in ASS. The potential sulfidic acidity in ASS is defined as the latent acidity released if all sulfide minerals they contain are oxidised [27].

The retained acidity is the acidity stored in largely insoluble compounds such as jarosite and other iron and aluminium sulfate minerals; in other words, it refers to the more recalcitrant sulfidic elements contributing to the net acidity when they progressively oxidize over time [8,27].

The acid neutralising capacity (ANC) indicates the buffering potential of the soil to acidification and to maintain pH to acceptable levels (e.g., pH 6.5–9.0). It depends on the types and quantities of clay minerals, carbonates or other minerals in the soil [27].

The acid trail of the SPOCAS method determines the titratable actual acidity (TAA), titratable peroxide acidity (TPA) and titratable sulfidic acidity (TSA). The TAA is measured in a 1:40 suspension of soil sample/1M KCl, while TPA is measured in a 1:40 soil sample/30% hydrogen peroxide [27,31]. TSA is the difference between TAA and TPA.

The sulfur trail of the SPOCAS method determines the peroxide oxidisable sulfur (SPOS), which is a measure of the reactive sulfides present in the soil sample. It is obtained from the difference between the sulfur determined in the peroxide digest (Sp) and the sulfur extracted by 1M KCl (S_{KCl}) [27].

Finally, the net acidity or ABA (acid base account) equation is calculated according to Ahern et al. [27] depending on the obtained pH KCl ranges.

3. Results and Discussion

3.1. Morphology and General Soil Characteristics of the Profiles

The general physicochemical soil characteristics of the studied area are shown in Tables 1 and 2. The topsoil has a crumb structure, with hydrophobic properties. The H horizons contain frequent reed residues with varying degrees of decomposition and charcoal fragments. At depths of 67 (profile 1) and 36 cm (profile 2) reddish mottles due to oxidation appear (hues 7.5YR and 5YR). The textures of the mineral horizons are sandy or sandy loam. Bulk densities of the organic horizons vary between 0.18 and 0.49 Mg/m³.

Profiles 1 and 2 were provisionally classified as Fluvaquentic Haplofibrists.

Table 1. Main physicochemical soil characteristics of profiles 1 and 2. EC: Electrical conductivity; OM: Organic matter; W&B: Walkley–Black method.

Depth (cm)	Horizon	Munsell Colour (moist)	Bulk Density (Mg/m ³)	EC(1:5) (dS/m at 25 °C)	Chloride Test	Sulfate Test	OM (%) W&B	OM (%) Calcination	pH(w) 1:1	pH(w) 1:2.5	pH(KCl) 1:2.5	pH(ox)
Profile 1												
0–18	Ap	7.5YR 3/2	0.48	3.9	Negative	Positive	15.2	48.9	3.4	4.2	4.0	1.6
19–55	H1	5YR 2/2	0.18	4.0	Negative	Positive	27.7	40.4	3.3	3.4	3.1	1.3
56–66	H2	7.5YR 3/2	0.49	2.8	Negative	Positive	9.6	10.4	3.4	3.4	3.2	1.5
67–80	2C	2.5YR 4/2	0.75	1.7	Negative	Positive	1.9	-	3.4	3.6	3.2	1.9
81–111	H3	5YR 3/3	0.23	8.2	Negative	Positive	22.1	27.6	2.1	2.3	2.3	1.0
Profile 2												
0–12	Oi	7.5YR 2/1	0.43	0.7	Negative	Negative	10.7	27.1	6.3	6.5	5.7	-
12–20	H1	5YR 2/2	0.37	0.4	Negative	Negative	29.1	32.2	5.1	5.2	4.3	1.8
21–35	H2	7.5YR 4/2	0.49	0.3	Negative	Negative	18.3	20.0	5.0	5.1	4.2	1.9
36–45	2Cg1	10YR 5/2	1.10	0.1	Negative	Negative	2.3	-	5.7	5.7	4.3	2.6
46–65	2Cg2	10YR 5/2	1.34	0.04	Negative	Negative	1.2	-	6.7	6.6	5.3	3.8

Table 2. Selected physicochemical soil characteristics of profile 3. EC: Electrical conductivity; OM: Organic matter; W&B: Walkley–Black method; CEC: Cation exchange capacity.

