

## Response to reviewers

**bg-2011-493**

### **Biogeochemistry of an Amazonian podzol-ferralsol soil system with white kaolin.**

In the following the reviewers comments are given in italic and our responses in normal font.

#### Response to reviewer 1

***Reviewer 1:** This manuscript presents the chemical composition of groundwaters measured at different sampling depths and locations in a well-documented podzol-ferralsol soil catena. Based on the results and their knowledge on the site, the authors proposed that two hydrological pathways exist in the soil catena and related groundwater compositions to soil mineral paragenesis. Eventually, they provide a geochemical scheme of the functioning of the studied podzol-ferralsol soil system.*

*General comments*

*The study site description is well documented and the database presented is impressive. However, I did not fully get the point of the study. The authors need to explain better why they did this study and then discuss what the conclusions and implications of their work are. It is all the more crucial for the impact of this study that it is easy to get lost in all the presented data tables. I would have needed more explanations in the introduction on why it is interesting to know about the biogeochemistry of this catena and why the adopted approach was thought to be fruitful.*

**Authors:** The introduction was rewritten to address these remarks as well as those of the other reviewers, see particularly lines 104 to 111.

***Reviewer 1:** For instance, Is there any scientific controversy about the biogeochemical functioning of podzol-ferralsol soil systems with white kaolin? Why groundwaters measurements would be the key for significant advances?*

**Authors:** DOM issued from podzols favours the dissolution of all type of clay minerals because of Al complexation by dissolved organic matter, so how can such processes favour the genesis of thick kaolin horizons? Montes et al. (2007) hypothesized that the mineralization in the deep Bh-Bhs horizons of an organic matter transferred at depth by podzolic DOM-rich waters can turns the acidic percolating water more reductive, favouring the leaching of the iron. Such hypothesis, however, needs to be assessed by studying pH, Eh, DOM and iron species in percolating groundwaters.

***Reviewer 1:** If so, why the locations of the sampling sites are appropriated?*

**Authors:** The introduction was rewritten to better expose the problem (lines 76-89).

***Reviewer 1:** Have the authors any a priori hypotheses on how groundwater elemental concentration will change with the location of the sampling site?*

**Authors:** Yes, we had an a priori hypothesis based on the fact that, in such old systems, horizon morphologies and solid phase characteristics are very similar from one system to the other: soil age and high weathering rates have resulted in obliteration of most small scale spatial variability due to parent rock heterogeneity. In such soil covers soil variations are spatially explicit and depend on soil forming processes, closely related to water pathway and residence time. Sampling points were thus selected based on the morphology of the soil cover and on the water pathways that could be inferred from soil patterns and topography. We explained this in the first § of section 2.2.2.

***Reviewer 1:** Concerning the conclusions and implications, the authors wrote in the end of the introduction that “Such knowledge is necessary to evaluate the possible changes in the natural*

organic matter (NOM) dynamics through global change, as well as to understand the relationships between soil, kaolin and landscape features, in order to preview the soil characteristics and the possibility of kaolin ore from remote sensing. (PP2236L19-24)" Unfortunately these aspects were absolutely not discussed in the manuscript. To my point of view, the authors need to rewrite the abstract, introduction, discussion and conclusion sections to present more clearly the objectives of their work and what are the important conclusions of their findings.

**Authors:** This remark was also made by the other reviewers. We changed the introduction, the discussion and the conclusion sections to address it. Changes are detailed in the followings.

**Reviewer 1: Specific comments**

*The role of the vegetation is very little discussed. It may be due to the fact that the authors focused on Al, Si and Fe. However, I would have appreciated a discussion about the role of the vegetation that may have different characteristics along the catena on DOM concentration and Si cycle. In its present form the manuscript is more a geochemistry paper rather than a biogeochemistry paper.*

**Authors:** We agree with the reviewer. The role of the vegetation is evident for who used to work with podzolic processes, but worth to be discussed for other scientists. The role of vegetation on DOM concentration and Si cycle was already addressed in a paper from Lucas, 2001 in Annual Rev. Earth Planet Sci. that was not cited here. We corrected this by giving more details about vegetation in §2.1 and better discussing the role of DOM on §4.2.

*Reviewer 1: By the way, the results on other elements than Al, Fe and Si are not discussed. In this case, I suggest the authors present the results on the other elements as supplementary materials*

**Authors:** We agree, table 3 was displaced in supplementary materials.

*Reviewer 1: The part on the characteristics of DOM is not convincing. The fitting with the PROSECE model is intriguing. The authors wrote "Here we chose 4 acidic sites, a sufficient number to ensure a good fitting of the experimental curves (PP2248L25)". Is there any objective criterion to choose 4 acidic sites? If not what would have been the results if the fitting was done using 3 or 5 sites?*

**Authors:** The authors agree that this sentence is not sufficiently detailed, so that we rewrote it. Briefly, the PROSECE software has been used in numerous studies, fitting various types of experimental set of data (ex. acido-basic titrations, fluorescence quenching, voltammetry, ...) to evaluate binding properties of organic ligands. As explained in a previous paper (Garnier et al., 2004, Water Research), PROSECE fitting of acido-basic curves consists in modelling the data with different number of acidic sites, and to determine the optimal combination. This combination respects the following criterions: the simplest combination of acidic sites which leads to the minimal fitting bias value (sum of the absolute differences between experimental and calculated pH values). In the present study, a distribution of 4 acidic sites was sufficient to allow a correct fitting of experimental curves.

Accordingly, the sentence: "Here we chose 4 acidic sites, a sufficient number to ensure a good fitting of the experimental curves." was modified by: "The optimal number of acidic sites is defined as the simplest combination which conduces to the minimal fitting bias value (sum of the absolute differences between experimental and calculated pH values). Accordingly, a distribution of 4 acidic sites was sufficient to allow a correct fitting of experimental curves."

*Reviewer 1: It is speculated about the composition of DOM that "This DOM has thus likely a high proportion of small carboxylic acids such as formic, oxalic or citric acids whose site densities are 83.3, 83.3 and 41.7 meq gC-1, respectively (PP2252L25)" or "The DOM circulating in depth in the kaolinitic horizons was quite different. (PP2252L22)" Why did the authors not look at the DOM using more advanced analytical tools (chromatography, IR...)?*

**Authors:** Our group has performed detailed characterization on DOM of these waters – UV, IR, ionic chromatography with a column dedicated to small organic acids, RMN, RPE, 3D-fluorescence, LIFS, time-resolved LIF. The results, however, would need another publication! To respond the reviewers

comment, we added here the results we obtained by ionic chromatography: method is given on section 2.2.3., lines 314-321, results in section 3.3. and discussion was modified accordingly in section 4.2, lines 597-599. The

**Reviewer 1:** *The justification about the selection of the sampling points is not convincing. "The sampling points were selected with the purpose of identifying the main biogeochemical compartments of the soil system. (PP2240L7)" What does that mean? It seems like the authors knew what the zones of interest for sampling were and decided to sample there. That is not necessarily a problem but they should present the story like that and specify why these zones were selected.*

**Authors:** The sampling points were selected based on the morphology of the soil cover and on the water pathways that could be inferred from this morphology and from topography. Justification about the selection of the sampling point was developed on §2.2.2.

