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The Genesis and Transformation of Organo-Mineral Colloids in a Drained Peatland Area

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Abstract. The spatial evolution of colloids from a drained peat bog to a river was studied in a karstic watershed (Jura Mountains, Switzerland) by bulk chemistry and electron microscopy. Raw waters (peat bog pore water, water from artificial drains and river water) were analyzed using ICP (Fe, Ca), Colorimetry (Fe^{2+}), TOC and UV (organic matter) and analytical electron microscopies (TEM-EDS, STEM-EDS, EF-TEM). Microscopic analyses correlate bulk sample results and highlight interesting features at the level of the individual colloids. In the peat, TEM-EDS shows the presence of individual globular entities made of carbon (0.4 to 1 μm), while in the river STEM-EDS reveals Fe-Ca-rich globular colloids with a core of carbon determined by EF-TEM. In parallel, bulk chemical analyses show that the ratio $[Fe^{2+}]:[Fe]_{tot}$ decreases from the peat to the river as an inverse function of pH and $[O_2]$, while $[Ca^{2+}]$ increases. We may thus postulate that Fe-Ca-C rich entities found in the river originate from the oxidation of Fe^{2+} and adsorption of Ca^{2+} at the surface of organic colloids, as they are transported by drains from the peat to the river.

1 Introduction

Colloids, particles of small size with great specific surface, are known to be carriers of pollutants in natural waters (Buffle, 1988; Honeyman and Santschi, 1992). Although they are defined according to a size parameter (< 1 μm), they represent a large variety of particles (e.g., clays, organic matter, iron oxyhydroxides, organo-mineral complexes, silica) which may offer selective reactivities.

In this work, we have used a combination of bulk chemical analyses and analytical electron microscopies; the latter are powerful techniques to selectively characterize particles in heterogeneous environmental samples (Lienemann et al., 1997; Perret et al., 1995; Mavrocordatos et al., 1994).
The studied site is a river draining peatlands in a karstic watershed in the Jura Mountains (Switzerland). As peats may deliver numerous particles, we first characterized the distribution of colloids in the river as a function of their size and nature. We then focused our interest on iron-calcium-rich entities, which predominate in the river. The preliminary results presented here attempt to address the genesis of these Fe-Ca colloids from anoxic peats to river, through drains.

2 Site description

The studied area is located in the Swiss Jura, in the Vallée des Ponts (20 km from Neuchâtel), a flat valley covered by peat bogs after the last glaciation (Atteia et al., 1996). Waters from this valley flow into a karstic aquifer located in 500 meters thick Upper Jurassic and Lower Cretaceous limestone. The altitude is ranging from 1000 meters (bottom of the valley) to 1300 meters (surrounding anticlines). Most of the peats have been converted to agricultural land but primary and secondary peats are still present in the western part of the basin, where we focused our attention. Waters from peat bogs and agricultural soils in the central valley are gathered respectively by the Little Bied brook and the Big Bied brook which meet prior to flowing into a sinkhole and then within the karst network. Peats were drained at the beginning of the century; these drains are the preferential passage of waters from the peats to the Bied brook.

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3 Methods

Chemicals used throughout were pro analysis grade. Dilutions and blanks were prepared with ultrapure, ultrafiltered, UV-irradiated water (Elgastat UHQ-II). For this study, a piezometer was installed in the peat to sample pore water. Drain water was sampled from a manhole and at the outlet of the drain. In the Little Bied brook, samples were taken a few meters downstream of the outlet of the drain and 2 kilometers downstream. Raw samples were acidified on the field (HCl 10^{-2} M or HNO_3 2 %), except for microscopy and UV measurements which were processed within 4 hours from sampling.

3.1 Bulk chemical analyses

pH (Metrohm 704), conductivity (WTW-LF323), dissolved oxygen (Orbisphere 27141) were measured directly on the field. Fe and Ca in suspensions were measured by ICP-AES (Perkin-Elmer, λ_{Ca}= 315.887 nm, λ_{Fe}= 259.940 nm). Fe^{2+} was determined by colorimetry (Hach DR2000; measurement at 562 nm with ferrozine; Stookey, 1970; subtraction of the absorbance caused by the color of the sample). Total organic carbon (TOC) was measured after high temperature combustion (Shimadzu TOC 5000). UV absorbance was measured at 285 nm (Perkin Elmer Lambda 7).