Depth (cm)	Horizon	Munsell Colour (moist)	Textural Class (USDA)	EC (1:5) (dS/m at 25 °C)	OM (%) W&B	CEC (cmol(+)/kg)	pH(w) 1:2.5	pH(w) 1:5
0–20	A	10YR 4/3	Sandy loam	1.7	4.0	11.5	3.7	-
21–38	H1	10YR 2/1	-	4.7	30.2	54.8	-	2.8
39–50	H2	2.5YR 3/2	-	9.2	38.4	49.2	-	2.3
51–70	H3	10YR 2/1	-	5.9	33.9	61.4	-	3.4
71–100	2Bg	5/5GY	Sandy loam	1.4	2.2	5.6	3.7	-

3.2. Organic Matter

Peat bogs are soils formed by the accumulation of organic matter (OM) in areas with poor drainage. Tables 2 and 3 show that the maximum OM content is normally found at the surface. Down the profile, it gradually decreases in the first few centimeters until reaching a point where it decreases drastically (profile 2). Moreover, profile 1 contains an organic layer at a depth of one meter deeper than the others—below a 2C horizon that represents an intercalation of slope colluvium.

Table 3. Micromorphological description of organic horizons of profiles 1 and 2.

Feature	Profile 1, Horizon H2	Profile 2, Horizon H2
Porosity and microstructure	50%, compound packing pores. Fine crumb structure.	40%, compound packing pores and fissures. Juxtaposed fine crumb structure and fine subangular blocky.
Organs and tissues	Large (max 1 cm) reed remains, layered, moderately decomposed, tissue (parenchima) fragments, phlobaphenized, coarse sand size, random and layered. About 20% of the volume.	Medium (2 mm) plant remains, layered, mainly roots and shoots, phlobaphenized. Some fungal sclerotia. About 15% of the volume.
Amorphous organic material	Reddish amorphous material, speckled. Undifferentiated b-fabric.	Brownish amorphous material, speckled. Undifferentiated b-fabric.
Faunal excrements	Abundant small excrements, as infillings of channels and also associated with plant remains.	Frequent small excrements, as infillings of channels and associated with plant remains.
Mineral components	Medium sand of schists and quartzites	Medium sand of schists and quartzites
Other pedofeatures	Very abundant gypsum rosettes (fan-like) made of prismatic gypsum crystals, medium sand size. Nodules, coatings and impregnative hypocoatings of jarosite around plant remains.	Very few gypsum rosettes, in plant rests. Nodules, coatings and impregnative hypocoatings of jarosite around plant rests. Hypocoatings and nodules of iron oxides, associated with plant rests.

OM contents obtained by the Walkley–Black and calcination methods differ from each other, although the techniques are not comparable. The organic matter values according to the Walkley–Black method (which underestimates soil organic carbon) [30] have a range of 9.6 to 29.1% in the genetic horizons designated as H in the field, while in the rest they do not exceed 15.2%. The results of the calcination method range of 10.4 to 40.4% of organic matter in the organic H horizons.

The Ap horizon of profile 1 has the highest content of organic matter (48.9%, calcination method) compared to those designated in the field as H. The high content of organic matter could be due to ploughing, which mixes materials of the topsoil with the H1 horizon. However, according to soil taxonomy [17] and the Soil Survey Laboratory [30], this horizon would have to be designated as an H horizon, the sequence of genetic horizons of the profile being the following: H1, H2, H3, 2C and H4. In the case of the Oi horizon of profile 2, the organic carbon content does not exceed 20%; therefore, it would be more suitable to designate it as A.

3.3. Micromorphology

A summary of the micromorphological descriptions of the two thin sections of the H horizons of profiles 1 and 2, following the criteria of Zaiets and Poch [32] can be seen in Table 3.

The fabric of both materials is similar: Mainly layered (medium to large organic remains with a subhorizontal orientation referred to the soil surface) and a juxtaposed fine granular structure due to faunal activity. Both materials have an undifferentiated b-fabric due to the masking effect by the organic matter, and the plant residues are phlobaphenized (containing reddish compounds from the oxidation of tannins). The H2 horizon of profile 1 has abundant fan-like arranged prismatic gypsum crystals as pedofeatures (gypsum rosettes), showing the typical prismatic habit of acidic environments [33,34] (Figure 2). It agrees with the positive qualitative reaction to sulfates (Table 1), while in profile 2 it is negative. The origin of gypsum is therefore the oxidation of pyrite-sulfur present in soil and its combination with Ca^{2+} in the soil solution. The precipitation of gypsum did not buffer all the potential acidity, probably due to the depletion of the Ca^{2+} source (low Ca^{2+} availability), since the present pH are strongly acidic, and also because jarosite formed in both profiles (Figure 2). It is found associated with plant rests and also as aggregates, which can be indicative of former pyrite-bearing soils. Indeed, no pyrite frambooids have been observed in the horizons, although possible pseudomorphs after pyrite were detected associated with organic remains (Figure 2d). Therefore, we think that the oxidation of fine primary pyrite contained in the Cambro-Ordovician parent material, not observable in thin sections, could be the main cause of the existence of sulfidic materials [34]. The H horizon of profile 2 shows almost no gypsum.