**Reviewer 1:** *I would need that the authors discuss the spatial variability of the site. They do not have replicates. If chemical groundwaters composition can vary strongly within the same soil horizon, it would be a problem. Can the authors comment on that?*

**Authors:** The response to this question is the same that these regarding the location of the sampling sites. A response is now given in the first § of section 2.2.2

**Reviewer 1: Minor comments**

P2235L23 : *"at least 13.6 1.1 PgC is stored in Amazonian podzols and could return the atmosphere if the climate changes with the onset of a dry season." Hopefully only part of it could return to the atmosphere!*

**Authors:** What part will return to the atmosphere is indeed the problem! We are currently studying this question using organic matter mineralization tests and the first results, to be published in 2013, suggest that 1/4 of this OM could return to the atmosphere within some years and 1/2 within some centuries.

**Reviewer 1: PP2240L23 was the driest instead of drier**

**Authors:** This was corrected

## Response to reviewer 2

**Reviewer 2:** *This study examines groundwater properties at a number of sites in a podzol-ferralsol soil catena located in the Alto Rio Negro region. The authors focus upon identifying the soil mineralogy and dissolved organic matter (DOM) concentration through their defined catena. By comparing groundwater sample availability during three precipitation events they conclude that there are two groundwater pathways in their studied catena. The first, permanent pathway is located at an approximate depth of 2 m, within the kaolin horizon. The second, more temporal pathway is located just below the surface and only occurs during heavier precipitation events. In the context of these two pathways, the authors present their mineralogical and DOM concentration data with the objective of understanding these soils more fully.*

*The study of the podzol-ferralsol soils in the Amazonian area is interesting, and understanding the soil processes governing these environments is important. However, the overall reasoning behind such a study is unclear. The authors state that they are constructing a database to study ground waters in a podzol-ferralsol region due to a lack of geochemical information in the study by Montes et al. (2007) The novelty of the podzol-ferralsol environments and their importance in soil dynamics is not clearly indicated in the abstract or the introduction and so it makes putting the data in the manuscript within an appropriate context difficult. The choice to study ground waters rather than other pools seems mainly due to the fact that other previous studies were unable to do so. The authors do not clearly describe why ground waters are so important to these environments, other than that they can potentially contain high levels of dissolved organic carbon (DOC). The objectives of the study stated in*

*the introduction are vague and I am not entirely sure they are all fully addressed with the current data presentation. After reviewing this paper, I still do not feel able to 'evaluate the possible changes in the natural organic matter (NOM) dynamics through global change'.*

**Authors:** The introduction was rewritten to address these remarks.

**Reviewer 2:** *The number of study sites within the catena seems appropriate and well placed, and in theory much information could be yielded from their investigation. However, much of the methods, results and discussions sections were difficult to understand due to many grammatical errors and poor explanations.*

**Authors:** The paper is being corrected by a native English speaker for final manuscript.

**Reviewer 2:** *Although the mineralogical aspect of this study was thorough, due to a lack of further chemical study of the DOC, often broad and poorly evidenced conclusions were made throughout the results and discussions sections.*

**Authors:** We added chemical identification and characterization of small carboxylic acids and data on aromaticity obtained by UV absorption, see hereafter.

**Reviewer 2:** *Much of the basis of this study is upon the setup of two water pathways. The authors define the two pathways upon only three sampling periods at seemingly random precipitation events. A more strategic sampling plan would have yielded a much more convincing definition. With the evidence presented thus far, the two defined pathways seem valid but I am not sure how well they expand to other times of the year.*

**Authors:** thanks also to other reviewers, we explained better in the first § of section 2.2.2. Water pathways were deduced (1) from the morphology of the soil cover, following the line of greatest slope along the catena as explained in section 2.2.2. (see also what is the structural analysis approach explained by the authors cited at lines 139-140) and (2) from field observation as explained in section 3.1.

**Reviewer 2:** *Overall, the objectives of this study are not clear, and need to be stated in both the abstract and introduction instead of a vague mention. The number of grammatical and spelling errors throughout the manuscript is extensive, and this needs to be corrected.*

**Authors:** The manuscript is being corrected by a native English speaker, abstract and introduction were rewritten.

**Reviewer 2:** *A major overhaul of much of the manuscript is required in order to provide a more succinct, easily followed study description.*

**Authors:** We tried to address this comment throughout all corrections in the manuscript, see further responses to the reviewer's comments.

**Reviewer 2:** *Specific comments*

*Abstract*

*-The aims of the study need to be clearly defined in the first paragraph and how the authors set about solving these.*

*-There does not seem to be a logical explanation of the most important points of the data, rather seemingly random parameters are presented with no clear story.*

*-The author's mention a database L6 P2234 but they do not state what was in the database and why did they study those parameters. Also 'the sampling periods allowed to sample under high- and low-level water-table conditions' makes no sense, rewrite.*

*-L10 P2234 what are the currently observed mineral and organic paragenesis? What is this compared to?*

*- The second and third paragraphs should be switched.*

*-L13 P2234 what is the aggressiveness of groundwater? This is the wrong word to use here, please replace.*

**Authors:** All these comments were taken in account in the new version of the abstract.

**Reviewer 2:** *-L17 P2234 this is an extremely broad statement, and there is no chemistry in this study to back this statement up, please revise.*

**Authors:** We added here the results we obtained by ionic chromatography: method is given on section 2.2.3., lines 314-321, results in section 3.3., lines 479-486 and discussion was modified accordingly in section 4.2, lines 597-599.

**Reviewer 2:** *-L27 P2234 this sentence makes no sense, rewrite for clarity.*

**Authors:** The sentence was modified (lines 50-51).

**Reviewer 2:** *Introduction*

*-Similar to the abstract, a clear logical reasoning for the study needs to be developed in this section. Restructure this section to begin with broad, widely applicable information important for your site, and then work towards focusing upon the most salient objectives of the study.*

**Authors:** We rewrote the introduction following the reviewer comments, lines 22 to 51.

**Reviewer 2:** *-L6 P2235 replace 'allowed' with 'allow'.*

**Authors:** The replacement was done.

**Reviewer 2:** *-L12 P2235 a positive feedback of what? Separate this sentence into two, and rewrite the second part for clarity.*

**Authors:** The feedback was defined and the sentence was separated and rewritten.

**Reviewer 2:** *- L18 P2235 restructure this sentence.*

**Authors:** The sentence was restructured

**Reviewer 2:** *- L22 P2235 which authors? State the name.*

**Authors:** OK

**Reviewer 2:** *- L23 P2235 this is the only mention of atmospheric importance and this statement is not supported in the manuscript explanation, suggest deletion.*

**Authors:** This was deleted.

**Reviewer 2:** *- L2 P2236 split this sentence into two after 'Montes et al. (2007).'*

**Authors:** The sentence was split.

**Reviewer 2:** *-L5 P2235 delete 'the' between of and iron.*

**Authors:** The sentence was rewritten

**Reviewer 2:** *- L7 P2236 what type of geochemical properties?*

**Authors:** Geochemical properties were defined: " Such hypothesis, however, needs to be assessed by studying pH, Eh, DOM and Fe and Al species in percolating groundwaters." (lines 93-94).

**Reviewer 2:** *- L13 P2236 Why is studying groundwater solutions so important?*

**Authors:** Response to these question is now given in the last § of the introduction, lines 104 to 111.

**Reviewer 2:** *- L15 P2236 is there a reference for this statement?*

**Authors:** No, this is a statement resulting from the analysis of existing literature.

**Reviewer 2:** - L16 P2236 rewrite the objectives to reflect the data presented. Also briefly mention how/what will be studied.

**Authors:** This was done on lines 104 to 111.

**Reviewer 2:** - L19 P2236 Delete the last sentence this is not answered in the study.

**Authors:** The sentence was modified (lines 104 to 111) and the answer to this question, which was indeed unclear, is now better addressed in the conclusion, lines 690 to 694 and 714 to 717 .