3.2 Electron microscopic analyses

Specimens were prepared on TEM grids (Cu 200 mesh; collodion covered, carbon coated) by a non perturbing ultracentrifugation procedure (Perret et al., 1991). Suspensions were directly ultracentrifuged onto TEM grids in a swing-out rotor (135'000 g, 4 h). Microanalyses of the resulting whole mount preparations were performed with 4 different microscopes in a correlative approach, in order to obtain maximum information on the particles.
Particles in the brook were randomly analyzed with a scanning transmission electron microscope (STEM; Jeol TEMSCAN 1200 Ex II, source LaB_6; 80 keV) coupled to an energy dispersive spectrometer (EDS; Princeton Gamma Tech) used in spectrum mode. The intimate structure of the Fe rich entities was investigated with a scanning transmission electron microscopes (STEM; Jeol 2010F, source Field Emission Gun; 200 keV) coupled to an energy dispersive spectrometer (EDS: Link) used in imaging mode. To ascertain the composition of these particles, in particular for light elements, analyses were performed with an energy-filtered transmission electron microscope in spectrum mode (EF-TEM; Zeiss CEM-902 equipped with a Castaing-Henry filter; source W; 80 keV; Perret et al., 1995). Preliminary results on the formation pathway of particles from peat to river were obtained with a TEM-EDS (Philips CM12, source W, 80 keV).

4 Results and discussion

4.1 Composition and size distribution of the colloids in the river

A distribution of the colloids as a function of their size and composition (major elements present in the particles) was determined by STEM-EDS. Samples were collected in the Little Bied brook at four dates during summer 1995. A random analysis of ca. 300 individual particles showed that the number concentration of particles was strongly dominated (> 50 % of the total number of particles) by Fe-Ca-rich entities in the < 0.5 µm size range (Figure 1). Clay particles were also significant (ca. 30%) in a larger size range (0.5-1 µm). The number of particle types was fairly limited and this study revealed only few particles in the size range > 1 µm.

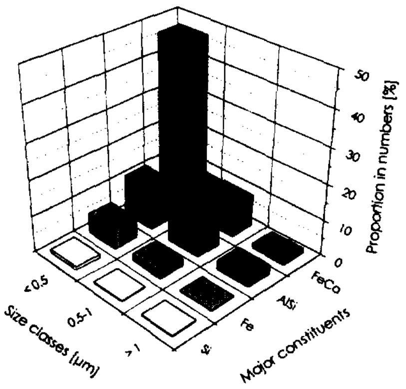


Fig.1. Characterization of the colloids in the Little Bied brook. Random analysis of 300 individual entities by STEM-EDS.

This distribution does not take into account the organic matter, which may be present as humic substances, polysaccharides or proteins (Volk et al., 1997). To evaluate its proportion and its nature in our system, organic matter was characterized by its carbon content (TOC) and its UV absorbance at 285 nm (Buffle et al., 1982).

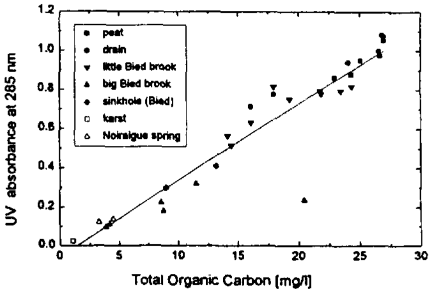


Fig.2. UV absorbance (285 nm) vs. Total Organic Carbon of raw water samples collected throughout the site.

Figure 2 shows the relation between TOC and UV absorbance on raw water samples collected at different dates throughout the basin. The correlation between both parameters is tight (R= 0.943), indicating the dominant humic/fulvic nature of organic matter. This result is not surprising and confirms the impact of peatlands on the water quality. Moreover, the higher TOC content in the Little Bied brook shows a greater impact due to the presence of secondary peats in this part of the valley.

4.2 Genesis of the Fe-Ca-rich colloids

The strong predominance of the Fe-Ca-rich colloids in the river led us to investigate the mechanisms of their formation.

4.2.1 Characterization by bulk chemical analyses

Figure 3 presents the results of bulk chemical analyses of samples collected in peat, drains and river. pH, % oxygen saturation, conductivity and Ca increase from peat to river, while the proportion of Fe^{2+} to Fe_{tot} decreases. It clearly appears from these data that the increase in pH and oxygen is followed by the oxidation of Fe^{2+} from peat to river, the major step being observed from peat to drain, where physico-chemical conditions drastically change. In fact, in the drain, peat pore water is in contact with air and mixed with clay pore water, rich in calcium; this influences equilibrium with carbonates and raises the pH. The high proportion of Fe^{2+} remaining in solution, although under unfavorable physico-chemical conditions (neutral pH, 60 % oxygen saturation), can be relied to the high concentration of humic substances in the system (ca. 20 mg C/l) which can stabilize Fe^{2+} by complexation.