3.4. Electrical Conductivities and Chloride and Sulfate Tests

The electrical conductivity values are highly variable between profiles and within profiles. Profile 1 shows EC (1:5) values of 4 dS/m to 1.7 dS/m at 25 °C, increasing with depth until the deepest horizon, with a value of 8.2 dS/m at 25 °C. Profile 3 is also highly saline, with values between 1.3 and 9.2 dS/m at 25 °C. On the other hand, the EC (1:5) of profile 2 is higher at the topsoil (0.7 dS/m at 25 °C) and decreases with depth. The high values of EC are associated with the qualitative presence of sulfates and not of chlorides; therefore, the salinity would have been developed by oxidation of sulfides.

From the tests, the hypothesis that the origin of the high conductivity in some horizons is the salt applied to the roads to prevent frost can be discarded. Instead, the origin of the high conductivity is the sulfur in the parent material of the study area as indicated by Losantos [22].

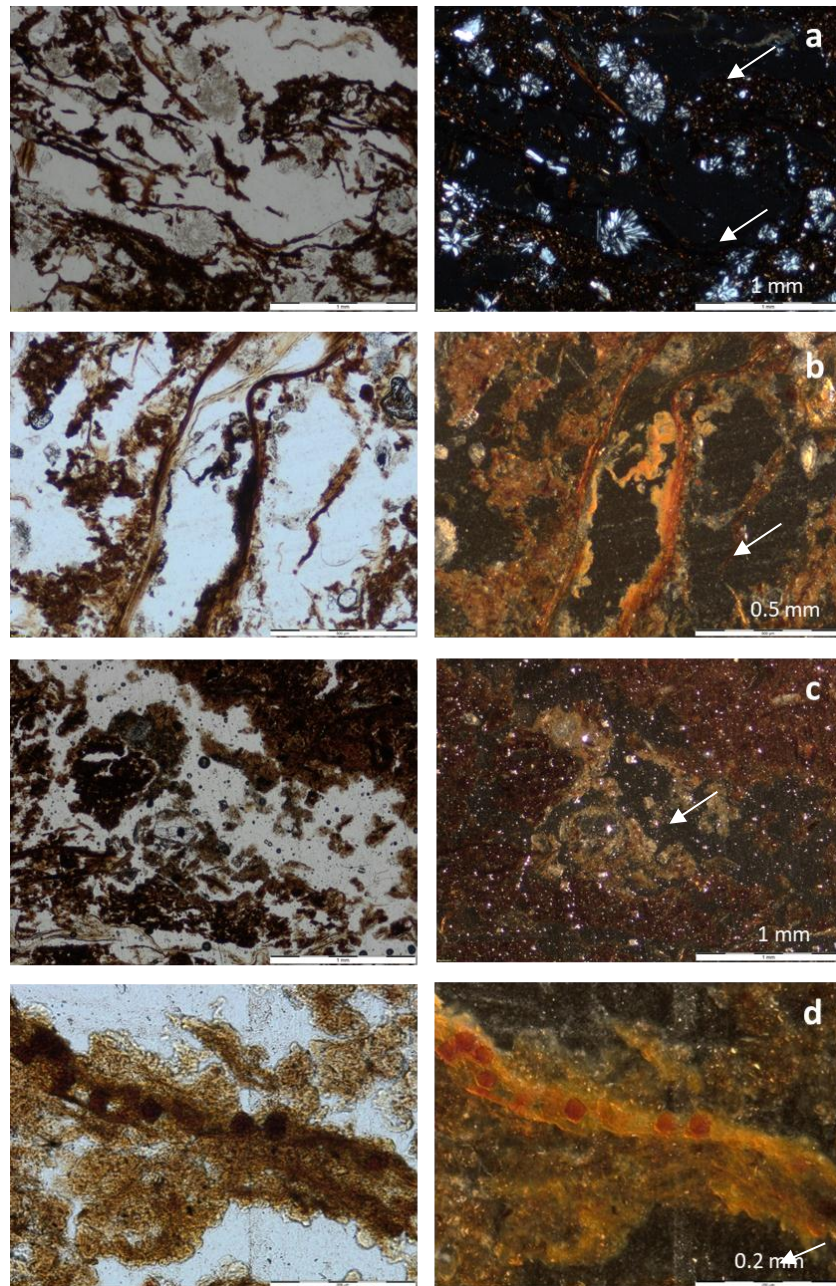


Figure 2. Microphotographs of selected features: (a) Gypsum rosettes in profile 1 (left: Parallel polarizers (PPL), right: Crossed polarizers (XPL)); (b) jarosite coating in a plant residue, profile 1 (left: PPL, right: Oblique incident light (OIL)); (c) jarosite hypocoating of around a pore, profile 2 (left: PPL, right: OIL); (d) iron oxide nodules, possibly pseudomorphs after pyrite framboids, profile 2 (left: PPL, right: OIL). PPL: Parallel polarizers, XPL: Crossed polarizers, OIL: Oblique incident light.

3.5. Soil Reaction

Most of the horizons have very acidic values, lower than pH 4 (Tables 1 and 2, Figure 3).

In profile 1, the pH in water varies between 2.1 and 4.2 while in profile 2 the range is from 5 to 6.7. Isbell [4] defines that values of $\text{pH}(w) \leq 4$ are indicative of sulfide oxidation processes. Therefore, all layers of profile 1 undergo sulfide oxidation processes and meet the characteristics of an acid sulfate soil. On the other hand, profile 2 has acidic to neutral pH values, which is why, so far, it has not been designated as an acid sulfate soil.