**Reviewer 2: Materials and Methods**

- L8 P2237 what is the name of the river network?

**Authors:** In such areas small rivers have no name.

**Reviewer 2:** -Section 2.1 is overly descriptive and could be shortened.

**Authors:** We tried to shorten, but we also need to explain for non-specialists and reviewer 1 for example asked for more detail about vegetation

**Reviewer 2:** - L20 P2237 Mineralogy: : : sentence is repeated in the next paragraph and only one is needed.

**Authors:** The repetition was deleted.

**Reviewer 2:** Also a very brief description of the methodology would be helpful.

**Authors:** X-ray diffraction on powder samples, diffuse reflectance spectroscopy and thermogravimetric analysis are broadly used mineralogical tools and we think that Biogeochemistry's readers would easily find information about. We specified that detailed methodology is given in Ishida, 2010.

**Reviewer 2:** -One point of confusion was the labelling system for the studied sequence. CA2-20 and CA1-150 are described but there seems to be no reasoning or ease to follow the sampling points in the sequence shown in Fig.2. I suggest a relabeling for clarity.

**Authors:** All points were relabeled: W1 and W2 in the waterlogged podzol area and from S1 upslope to S6 downslope along the catena.

**Reviewer 2:** Also what is the difference between an observation pit and borehole?

**Authors:** We specified "hand auger borehole" in the text. A soil pit is a soil pit, just try for example "soil pit" in Google Images.

**Reviewer 2:** Is it necessary to include these on Fig. 2?

**Authors:** We think it is necessary because it gives the accuracy of the soil horizons geometry along the catena.

**Reviewer 2:** Spell out FAO in the Fig. 2 legend.

**Authors:** For brevity, we referred in the legend to FAO, 1993 and we gave the reference in the ref. list.

**Reviewer 2:** Can the Spring point be indicated on Fig. 1 or Fig. 2?

**Authors:** Yes, we indicated on Fig. 1.

**Reviewer 2:** -Fig. 3 is this for pit 1?

**Authors:** Yes, we have specified in the legend.

**Reviewer 2:** Why are only these parameters plotted? What about plotting the other pits in a similar plot for easy comparison?

**Authors:** Because those are the parameters of interest for the biogeochemical interpretation: relative positions of the TOC, kaolinite and gibbsite peaks within and beneath the Bh horizon. Other pits would not add more for the purpose of the paper.

**Reviewer 2:** *Why is TOC not stated in mg/L? Is this supposed to be DOC, were the samples filtered prior to this measurement? If so, how?*

**Authors:** Fig. 3 refers to the soil solid phase! We modified the legend to avoid any ambiguity.

**Reviewer 2:** *- Section 2.2.2 the choice of these three periods does not seem entirely logical, and even though the original reason for their choice did not come true, it is not necessary to state this. Only discuss what was more importantly different between them. What are the seasons for each of the collection times?*

*What are the average rainfall numbers for past years and how does these sampling periods compare, with cited numbers?*

**Authors:** These three questions are linked to each other. In these regions there are no marked season and a great interannual variability, we changed section 2.1 (lines 123-124) to explain that. We also shortened the first § of section 2.2.3.

**Reviewer 2:** *-L10 P2241 what analyses were conducted on each of the four aliquots?*

**Authors:**  $\text{H}_4\text{SiO}_4$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , we added "separately" to avoid ambiguity.

**Reviewer 2:** *What was the fifth container poisoned for?*

**Authors:** We specified "for laboratory analysis of DOC and other dissolved species", those are listed in the 4<sup>th</sup> §.

**Reviewer 2:** *Were blanks also filtered to ensure no additional contributions?*

Yes, we specified that on line 277.

**Reviewer 2:** *-L16 P2241 a reference for past use of this method would be appropriate here.*

**Authors:** We did not found comparable groundwater study to refer to. We had tested the method in the lab before field studies.

**Reviewer 2:** *-L20 P2241 if iron measurements were made within an hour, what is the point in testing whether it is the same after 6 hours?*

**Authors:** No significant differences were observed between measurements 10mn and 6 hours after sampling. This assessed that no significant oxidation of  $\text{Fe}^{2+}$  had occurred between 10mn and 1 hour, which is the maximum time between sampling and analysis.

**Reviewer 2:** *-L23 P2241 what were the absorbencies used for each of the parameters measured? How significant is DOM contribution at these specific absorbencies? Can you provide some references for this?*

**Authors:** Absorbencies are now given on lines 263-264. As DOM absorbency exponentially decrease from UV to IR, DOM contribution is low for  $\text{Al}^{3+}$  and  $\text{H}_4\text{SiO}_4$  measurements realized at 620 and 695 nm, respectively, but can be significant for  $\text{Fe}^{2+}$  measurement at 485 nm. Details and a reference are given lines 269 to 274.

**Reviewer 2:** *-L26 P2241 how long after sampling was DOC analyses performed? Delete equipment in this sentence.*

**Authors:** Between 10 and 45 days, this was specified in the text on line 275. The word equipment was deleted.

**Reviewer 2:** *-L4 P2242 change 'but' to 'and'.*

**Authors:** This change was done.

**Reviewer 2:** -L7 P2242 include a reference to substantiate this oxidation of DOM test.

**Authors:** Reference was added (Patel-Sorrentino et al., 2004)(line 286).

**Reviewer 2:** -L23 P2242 change 'depending' to 'dependent'.

**Authors:** This change was done.

**Reviewer 2:** -L21 P2242 DOM being charged is no great surprise, and of course it affects pH values. I wonder how much this adjustment in pH affected some of the conclusions later in the paper. An example of how much one or two of the pH values changed would be helpful.

**Authors:** We gave an example lines 303 to 305.

**Reviewer 2:** -P2242 last paragraph the reasoning for the microtitration is not clear, and I am not sure doing this experiment is necessary for this study.

**Authors:** the behavior of the percolating solution with regard to Al and Fe transport depends on specific metal exchange sites, poorly sensitive to variations in pH and few in number, and numerous exchange sites where occurs competition between H<sup>+</sup> and metal, as carboxylic sites. Microtitration is a useful tool to identify and quantify the latter sites.

We substituted the last paragraph for the following (lines 306 to 313):

"In order to evaluate the behaviour of the studied solutions with regard to H<sup>+</sup>, acid-base logarithmic scale microtitrations of selected samples were performed using the procedure describe by Garnier et al. (2004a). Briefly, sample solutions were acidified by 0.2 mol l<sup>-1</sup> HNO<sub>3</sub> additions until pH 2.5, N<sub>2</sub> purged, and then titrated using 0.1 mol l<sup>-1</sup> KOH until pH 11.5. Acid-base titrations were performed using two Titrino 716 apparatus controlled by a Tinet 2.4 software (Metrohm). The combined pH-micro-electrode used (Mettler, Inlab422, reference: Ag/AgCl/KCl 3.0 mol l<sup>-1</sup>) was calibrated daily by the titration of a HNO<sub>3</sub> 0.01 mol l<sup>-1</sup> solution followed by theoretical fitting of the titration curve."

**Reviewer 2: Results**

-Similar to the previous sections, the authors need to thoroughly revise this section to make a more easily followed argument.