4.2.2 Characterization by analytical electron microscopy

TEM observations and TEM-EDS analyses were performed in parallel to bulk chemistry (Figure 4). In the peat, micrographs show the presence of spherical electron-dense particles revealing only carbon. Their size ranges from 0.4 to 1 µm. In the drain, particles, with a similar morphology but with a smaller size range (0.2 to 0.4 µm), are detected but their composition differs: besides carbon, iron and calcium are revealed as major components of the particles. In the Little Bied brook, Fe-Ca colloids exhibit the same shape, size and composition as the ones in the drain. The similar morphology of the particles from peat to river and the correlation with bulk chemistry led to the hypothesis of iron precipitation on the surface of globular carbon entities in the drain. On the contrary chemical conditions do not favor calcium precipitation (undersaturation with respect to calcite). So, as suggested by the relatively high intensity of Ca EDS peaks (ca. 1/5 to 1/2 of Fe EDS peaks), calcium is postulated to be incorporated into the particles via successive adsorption onto the surface of continuously growing iron oxyhydroxide during its formation. Furthermore, given their morphology and composition, Fe-rich colloids seem to undergo only little transformation from drain to river.

To further describe the Fe-Ca colloids, elemental mapping was performed by STEM-EDS on particles from the Little Bied brook (Figure 5). This results in electronic pictures localizing the position of an element in the particles, with a signal intensity proportional to its concentration (Reed, 1993). The analysis reveals that iron and calcium maps can be perfectly superimposed, and that the two elements are localized at the outer of the particles whereas, the core presents a depletion of iron and calcium. No other element could be detected by EDS in the center of the particles, but this technique is not the most appropriate for detecting light elements (Z < 13). Moreover, the supporting film of the specimen is made of collodion/carbon, so that the intense peak of carbon in TEM-EDS spectra might be attributed to this film. To establish the presence of carbon in the Fe-Ca entities, a fine EF-TEM analysis was processed on the dominant Fe-Ca-rich entities from the Little Bied brook. The EF-TEM technique, as opposed to EDS, allows a better signal-to-noise ratio and a higher spectral resolution for light elements. Consistent EF-TEM spectra of the film and of the supporting film plus Fe-Ca-rich colloids revealed that the latter contain significant

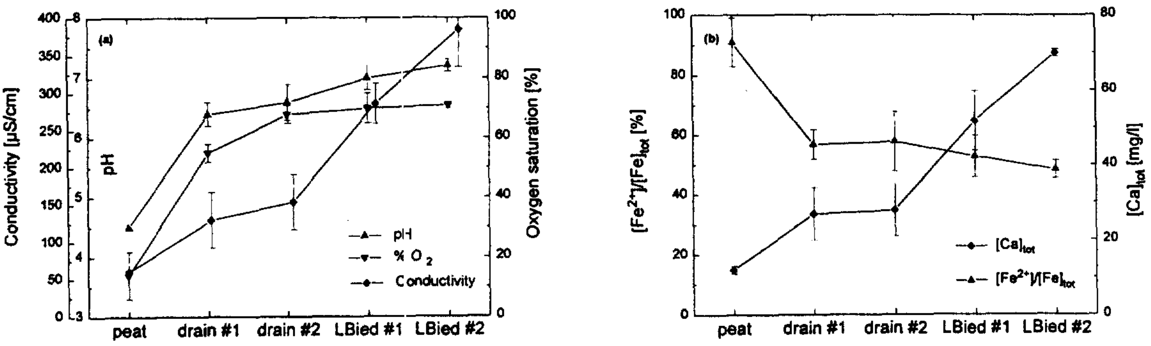
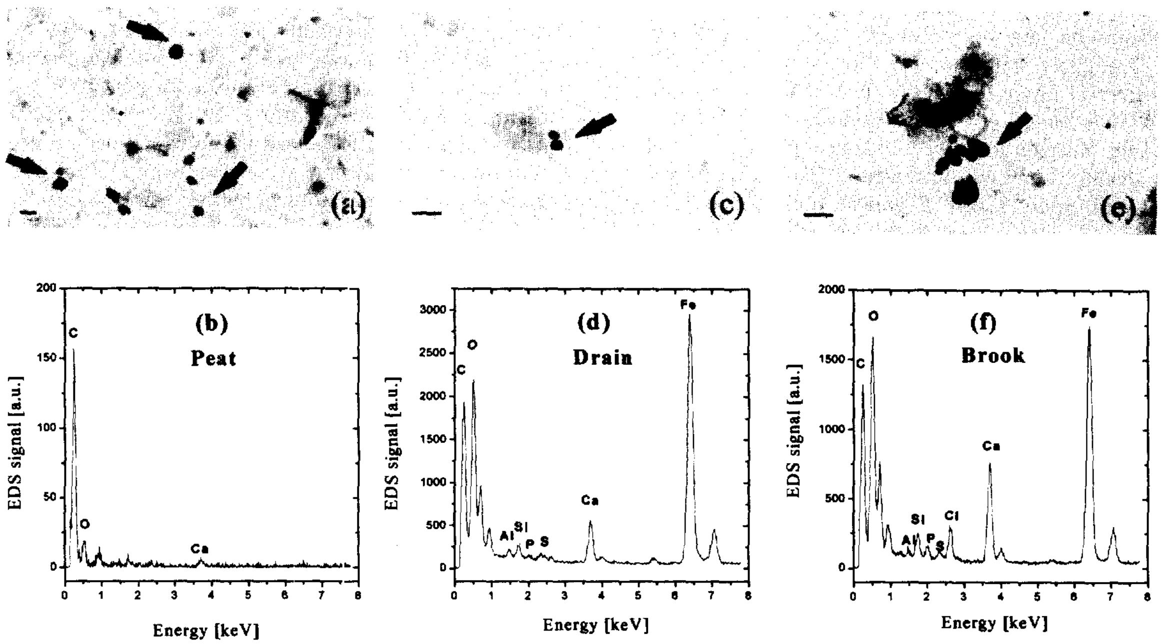