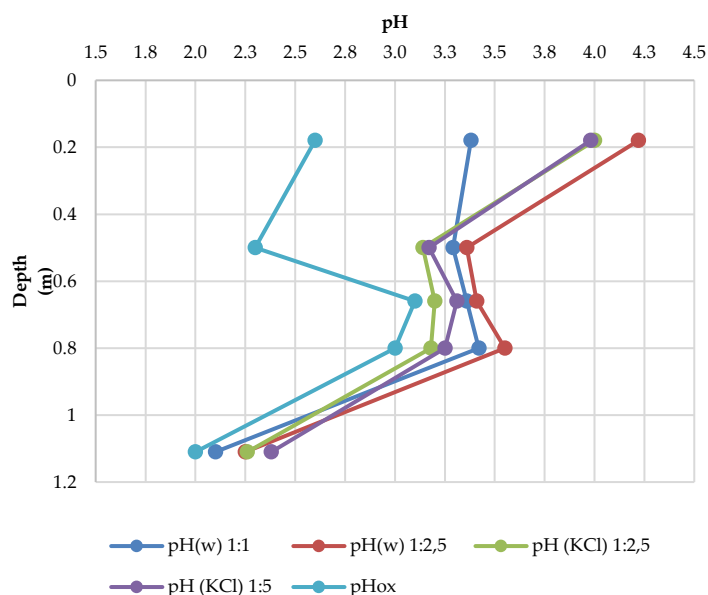


Figure 3. Variation in depth of the different types of pH obtained for profile 1.

In profile 2, the pH in KCl presents values, in general, lower than the pH in water, usually between 0.5 and 1 pH units, as is the case in soils with a cation exchange capacity. However, in some horizons of profile 1, the pH (KCl) is equal or higher than the pH(w), indicating that they have a variable charge and are close to the zero point of charge or the isoelectric point, probably caused by amorphous organic matter.

The pH(ox) values of profile 1 are similar along the profile, with the organic horizons having the lowest values, and they comply with the $\text{pH(ox)} \leq 2$, indicative of a high sulfide content [27]. In contrast, in profile 2, the inorganic horizons, 2Cg1 and 2Cg2 have values higher than 2, 2.6 and 3.8, respectively. These, together with horizon A of profile 3, would confirm their low sulfide content. In addition, the reaction to hydrogen peroxide (30% H_2O_2) of those samples with lower pH(ox) is strong, indicating high sulfur content.

Finally, the comparison between pH(w) and pH(ox) allows us to designate profile 1 as a current acid sulfate soil, while profile 2 should be a potential acid sulfate soil [28]. However, since profile 2 is completely drained (and oxidized at present) the designation of potential acid sulfate soil would not be correct. Another option would be to designate it as a recently post-active acid sulfate soil. On the other hand, this classification has been made from the data obtained in the laboratory when it is recommended that the assignment of the SSA typology be carried out in the field using the values obtained of pH (F) and pH (FOX), that is, pH in water in the field and pH with peroxide in the field, to avoid redox reactions after taking the samples.