**Authors:** We revised the whole section following the 3 reviewers comments.

**Reviewer 2:** -L8 P2243 change '2dn' to '2nd'.

**Authors:** The change was done.

**Reviewer 2:** -L15 P2243 description of PMVB-15 point in next paragraph should be moved forward to this point.

**Authors:** The description of this point was moved and the text adapted for.

**Reviewer 2:** -L19 P2243 delete 'ing' in excepting. Do this for the rest of the paper.

**Authors:** This correction was done throughout the manuscript.

**Reviewer 2:** -L10 P2244 What is the objective in including Supplemental Table 1? The summary tables included in the main text are more than adequate. I suggest this table be removed.

**Authors:** Here we do not agree with the reviewer. The whole database can be fruitful for future research topics we do not imagine even now and as the database is in Supplements, it does not hinder the reading of the manuscript.

**Reviewer 2:** In the Table 2 legend, I suggest changing 'statistics' to 'summary'.

**Authors:** We changed the legend, we also changed the text accordingly, line ?? ("summary from these data is given in Table2").



**Reviewer 2:** -L18 P2244 *'This assessed: :.'* rewrite this sentence or delete it is confusing.

**Authors:** The sentence was deleted.

**Reviewer 2:** -L25 P2244 Change *'one sampling day to the other'* to *'sampling days'*.

**Authors:** The change was done.

**Reviewer 2:** -Fig. 5 is this figure really important to include in the main text? This could be moved to the supplementary. Also there are commas in the y axis, these should be periods.

**Authors:** We agree with the reviewer, this information is contained. We suppressed this figure and we added a comment about standard deviations and moved the figure to the supplementary material. We substituted commas per periods in the y axis.

**Reviewer 2:** -Fig. 6 is very difficult to see, and really there are few differences between a-d, as stated on L26 P2242. Therefore, to make it clearer the authors could consider just showing Fig. 6d and stating the differences in a-c.

**Authors:** We agree with the reviewer on both points. The information given in Fig. 5 is contained in the standard deviation bars of other figures. We suppressed this figure and we added a comment about standard deviations. Regarding Fig. 6 and 7, we moved the part giving average composition by sampling periods in supplementary material (Fig. S3 and S4) and we merged the overall average in a single figure (new Fig. 5). The manuscript is thus lighter and more easily readable. Legend of figures and text were changed accordingly, the whole paragraph was rewritten (lines 366 to 372).

**Reviewer 2:** -L27 P2242 rewrite this sentence on this line, it is confusing.

**Authors:** The sentence was suppressed following rewriting of the whole paragraph, see previous point.

**Reviewer 2:** -L11 P2245 a statistical test to demonstrate this would be helpful.

**Authors:** We specified (line 384-385): "T-test values of the difference between points separated by at least 2 other points in the sequence were all higher than 2".

**Reviewer 2:** -L17 P2245 *diminution* is used many times in the text; this is incorrect and should be revised.

**Authors:** We replaced with "decrease" (3 replacements in the manuscript)

**Reviewer 2:** -L1 P2246 swap *always* and *had*.

**Authors:** We swapped these words.

**Reviewer 2:** -L11 P2246 a strong decrease is not really accurate, since they both decreased by about a half.

**Authors:** We substituted "a strong decrease" by "a decrease by more than half".

**Reviewer 2:** -L13 P2246 shorten, split and revise this sentence for clarity.

**Authors:** We shortened, divided and revised the sentence.

**Reviewer 2:** -L22 P2246 what is the quantification limit?

**Authors:** The quantification limit is given in the method section (0.01 mg L<sup>-1</sup>).

**Reviewer 2:** -Just looking at the redox numbers and the iron concentrations, there seems to be some disparity based on normal logic. A more thorough discussion and consideration of these numbers should be conducted.

**Authors:** this section only describes the results. Discussion and consideration of these numbers are given in section 4.3.2.

**Reviewer 2:** -L20 P2247 rewrite these next two sentences for clarity.

**Authors:** The two sentences were rewritten (lines 439 to 443).

**Reviewer 2:** -L3 P2248 delete 'the' between on and average.

**Authors:** We deleted this word.

**Reviewer 2:** -L13 P2248 shouldn't there be a correlation? This needs further thought and consideration.

**Authors:** Yes, a correlation was expected but not observed. This point is discussed in section 4.3.2. (lines 672-675).

**Reviewer 2:** -L20 P2248 rewrite for clarity.

**Authors:** We rewritten the sentence (line 465).

**Reviewer 2:** -L26 P2248 only 4 acidic sites to represent all of the DOM molecules seems very low, and I wonder how well this model works.

**Authors:** We explained better how the model works by substituting the sentence: "Here we chose 4 acidic sites, a sufficient number to ensure a good fitting of the experimental curves." by: "The optimal number of acidic sites is defined as the simplest combination which conduces to the minimal fitting bias value (sum of the absolute differences between experimental and calculated pH values). Accordingly, a distribution of 4 acidic sites was sufficient to allow a correct fitting of experimental curves." (lines 467-472). The laboratory method was also better described in the 2.2.3 section (lines 306-313).

**Reviewer 2:** Discussion -This section can be shortened to the most pertinent points, and a logical discussion needs to be developed. This section is particularly difficult to follow.

**Authors:** We shortened and rewritten many parts of this section: the 2<sup>nd</sup> § of 4.1.1,

**Reviewer 2:** -L11 P2249 is the soil and vegetation exactly the same? This seems difficult to believe.

**Authors:** We substituted "same" by "similar", but it must be considered that most of Amazonian soils are thick, old soils which can be considered as end-members of pedogenetic processes; most differences in parent rocks were wiped out during pedogenesis. Regarding podzols all minerals, but quartz and scarce heavy minerals, were completely weathered and disappeared from the first 2, 3 or more meters of the soil. If the quartz grains size is similar between two different types of rocks, the podzols developed on these two rocks will be very similar. If climate is similar, the vegetation too will be very similar. Another consequence is that the soils – podzols or ferralsols – are quite homogeneous: sampling is quite reproducible from one place to the other for two soils having the same position in the soil system.

**Reviewer 2:** -L21 P2249 shorten, split up and rewrite this sentence.

**Authors:** The whole was rewritten.

**Reviewer 2:** -L25 P2249 why are molar ratios calculated? The point is already made.

**Authors:** We agree – we deleted the molar ratios.

**Reviewer 2:** -L2 P2250 The last sentence of this section, seems like an afterthought and not thoroughly thought out and discussed. Also the data presented do not unambiguously confirm this statement. Either remove or expand and reword.

**Authors:** We referred in the text to the papers where such adsorption has been observed (lines 513-516).

This statement was not explained because it seemed evidence to the authors. In Amazonian podzols, DOC adsorption on clay or Fe-oxides surfaces was frequently observed and observed everywhere a DOC-rich water table leaves a sandy material and passes through a material having some clay or oxides – 4% of clay minerals is enough to observe such adsorption, described for example Fig. 4 in Chauvel et al., 1987 which is the sketch of the following photograph.

The white sand as well as the sandy yellow material have high hydraulic conductivity. The water table that fluctuate in the white sand is DOC-rich, but when it passes through the yellow material it leaves the DOM at the transition, here is a detail.



**Reviewer 2:** -L8 P2250 suffered is not appropriate to describe water. A better word is exhibited.

**Authors:** The word suffered was replaced by exhibited.

**Reviewer 2:** -L9 P2250 this cannot be confirmed, therefore, 'is' should be changed to 'can be'. Also a reference would be appropriate here.

**Authors:** Same answer than for L2 P2250, however, we changed "is" to "can be".

**Reviewer 2:** -L10 P2250 rewrite this sentence it is confusing.

**Authors:** We substituted the sentence by "The low percentage of DOC observed in the water percolating in the deep kaolin horizons, however, shows that a small proportion of DOM was not retained in the Bh and is able to migrate through a clayey material."