Fig.3. (a) Evolution of pH, % oxygen saturation and conductivity between the peat and the Little Bied brook; (b) evolution of calcium and Fe^{2+}: Fe_{tot} between the peat and the Little Bied brook. Each point represents an average of 5 samples taken between February and March 1997.



amounts of carbon (Mavrocordatos, 1997). These two fine analyses on the composition and structure of the Fe-Ca entities in the brook fit the hypothesis on iron precipitation onto the surface of organic globular colloids, iron and calcium being localized on the outer portion of the particle, whereas the core contains carbon. Moreover, the presence of globular carbon entities in the peat can be related to the ability of humic substances to form rigid «spherocolloids» at high concentration and low pH (Ghosh and Schnitzer, 1980).

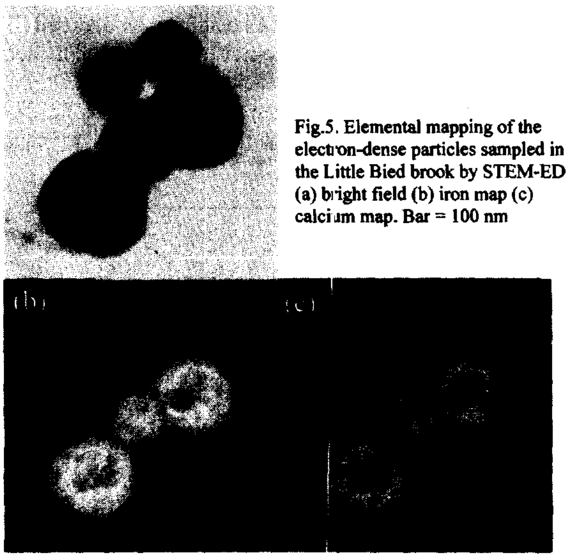


Fig.5. Elemental mapping of the electron-dense particles sampled in the Little Bied brook by STEM-EDS; (a) bright field (b) iron map (c) calcium map. Bar = 100 nm

5. Conclusion

Several observations in natural waters have shown that organic matter often consists of fibrillar networks covered by mineral elements (Leppard, 1992). On the contrary, in our system, ferrous iron seems to oxidize and precipitate at the surface of spherical organic entities whose nature is most probably of humic/fulvic origin. This precipitation is related to variations of the chemical conditions, in particular from an acidic and anoxic (peat) to a neutral and oxic (drain) medium. Calcium incorporation into these particles is not clearly understood yet, but may proceed via adsorption. Nevertheless, more investigations on these particles are necessary and the work is still in progress. Amongst others, the ability of these colloids to move from peat to drain will be explored; additionally, laboratory-controlled syntheses with field samples, coupled to electron microscopic analyses, will lead to more accurate information on the formation processes of these particles.

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