3.6. Peroxide Oxidation Combined Acidity and Sulfur (SPOCAS) Method

The results of the application of this set of analyses are found in Table 4. Profile 1 shows TAA values of $247.6 \text{ H}^+/\text{t}$ to $903.9 \text{ mol H}^+/\text{t}$, increasing with depth until the deepest horizon, with a value of $903.9 \text{ mol H}^+/\text{t}$. On the other hand, profile 2 has less acidity, since the values are between 8.5 and $4.8 \text{ mol H}^+/\text{t}$, the maximum value being $144.2 \text{ mol H}^+/\text{t}$ in H1 horizon. This horizon may still have some acidity resources and it is important to determine the acid sulfate soil type because this acidity could be discharged after a strong rainfall, for example.

Table 4. SPOCAS results obtained in profiles 1 and 2. TAA: Titratable actual acidity; TPA: Titratable peroxide acidity; TSA: Titratable sulfidic acidity; S(POS): Peroxide oxidisable sulfur; (p): Peroxide; (a): Reactive.

Profile and Horizon	pH _(KCl)	pH _(ox)	TAA	TPA	S _(KCl)	S _(p)	Ca _(KCl)	Ca _(p)	Mg _(KCl)	Mg _(p)	TSA	S _(POS)	Ca _(a)	Mg _(a)
	pH Units		Mol H ⁺ /t		%S		%Ca		%Mg		Mol H ⁺ /t	%S	%Ca	%Mg
Profile 1														
A	4.3	2.6	247.6	1336.0	0.57	1.2	0.99	1.29	0.04	0.06	1088.4	0.58	0.30	0.02
H1	3.4	2.3	330.9	1490.0	0.70	1.5	0.69	0.83	0.01	0.03	1159.1	0.79	0.14	0.02
H2	3.8	3.1	121.9	230.2	0.38	0.4	0.34	0.34	0.01	0.01	108.3	0.06	0.00	0.00
2C	3.8	3.0	67.3	85.0	0.19	0.2	0.18	0.20	0.00	0.01	17.6	0.06	0.02	0.00
H3	2.8	2.0	903.9	1580.0	1.78	2.5	0.70	0.76	0.04	0.05	676.2	0.73	0.06	0.01
Profile 2														
O _i	6.2	5.4	8.5	0.0	0.03	0.2	0.56	0.46	0.05	0.05	< 0	0.16	0.00	0.00
H1	4.4	3.5	144.2	572.5	0.05	0.4	0.32	1.11	0.02	0.04	428.3	0.31	0.79	0.02
H2	4.5	3.6	63.8	272.5	0.03	0.2	0.28	0.34	0.02	0.03	208.8	0.17	0.06	0.01
2Cg ₁	4.6	4.1	12.3	0.0	0.02	0.0	0.06	0.08	0.01	0.01	< 0	0.01	0.02	0.00
2Cg ₂	5.4	5.8	4.8	0.0	0.02	0.0	0.07	0.08	0.01	0.01	< 0	0.02	0.02	0.00

The titratable peroxide acidity or TPA is zero in the Oi, 2Cg1 and 2Cg2 horizons of profile 2. It indicates that the soil's buffering capacity equals the potential acidity from oxidation of sulfides [27]. On the other hand, the TPA > 0 in the rest of the samples indicates the opposite, this means that in profile 1 and some horizons (H1 and H2) in profile 2 there is a varying amount of pyrite and the reactivity of the carbonate is low.

The reacted calcium and magnesium (CaA and MgA) in both profiles are low (not higher than 0.5%). For this reason they should be ignored in the ABA equation [27].

The 'sulfur trails' of SPOCAS (S_{KCl} and Sp) are shown in Table 4. The SPOS results obtained in both profiles are between 0.01% and 0.79% and have a maximum of 0.79% in profile 1 (H3) and 0.31% in profile 2 (H1). Generally, high values of SPOS are indicative of reduced or PASS (potential acid sulfate soils) samples because they have a lot of recalcitrant oxidizable sulfur, but may differ on partially oxidized and surface samples [27].

Finally, the net acidity or acid base account equation is calculated using the results of Table 4. Some of the horizons of profile 2 have TPA < 0 and pH ranges between 6.2 and 4.6 units; therefore, net acidity cannot be calculated since, according to the values obtained for the SPOCAS method, they do not represent a risk. The results of net acidity (%S and mol H⁺/t), S_{POS} and TAA with unit conversion are shown in Table 5.

Table 5. Conversions and net acidity results for profiles 1 and 2. s-TAA: Actual acidity with sulfur units; a-SPOS: Potential acidity with acidity units.