**Reviewer 2:** -L13 P2250 a few references in these explanations in this paragraph would be helpful. Also how long do the authors anticipate the mineralization to take? Is this a realistic time period for their study and observations?

**Authors:** References were added. We also specified that “The assumption of a relatively rapid turn-over of the OM is strengthened by the young apparent  $^{14}\text{C}$  ages (<3000 y) measured for a DOM of similar deep Bh from the Manaus area (Montes et al., 2011).

**Reviewer 2:** -L23 P2250 delete ‘progressive’. This whole sentence is confusing and should be rewritten.

**Authors:** We deleted “progressive”, rewritten and shortened the sentence.

**Reviewer 2:** -L5 P2251 change ‘loosed’ to ‘lost’.

**Authors:** The change was done.

**Reviewer 2:** -L6 P2251 ‘Such water: :’ this is confusing and should be rewritten.

**Authors:** The two first sentences of the § were rewritten and substituted by: “When flowing from the white sand to the non-podzolic leached horizon Ef, passing the Bhs, the groundwater lost most of its DOC, but remained with DOC concentrations higher than  $5\text{ mg L}^{-1}$  thus aggressive with regard to secondary minerals. It can therefore favour the clay impoverishment of the Ef horizon with a positive feedback due to higher water flow after clay impoverishment.”

**Reviewer 2:** -L7 P2251 Change ‘is’ to ‘can be’.

**Authors:** The change was done

**Reviewer 2:** -L10 P2251 PMVB-15 is so different from all other points, and this short discussion should be expanded.

**Authors:** We explained the role of the litter degradation by adding the following sentence: “It has indeed been shown that the forest recycles a great amount of Si through litterfall and that litter dissolution in the topsoil can increase groundwater Si concentration up to saturation with kaolinite (Lucas, 2001).”

**Reviewer 2:** -Section 4.3 there is no reasoning behind why this first calculation is performed. I am not sure ZDOM really means anything. If it does, then this is not clear and warrants much more explanation. Also what is COD in equation 1? Calculation of the acid site density is intriguing but without more chemical evidence, I strongly question the validity of the conclusions made in regard to these calculations. There are methods that could help to confirm the idea that carboxylic groups are important, e.g. IR, NMR, GC-MS.

**Authors:** Characterization of DOM functional group or of compounds by spectroscopic or chromatographic methods does not give measurement of DOM chemical behavior. Here we give informations about this chemical behavior. Our group also performed detailed characterization on DOM of these waters and of SOM of the Bh – UV, IR, ionic chromatography with a column dedicated to small organic acids, RMN, RPE, 3D-fluorescence, LIFS, time-resolved LIF. The results, however, need another publication! To respond the reviewers comments, we added here the results we obtained by ionic chromatography and by UV absorption.

To introduce why we performed such calculations we added the following sentence at the beginning of §4.2.: “The remaining negative charges due to the DOM were calculated in order to calculate the DOM acid site density.”

**Reviewer 2:** -Table 4, I cannot find any discussion of this table. Therefore, maybe it should be omitted and discussed only since there are so few numbers within it.

**Authors:** We think that such data may be useful for scientists studying podzol-issued waters, so we think it is better to leave the table. The data are discussed in section 4.2., line ??, where we added a reference to the table.

**Reviewer 2:** -L22 P2253 this sentence is confusing and should be rewritten.

**Authors:** We agree, the sentence is confusing and non-useful, it was deleted.

**Reviewer 2:** -L25 P2253 insert 'the' between in and upper.

**Authors:** This insert was done.

**Reviewer 2:** -L2 P2254 I don't think that all of the points are close to the "kaolinite 1" line, but they seem to be spaced between that and the second kaolinite line. I suggest a revision of this sentence.

**Authors:** We agree, the sentence was rewritten.

**Reviewer 2:** -L14 P2254 why test the complexation by DOM? The calculation seems odd and it does not add anything extra, so why include this?

**Authors:** We agree, we removed the corresponding points from Fig. 7 and the corresponding paragraph in section 4.3.1.

**Reviewer 2:** -Section 4.4.2 the fact that Fe<sup>2+</sup> is so predominant in these oxic soils is really interesting. Testing some of the explanation for the rapid change in redox condition in a laboratory setting to validate the suggestions made here would be a good addition to this section.

**Authors:** We actually plan to test changes in redox conditions in a laboratory setting. Such an experiment, however, is heavy. We need to bring back from the camp undisturbed samples taken at 1.5 to 3 m in depth, to store them until the return to the laboratory (at least 1 week) with microbial activity as small as possible, then to place them under controlled hydric potential using groundwater also sampled at site. We applied for funding for that.

**Reviewer 2:** - P13-160 point does not seem very differently positioned than the others around it, this statement should be rethought out.

**Authors:** We disagree with that comment. The point P13-160 (now S2-160) is 100mV lower than points.

**Reviewer 2:** -L12 P2255 many broad statements are made in this paragraph which are currently very thinly substantiated. These suggestions need more thought and evidence before this paragraph can be included as it stands.

**Authors:** This paragraph made two statements: (1) the Eh hypothesis, that is discussed in the previous §, and (2) the carboxylic hypothesis that is now more substantiated with the new data given regarding small carboxylic acids.

**Reviewer 2: Conclusions**

*-This section is not very conclusive. It is extremely confusing at times and there is no logical thought pattern. This section is designed to be understandable without having read the paper beforehand, and currently this is not possible. The authors should think about the most salient points of their study, and then put them together in a logical conclusion for a more easily understood section.*

**Authors:** The conclusion was rewritten.

### Response to reviewer 3

**Reviewer 3:** *The authors present an impressive dataset for groundwater samples collected along a podzol---ferralsol catena overlying a kaolin depot in Amazonia. They were able to distinguish two flow pathways with characteristic water chemistries with regard to Al, Si, Fe and DOC mobility and transport, and infer new insights in the genesis of these soil systems.*

*The authors demonstrate great knowledge of this soil system. Despite the fact that this manuscript represents only an excerpt of a comprehensive dataset on this soil system --- publications that include more in---depth characterizations of the mineralogy and DOC chemistry appear to be in prep – the manuscript presented here has significant shortcomings that need to be addressed before I can recommend publication*

*In the following, I will use the abstract as an example to briefly illustrate my main concerns: While the authors state that podzol--ferralsol systems are widespread in Amazonia and are frequently associated with kaolin deposits, there is no mention of the general research problem addressed in this manuscript. The authors then go on to describe the wealth of their results without stating a specific research question or hypothesis. Finally, the manuscript ends in a statement of possible implications that will confuse even the informed reader. This is symptomatic for the whole paper and I advise the authors to make a serious attempt to revise the presentation of the abstract, introduction, discussion and conclusion sections. It is not clear to me what is unknown, what the specific research questions are, and why the relevant in the context of global change and C cycling. Moreover, I suggest trying to disentangle the main angles the authors provided in this manuscript: (i) the dynamics of DOC in these soil systems, their sensitivity to global change, and the implications for global C cycling; and (ii) the relationship between soil processes, kaolin deposits, and landscape forms, and what this all means for kaolin ore exploitation. How are they related/not related? What specific aspect can be resolved with this study*

**Authors:** All changes we made in introduction, discussion and conclusion section were conducted in order to address these comments. At the end of introduction, we clearly expressed the twofold aim of the paper (lines 104-111). Many changes were made in the discussion section, thanks also to the other reviewers. The conclusion was rewritten too.