Horizon	s-TAA	a-SPOS	Net Acidity	Net Acidity
	S%	mol H ⁺ /t	S%	mol H ⁺ /t
Profile 1				
A	0.40	362.99	0.98	610.6
H1	0.53	489.60	1.32	820.5
H2	0.20	37.42	0.26	159.3
2C	0.11	34.93	0.16	102.2
H3	1.45	452.81	2.18	1356.7
Profile 2				
H1	0.23	192.72	0.54	337.0
H2	0.10	102.91	0.27	166.7

In profile 1, the content of actual acidity is between 67.3 mol H⁺/t and 903.9 mol H⁺/t; this is directly related to the low pH values and the higher actual acidity values. In profile 2, the values of actual acidity are lower (272.5 and 572.5 mol H⁺/t). On the other hand, the content of potential acidity is between 34.9 and 489.6 mol of H⁺/t in profile 1 and lower (192.7 and 102.9 mol of H⁺/t) in the H horizons of profile 2. These differences between profiles and horizons could be due to:

- The initial content of pyrite in the horizons. The successive accumulation of detrital materials from upslope combined with periods of peat formation could be the cause of varying pyrite contents along the profile, and therefore of variable potential acidity.
- Part of the pyrite content having already been oxidized due to the drainage works. Again, the degree of oxidation varies depending on local profile conditions and also on the position and characteristics of the horizons.

As a consequence, the potential acidity of the study area should be calculated based on the assignment of a profile type. For soils similar to profile 1, the acidity that can be produced is 261 mol H⁺ while for soils similar to profile 2 it is 22.3 mol.

3.7. Implications for Acidification Risk Assessment in the Pyrenees

Our study is the first record of ASS in the Pyrenees. A comprehensive assessment of the effect of acid effluents due to the drainage of existing peatlands has never been made. In spite of that, acidic drainage has indeed been reported in some small rivers of Pyrenean valleys (pH between 4.4 and 5.2) subjected to alternating dry and wet seasons and causing the precipitation of Al-hydroxysulfates on river gravels [35,36].

The survey and mapping of the geological hazards in Catalonia is at present carried out by the ICGC, which could include these risks as in Bui [37], through a detailed location of peat bogs and of Fe-rich parent materials, together with the analytical characterization of selected sites.

4. Conclusions

The presented scheme provides a nearly complete analytical procedure for the characterization of acid sulfate soils (ASS) present in the first ASS reported in the Catalan Pyrenees. The results permit the distinction between different acid sulfate soil types and provide information about potential acidity. The potential acidity that can be generated in the next few years is 283.3 mol H⁺ if pH correction methods are not applied. The difference between profiles in terms of potential acidity could be due to: (1) The initial content of pyrite or (2) that part of the pyrite that has already been oxidized. This is reflected in the micromorphology of the profiles, one of them more oxidized (profile 1) and with the sulfate partly buffered by gypsum precipitation, and the other (profile 2) with more jarosite. Besides this first characterization of acid sulfate soil in Catalonia, this study will help to assess potential locations of other ASS in the Catalan Pyrenees with similar conditions (e.g., iron-rich parent material, udic moisture regimes, waterlogging) and to evaluate environmental risks related to their management.

Author Contributions: Conceptualization, R.M.P.; methodology, A.C., M.A.; investigation, A.C.; resources, R.M.P.; writing—original draft preparation, A.C.; writing—review and editing, A.C., R.M.P.; supervision, R.M.P.; funding acquisition, R.M.P.

Funding: This research was funded by Institut Cartogràfic i Geològic de Catalunya (ICGC).

Acknowledgments: We acknowledge José Manuel Plata for the preparation of the soil thin sections.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Pons, L.J. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils. In *Acid Sulphate Soils, Proceedings of the International Symposium, Wageningen, The Netherlands, 13–20 August 1972*; Dost, H., Ed.; International Land Reclamation Institute Pub. 18: Wageningen, The Netherlands, 1973; Volume 1, pp. 3–27.
2. Fanning, D.S.; Fanning, M.C.B. *Soil Morphology, Genesis, and Classification*; John Wiley and Sons: New York, NY, USA, 1989; p. 395.
3. Dent, D.L.; Pons, L.J. A world perspective on acid sulfate soils. *Geoderma* **1995**, *67*, 263–276. [[CrossRef](#)]
4. Isbell, R.F. *The Australian Soil Classification System*; CSIRO Publishing: Melbourne, VIC, Australia, 1996.
5. Fanning, D.S.; Rabenhorst, M.C.; Burch, S.N.; Islam, K.R.; Tangren, S.A. Sulfides and sulfates. In *Soil Mineralogy with Environmental Applications*; Dixon, J.B., Schulze, D.G., Eds.; Soil Science Society of America Book Series #7: Madison, WI, USA, 2002; pp. 229–260.
6. Powell, B.; Martens, M. A review of acid sulfate soil impacts, actions and policies that impact on water quality in Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Mar. Pollut. Bull.* **2005**, *51*, 149–164. [[CrossRef](#)] [[PubMed](#)]
7. Andriessse, W.; Van Mensvoort, M.E.F. Acid sulfate soils: Distribution and extent. In *Encyclopedia Soil Science*; Lal, R., Ed.; CRC Press: Boca Raton, FL, USA, 2006; Volume 1, pp. 14–19.
8. Hall, K.C.; Baldwin, D.S.; Rees, G.N.; Richardson, A.J. Distribution of inland wetlands with sulfidic sediments in the Murray-Darling Basin, Australia. *Sci. Total Environ.* **2006**, *370*, 235–244. [[CrossRef](#)] [[PubMed](#)]

9. Fitzpatrick, R.W.; Fritsch, E.; Self, P.G. Interpretation of soil features produced by ancient and modern processes in degraded landscapes: V. Development of saline sulfidic features in non-tidal seepage areas. *Geoderma* **1996**, *69*, 1–29. [[CrossRef](#)]
10. Bescansa, P.; Roquero, C. Characterization and classification of tidal marsh soils and plant communities in north-west Spain. *Catena* **1990**, *17*, 347–355. [[CrossRef](#)]
11. Gómez-Miguel, V.D.; Badía-Villas, D. Soil Distribution and classification. In *The Soils of Spain*; Gallardo, J.F., Ed.; World Soils Book Series; Springer: Berlin Germany, 2007; Volume 2015, pp. 11–48.
12. Rubio, J.L.; Sánchez, J.; Corteza, J. *Proyecto LUCDEME: Mapa de suelos de la Comunidad Valenciana*; Conselleria d’Agricultura i Medi Ambient: Valencia, Spain, 1996.
13. Camarero, J.J.; Gutiérrez, E. Pace and pattern of recent treeline dynamics: Response of ecotones to climatic variability in the Spanish Pyrenees. *Clim. Chang.* **2004**, *63*, 181–200. [[CrossRef](#)]
14. Garcés-Pastor, S.; Cañellas-Boltà, N.; Pèlach, A.; Soriano, J.M.; Pérez-Obiol, R.; Pérez-Haase, A.; Calero, M.A.; Andreu, O.; Escolà, N.; Vegas-Vilarrúbia, T. Environmental history and vegetation dynamics in response to climate variations and human pressure during the Holocene in Bassa Nera, Central Pyrenees. *Palaeogeogr. Palaeoclimatol.* **2017**, *479*, 48–60. [[CrossRef](#)]
15. Pèlach Mañosa, A.; Pérez-Obiol, R.; Soriano López, J.M.; Bal, M.C. El paisatge vegetal de les Planes de Son i la mata de València: Una aproximació als darrers mil·lennis de geohistòria ambiental. In *Els Sistemes Naturals de les Planes de Son i la Mata de València*; Germain, J., Ed.; Treballs de la Institució Catalana d’Història Natural 16; Institució Catalana d’Història Natural: Barcelona, Spain, 2010; Volume 16, pp. 751–783.
16. Institut Cartogràfic i Geològic de Catalunya (ICGC). Documents of the Centre d’Interpretació de Sòls dels Pirineus, Unpublished. Available online: <http://www.icgc.cat/ca/L-ICGC/Agenda2/Centre-d-Interpretacio-dels-Sols-dels-Pirineus> (accessed on 25 June 2019).
17. Soil Survey Staff. Soil Taxonomy. A basic System of Soil Classification for Making and Interpreting Soil Surv. In *Agriculture Handbook 436*; US Department of Agriculture: Washington, DC, USA, 2014.
18. IUSS Working Group WRB. *World Reference Base for Soil Resources 2014, Update 2015: International Soil Classification System for Naming Soils and Creating Legends for Soil Maps*; World Soil Resources Reports No. 106, 192; FAO: Rome, Italy, 2015.
19. Fanning, D.; Rabenhorst, M.; Fitzpatrick, R. Historical developments in the understanding of acid sulfate soils. *Geoderma* **2017**, *308*, 191–206. [[CrossRef](#)]
20. Creeper, N.L.; Fitzpatrick, R.; Shand, P. A simplified incubation method using chip-trays as incubation vessels to identify sulphidic materials in acid sulphate soils. *Soil Use Manag.* **2012**, *28*, 401–408. [[CrossRef](#)]
21. Institut Cartogràfic i Geològic de Catalunya (ICGC). *Llegenda del Visualitzador Geoindex-Sòls*; ICGC: Barcelona, Spain, 2018; p. 43. Available online: <https://www.icgc.cat/Administracio-i-empresa/Eines/Visualitzadors-Geoindex/Geoindex-Sols> (accessed on 25 June 2019).
22. Losantos, M. La geologia de les Planes de Son i la mata de València. In *Els Sistemes Naturals de les Planes de Son i la Mata de València*; Germain, J., Ed.; Treballs de la Institució Catalana d’Història Natural 16; Institució Catalana d’Història Natural: Barcelona, Spain, 2010; pp. 21–75.
23. CBDSA (Comisión del Banco de Datos de Suelos y Aguas). *SINEDARES, Sistema de Información Edafológica y Agronómica de España*; Ministerio de Agricultura y Pesca: Madrid, Spain, 1981.
24. Stone, Y.; Ahern, C.R.; Blunden, B. *Acid Sulfate Soils Manual*; Acid Sulfate Soils Management Advisory Committee: Wollongbar, NSW, Australia, 1998.
25. Benyarku, C.A.; Stoops, G. *Guidelines for Preparation of Rock and Soil Thin Sections and Polished Sections*; Quaderns DMACS, 33; Universitat de Lleida: Lleida, Spain, 2005.
26. Stoops, G. *Guidelines for Analysis and Description of Soil and Regolith Thin Sections*; Soil Science Society of America Inc.: Madison, WI, USA, 2003.
27. Ahern, C.R.; McElnea, A.E.; Sullivan, L.A. *Acid Sulphate Soils: Laboratory Methods Guidelines*; Department of Natural Resources, Mines and Energy: Indooroopilly, QLD, Australia, 2004.
28. Jayalath, N. *Laboratory Protocols For. Acid Sulfate Soils*; CSIRO: Canberra, CBR, Australia, 2012.
29. Porta, J.; López-Acevedo, M.; Rodríguez-Ochoa, R. *Técnicas y Experimentos en Edafología*; Col·legi Oficial d’Enginyers Agrònoms de Catalunya: Barcelona, Spain, 1986.
30. Soil Survey Laboratory. *Soil Survey Laboratory Methods Manual*; United States Department of Agriculture Natural Resources Conservation Service: Washington, DC, USA, 2004.