**Reviewer 3:** *Finally, I recommend that the authors incorporate findings from the other publications on mineralogy and DOC chemistry. These are critical factors that need to be taken into consideration if one is to develop a thorough understanding of the pedogenic processes at work in this soil system. Without these data, any inferences appear a little premature.*

**Authors:** Mineralogy data were published in an already available document (Ishida, 2010) (<http://www.teses.usp.br/teses/disponiveis/44/44142/tde-08012011-011714/pt-br.php>) and a synthesis will soon be published in Geoderma. We think that adding more mineralogical data in this paper will not bring more to the paper and will turn the manuscript unnecessarily heavy. With regard to DOC chemistry, we added to the present papers the identification and quantification of small carboxylic acids by ionic chromatography and the SUVA<sub>254</sub> index characteristic of the aromaticity of the DOC: methods are given on section 2.2.2., lines 314-321, results in section 3.3. and discussion was modified accordingly in section 4.2, lines 597-599.

**Reviewer 3:** *Specific comments*

*Abstract:*

*L12: change to "... in THE acid podzolic ..."*

**Authors:** This change was done.

**Reviewer 3:** *It would be beneficial to the reader if the last sentence of the abstract was reworded. I suggest "... kaolin are likely to occur where active giant podzols are close to a slope gradient sufficient to ..."*

**Authors:** the sentence was changed in the reworked conclusion.

**Reviewer 3:** *Results:*

*P2244L16--19: Why is it necessary to report this data in the main manuscript? I suggest moving this information in the supporting materials.*

**Authors:** This was also suggested by Reviewer 2 and we moved the figure in the supplementary material.

**Reviewer 3:** *P2248L13: Please revise the wording – the following is confusing: "There is no, however, a good correlation ...". I understand that there is no correlation and that is what should be said.*

**Authors:** This was corrected (lines 456-457) and the R<sup>2</sup> (0.23) was given.

**Reviewer 3:** Fig. 7: I find it counter-intuitive that the sampling points are plotted in this sequence. In Fig. 2 it looks like water flow along this pathway reaches the sampling points in the following order: P4-240 – P13-160 – PMVB – P12-160. In any case, connecting the data points with a line is misleading as it suggests to the reader that water flows along this sequence.

**Authors:** We agree and we suppressed the line between point S3-160 and point SMVB-15 in Fig. 5 and Fig. S3.

**Reviewer 3: Discussion:**

P2251L7: What exactly is the positive feedback? Please expand

**Authors:** the sentence was modified in order to explain this point: "It can therefore favour the clay impoverishment of the Ef horizon with a positive feedback due to higher water flow after clay impoverishment."

**Reviewer 3: P2251L: Equation 1 --- Define the terms of the equation. COD?**

**Authors:** It was a mistake – COD in place of DOC - and was corrected.

**Reviewer 3: L22: change 'was' to 'whereas'**

**Authors:** the change was done

**Reviewer 3: P2252L4: Your aim is not to 'give an order of magnitude'. What the authors are trying to do here is to approximate the acid-site densities of DOC using a single carboxylic-acid type ligand as a model. Please rephrase.**

**Authors:** OK, we changed substituted the sentence by "The acid site density  $L_T$  expressed in  $\text{meq.gC}^{-1}$  was approximated by modelling for a single carboxylic-type ligand..."

**Reviewer 3: P2256L1517: How do reconcile your hypothesis that DOC becomes mineralized (or 'turned over') after adsorbing to mineral? Most publications indicate that adsorption to clays and Fe oxides protects DOC from microbial decomposition**

**Authors:** This is hypothesis of a relatively rapid turn-over of the OM is strengthened by the young apparent  $^{14}\text{C}$  ages (<3000 y) measured for a NOM from a similar deep Bh in the Manaus area (Montes et al., 2011). This is now specified on lines 531-534. It is likely that only a part of the organic matter suffers mineralization, another part, more aromatic and hydrophobic, being resistant. A response to this question will be sought in future work by dating of the different fractions of the Bh OM and by mineralization experiments.

1 **Biogeochemistry of an Amazonian Podzol-Ferralsol Soil System with White**  
2 **Kaolin**

3  
4 Y. Lucas<sup>1</sup>, C. R. Montes<sup>2</sup>, S. Mounier<sup>1</sup>, M. Loustau-Cazalet<sup>1,\*</sup>, D. Ishida<sup>3,\*\*</sup>,  
5 R. Achard<sup>1,\*\*\*</sup>, C. Garnier<sup>1</sup>, B. Coulomb<sup>4</sup> and A. J. Melfi<sup>5</sup>

6  
7  
8 <sup>1</sup> PROTEE, Université du Sud Toulon-Var, La Garde, Toulon, France

9 <sup>2</sup> NUPEGEL, CENA, Universidade de São Paulo, Piracicaba, Brazil

10 <sup>3</sup> NUPEGEL, IG, Universidade de São Paulo, São Paulo, Brazil

11 <sup>4</sup> LCE-DMCM, LCP, Aix-Marseille Université, Marseille, France

12 <sup>5</sup> NUPEGEL, ESALQ, Universidade de São Paulo, Piracicaba, Brazil

13 \* now at : LGCIE, INSA, Université de Lyon, Villeurbanne, France

14 \*\* now at : NUPEGEL, CENA, Universidade de São Paulo, Piracicaba, Brazil

15 \*\*\* now at : INERIS, Aix-en-Provence, France

16  
17  
18  
19 Correspondence email for proofs: lucas@univ-tln.fr



20 **Abstract**

21  
22 Podzol-ferralsol soil systems cover great areas in Amazonia and in other equatorial  
23 regions; they are an end-member of old equatorial landscape evolution, are frequently  
24 associated with kaolin deposits and store and export large amounts of carbon. Although  
25 natural organic matter plays a key role in their dynamics, little is known about their  
26 biogeochemistry, usually inferred from soil mineralogy and from spring or river water  
27 properties. In order to assess the role of dissolved organic matter (DOM) on NOM storage and  
28 kaolin genesis, we studied the groundwater composition of a typical podzol-ferralsol soil  
29 catena from the Alto Rio Negro region, Brazil.

30 Groundwater was sampled at three moments of the year corresponding to low,  
31 intermediate and high rainfall periods, using 13 tension-free lysimeters placed according to  
32 soil morphology. DOC,  $E_H$ , pH, dissolved Si,  $Al^{3+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$  were analysed for all samples  
33 and all values are given in a database. Quantification of other dissolved ions, small carboxylic  
34 acids and SUVA<sub>254</sub> index and acid-base microtitration were achieved on selected samples.

35 The groundwater produced by the hydromorphic podzols is acidic, DOM-rich with a high  
36 proportion of humic compounds. Part is directly exported to the black-water streams, another  
37 part percolates in depth and most DOM is adsorbed in the Bh horizons, allowing carbon  
38 storage at depth; humic substances are preferentially adsorbed with regard to small carboxylic  
39 compounds. The groundwater that passed the Bh underwent a more than 10-fold decrease of  
40 DOC and exhibits a high proportion (around 50% of DOC) of small carboxylic acids, which  
41 have the ability to percolate through kaolinitic materials.

42 With regard to the soil system dynamics, the aggressive DOM-rich groundwater  
43 circulating in the sandy podzol E horizons favours kaolinite and Fe- or Al-oxides dissolution  
44 and subsequent development of the sandy horizons at the expense of the clayey ones. In the  
45 deep groundwater circulating in the kaolin and in the kaolinitic ferralsolic horizons, Si and Al  
46 content is controlled by gibbsite and kaolinite precipitation/dissolution and by quartz  
47 dissolution. Fe is mainly transported as  $Fe^{2+}$ , due to acidity and relatively low  $E_H$ . Its mobility  
48 can be related to small  $E_H$  variations and enhanced by the significant concentration of small  
49 carboxylic acids. The long-term result of these processes is the bleaching and thickening of  
50 the kaolin and it can be inferred that kaolin is likely to occur where active giant podzols are  
51 close to a slope gradient sufficient to lower the water-table.

53  
54  
55

## 1 Introduction

56 More than 18% of the Amazonian area is covered by podzol-ferralsol systems (RadamBrasil,  
57 1978), which are characterized by the juxtaposition of podzols and ferralsols on the same  
58 landscape units (Lucas et al. 1984; Chauvel et al., 1987). Ferralsols are usual, climacic soils of  
59 equatorial areas where high weathering rates and long-time evolution allowed the leaching of  
60 all major elements but Al, Fe and Ti, the persistence of Si as kaolinite in the upper horizons  
61 being allowed by plant cycling (Lucas et al., 1993). The podzols appear and develop where  
62 dissolved organic matter (DOM) is able to percolate through soil horizons down to the rivers,  
63 allowing Al and Fe leaching and thus favouring the dissolution of clay and iron oxides (Lucas  
64 et al., 1996; Lundström et al., 2000; Nascimento et al., 2004). Once initiated, this process  
65 induces a positive feed-back for Al and Fe leaching, resulting in a progressive replacement of  
66 the ferralsols by podzols, even where ferralsols are clayey. Large podzol areas constitute thus  
67 one end-member of equatorial soils and landscape evolution (Dubroeuq and Volkoff 1998)  
68 (Fig. 1).

69 The podzolic areas of such systems have the ability to release great amounts of dissolved  
70 organic carbon (DOC) (Leenheer, 1980; Chauvel et al., 1996; Benedetti et al., 2003;  
71 Patel-Sorrentino et al., 2007) in the draining waters, which flow afterwards to the sea through  
72 the river network. Considering the Amazon basin, they provide a tenth of the 0.13 PgC  
73 annually exported to the sea (Tardy et al., 2009). They also can store large amounts of carbon  
74 in the upper and the deep Bh and Bhs horizons (Batjes et Dijkshoorn, 1999; Bernoux et al.,  
75 2002; Veillon and Soria-Solano 1988; Nascimento et al., 2004; Montes et al., 2011).  
76 According to Montes et al. (2011), hydromorphic podzols can store  $86.8 \pm 7.1 \text{ kgC m}^{-2}$  and at  
77 least  $13.6 \pm 1.1 \text{ PgC}$  is stored in Amazonian podzols. These soil systems thus take a significant  
78 part to the  $\text{CO}_2$  cycle at the global scale, but the dynamics of DOM transfer and soil organic  
79 matter (SOM) accumulation is still poorly known.

80 Podzol-ferralsol systems are also frequently associated with kaolin deposits (Montes et  
81 al., 2007), which are geological or pedological formations rich in kaolinite-type clays. In the  
82 Amazon area, thick white kaolin horizons (up to 10 m thick) were observed beneath ferralsol-  
83 podzol systems developed over sedimentary (Lucas et al., 1984; Chauvel et al., 1987; Costa  
84 and Moraes, 1998; Fritsch et al., 2009) as well as crystalline basement rocks (Dubroeuq and  
85 Volkoff, 1998; Montes et al., 2011), opening the question of the genetic relationships between  
86 podzolic processes and kaolin genesis in order to provide guidance for kaolin prospecting.  
87 Kaolin genesis is favoured where weathering enhances quartz and Fe-bearing minerals  
88 dissolution while maintaining kaolinite stability. As DOM issued from podzols favours the  
89 dissolution of all type of clay minerals because of Al complexation, how can podzolic  
90 processes favour kaolin genesis? Montes et al. (2007) hypothesized that the DOM transferred  
91 at depth by podzolic groundwater adsorbs within the Bh-Bhs horizon and that part of it is  
92 mineralized, which turns the acidic percolating water more reductive, favouring iron leaching  
93 and allowing bleaching of kaolin horizons. Such hypothesis, however, needs to be assessed by  
94 studying pH,  $E_H$ , DOM and Fe and Al species in percolating groundwaters. Several detailed  
95 studies of the solid mineral and organic phases have already been conducted on Amazonian  
96 podzols (Bravard and Righi, 1991; Nascimento et al., 2004; Bardy et al., 2008; Fritsch et al.,  
97 2009), showing that horizons morphology and solid phases characteristics are very similar  
98 from one system to the other, but the properties or composition of the circulating solutions  
99 were only inferred from the properties of solid phases. Few works (Cornu et al., 1997, 1998;  
100 Nascimento et al., 2008) have focused on sampling and studying the percolating solutions,  
101 mainly because of difficulties of sampling groundwater in these regions. More generally,

102 except for the surface horizons little is directly known about percolating soil solution in  
103 humid tropic soils.

104 In this context, the aim of the paper was twofold, both related to natural OM dynamics.  
105 First, what is the specific role of DOM with regard to the soil system dynamics, particularly  
106 soil OM accumulation in deep horizons and OM transfer towards the river network? Second,  
107 is there a relationship between kaolin formation and OM properties, and if so, will kaolin  
108 formation be favoured at specific locations within the soil system? Such knowledge would  
109 help in predicting the possibility of kaolin ore from remote sensing. The answer to these  
110 questions has been sought by studying groundwater percolating in a podzol-ferralsol system  
111 whose morphology and mineralogy had been studied in previous work.

112

## 113 **2 Material and methods**

114

### 115 **2.1 Description of the Studied Area**

116 The studied soil catena is situated near the São Gabriel da Cachoeira city, Amazonia State,  
117 Brazil, at 0° 6' 21"S and 66° 54' 22" W (Fig. 1), and was described in previous publications  
118 (Montes et al., 2007; Ishida, 2010). It was chosen amongst 11 similar catenas that have been  
119 studied on the same site, thereby ensuring its representativeness. It cuts the edge of a plateau  
120 where giant podzols developed from the plateau centre at the expense of reddish yellow, low  
121 activity clay ferralsols, as described elsewhere (Lucas et al., 1988; Dubroeuq and Volkoff,  
122 1998). It is related to a river network which enters the plateau by regressive erosion.

123 The climate is typically equatorial, with an annual rainfall around 3,000 mm, without a  
124 marked dry season and with a great interannual variability. Daily rainfall data were obtained  
125 from the airport station situated 6 km from the studied area. The geological substratum is  
126 composed of crystalline rocks having composition varying between monzogranitic,  
127 sienogranitic and quartzomonzonitic (Dall'Agnol and Macambira, 1992). The vegetation over  
128 the ferralsols and over well-drained podzols is a typical lowland tropical evergreen forest and  
129 over the hydromorphic podzols a specific forest called *campinarana* and characterized by a  
130 high density of smaller trees (20-30m). Such differences in vegetation are typical in podzol-  
131 ferralsol systems (Prance, 1978), and both forest type and soil characteristics result in high  
132 DOM differences between ferralsol and podzol groundwater (Bravard and Righi, 1991;  
133 McCain et al., 1997; Zanchi et al., 2011). In ferralsol areas, DOM adsorption and high  
134 decomposing rates accounts for low DOM concentrations in groundwater and streams (white  
135 or clear waters), with low C/N ratio and aliphatic, poorly aromatic fulvic and humic acids  
136 (FA and HA). In podzol areas, the lack of DOM adsorption and low decomposing rates  
137 accounts for high DOM concentrations in groundwater and streams (black waters), with high  
138 C/N ratio, poorly hydrolysable N, poorly aliphatic and highly aromatic FA and HA. The soils  
139 were studied using a structural analysis approach (Boulet et al., 1982; Fritsch and Fitzpatrick,  
140 1994; Delarue et al, 2009). Macromorphological features were observed through hand auger  
141 boreholes and pit descriptions. Mineralogy was determined by X-ray diffraction on powder  
142 samples, diffuse reflectance spectroscopy and thermogravimetric analysis. Only the data  
143 necessary to understand the water geochemistry are given here; detailed methodology,  
144 mineralogy and geochemistry are given in Ishida (2010).