31. McElnea, A.E.; Ahern, C.R.; Menzies, N.W. The measurement of actual acidity in acid sulfate soils and the determination of sulfidic acidity in suspension after peroxide oxidation. *Soil Res.* **2002**, *40*, 1133–1157. [[CrossRef](#)]
32. Zaiets, O.; Poch, R.M. Use of micromorphology for humus characterization and classification in some mediterranean calcareous soils. *Appl. Soil Ecol.* **2018**, *123*, 672–681. [[CrossRef](#)]
33. Poch, R.M.; Artieda, O.; Lebedeva, M. Gypsic features. In *Interpretation of Micromorphological Features of Soils and Regoliths*; Stoops, G., Marcelino, V., Mees, F., Eds.; Elsevier: Amsterdam, The Netherlands, 2018; pp. 259–287.
34. Mees, F.; Stoops, G. Sulphidic and Sulphuric Materials. In *Interpretation of Micromorphological Features of Soils and Regoliths*; Stoops, G., Marcelino, V., Mees, F., Eds.; Elsevier: Amsterdam, The Netherlands, 2018; pp. 347–376.
35. Institut Cartogràfic i Geològic de Catalunya (ICGC). *Les Pàtines Blanques a la Capçalera de la Noguera de Vallferrera. Composicions, Processos i Efectes Associats*. Technical Report IGC-GAO-003/2012. Available online: http://parcsnaturals.gencat.cat/web/.content/home/alt_pirineu/coneix-nos/centre_de_documentacio/fons_documental/biblioteca_digital/hidrologia/les_patines_blanques_a_la_cap_alera_de_la_noguera_de_vallferrera/3les_patines_blanques_de_la_cap_alera_de_la_noguera_de_vallferrera.pdf (accessed on 17 September 2019).
36. Jiménez Moya, M.; Madaula Izquierdo, E.; Molina García, O. Origen i Efectes Dels Drenatges Àcids a L'alta Muntanya. El Cas de la Capçalera Del Riu Freser. Bachelor's Thesis, Universitat Autònoma de Barcelona, Bellaterra, Spain, 2019.
37. Bui, E.N. High-resolution mapping of acid sulfate soils in Northern Australia through predictive models. *Environ. Chem. Lett.* **2018**, *16*, 1449–1455. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).