145 The soil catena (length 200m, difference in altitude 15m) is sketched on Fig. 2. Two main  
146 sets of horizons can be distinguished: (i) the horizons of the well-expressed podzols, at the  
147 upper part of the catena, and (ii) the oxic horizons coloured by Fe-oxides on the slopes. Thick  
148 kaolin horizons were observed below both podzolic and oxic horizons. Mineralogical data are  
149 summarized in Table 1.

150 The podzols have a typical vertical succession of horizons: O, A1, E, Bh, Bhs. The  
151 organic O horizons are peat-like, with a thickness varying from a few centimetres to more

152 than 50. The more water-logged the topsoil throughout the year, i.e. far from the plateau  
153 slopes, the thicker the O horizons. The humic A1 horizons are well-developed; they consist of  
154 clean white quartz sand and organic matter particles. The eluviated sandy Es horizons have  
155 thin (1-2 mm), dark-grey micro-horizons coloured by organic matter particles; they have  
156 traces of kaolinite and gibbsite and high porosity and hydraulic conductivity. The transition  
157 between Es horizons and the underlying kaolin shows the vertical following sequence: (1)  
158 Bh - the sandy Es horizon turns progressively darker, due to an increase of organic matter  
159 content; (2) Bhs - there is an irregular, finger-like transition towards a hardened, sandy-clay  
160 horizon, brown coloured (10YR 5/2) (colors are given according to Munsell, 1990) with dark  
161 brown (7,5YR 5/6) features formed by organic matter and Fe-oxides accumulation in cracks  
162 and tubular pores, the gibbsite content is higher, the quartz sand content diminishes quickly in  
163 depth, together with the increase of kaolinite and the hydraulic conductivity turns lower. The  
164 kaolin K1 and K2 horizons consist mainly of kaolinite, with gibbsite content around 8% at the  
165 upper part of K1 and decreasing in depth to be lower than 2% at the lower part of K2 (Fig. 3).  
166 The upper part of the kaolin is a clayey, whitish material with some orange-coloured coatings  
167 in tubular pores (K1 horizon). These coatings progressively diminish in depth, giving place to  
168 a homogeneous, white, clayey, butter-like material (K2 horizon). In depth, the C1 horizon is a  
169 silt-clay saprolite having muscovite and weathered feldspar.

170 Going downslope, podzolic horizons give place to oxic horizons coloured by Fe-oxides:  
171 A horizons, on the upper part of the profiles; B1 horizons, which progressively changes from  
172 sandy to sandy-clay in the downslope direction; B2 sandy-clay horizons; B3 horizons in the  
173 downslope position having water-logging features. Below the B1 horizon were observed a  
174 silty clay loam, pale yellow horizon with coarse quartz grains (Ef). It indicates a perched  
175 water-table and is associated with small micro-valleys (2 to 4 m wide and 1 to 2 m depth)  
176 whose the flat bottom is at the same altitude than the Ef horizon, the micro-valleys forming a  
177 hydrographical network on the slopes. In depth the thick kaolin horizons, the clayey K1 and  
178 K2 horizons extend downslope. The colours are yellow (10YR 8/6) and white (5Y 8/1 to 5Y  
179 8/2), for K1 and K2 horizons, respectively. A K3 horizon having some remaining quartz  
180 grains and some red and yellow nodules appears at the mid-slope at the upper part of the  
181 kaolin corp. Downslope, the K1 and K2 horizons give place to the K4 horizon characterized  
182 by more abundant unweathered muscovites and Fe red spots at its upper part. Gibbsitic  
183 nodules are located at the downslope half of the catena as indicated on the figure. In depth, C1  
184 and C2 horizons are saprolitic horizons having many muscovite and weathered feldspar. At  
185 the lower part of the catena, the water table had the typical odour of sulphurs.

186

## 187 **2.2 Water Sampling and Analysis**

188

### 189 **2.2.1 Lysimeters**

190

191 It appeared unnecessary for the purpose of the present work to collect and analyze rain  
192 openfall, throughfall and stemflow. Such a study is difficult because of highly spatial  
193 variability under forest cover and had already been conducted in a similar podzol-ferralsol  
194 system throughout a whole year (Cornu et al., 1998). The results showed that the precipitation  
195 input were negligible with regard to mineral-solution equilibrium in soil horizons. Mean  
196 concentrations and standard deviation in openfall were  $0.02 \pm 0.01$ ,  $0.03 \pm 0.02$  and  $0.04 \pm 0.02$   
197  $\text{mg L}^{-1}$  for dissolved Si, Al and Fe, respectively, in throughfall they were  $0.08 \pm 0.04$ ,  
198  $0.06 \pm 0.04$  and  $0.07 \pm 0.05$   $\text{mg L}^{-1}$ , respectively. Stemflow fluxes were insignificant.

199 Regarding groundwater, thirteen zero-tension lysimeters were installed inside drilling  
200 holes at different depths, 2 points (W1-20 and W2-150) within the podzolic campinarana area  
201 (Fig. 1) and 11 points along the soil catena (Fig. 2). After installing the lysimeters, each

202 drilling hole was tamped by filling with the previously extracted soil material at the  
203 corresponding depth. Each lysimeter was made of a 50 mL polypropylene bottle bored with 5  
204 mm diameter holes all around. A 2 mm diameter capillary PTFE tube was inserted through  
205 the bottle cap in order to permit extracting water from the topsoil with a manual vacuum  
206 pump. To prevent clogging of the capillary tube by soil particles, a cylindrical filter made of a  
207 SeFar Nitex 64 $\mu$ m polyamide open mesh was put inside the bottle. All lysimeters were acid-  
208 washed prior to installation.

### 210 **2.2.2 Sampling points**

211  
212 The studies already conducted on Amazonian podzol-ferralsol systems (see introduction)  
213 have shown that horizon morphologies and solid phase characteristics are very similar from  
214 one system to the other: soil age and high weathering rates have resulted in obliteration of  
215 most small scale spatial variability due to parent rock heterogeneity. As in many old, deeply  
216 weathered soil covers soil variations are spatially explicit and depend on soil forming  
217 processes, closely related to water pathway and residence time (Boulet et al., 1982). In such a  
218 context, sampling points were selected based on the morphology of the soil cover and on the  
219 water pathways that could be inferred from soil patterns and topography; the continuity and  
220 consistency of observed variations along the water pathways will determine the validity of the  
221 data.

222 Three points were located in the podzolic E horizons, where circulates the DOM-rich  
223 water-table perched over the Bh-Bhs horizons. The "W1-20" point was situated at 20 cm  
224 depth in the podzolic campinarana area. It allowed sampling the upper part of the water-table  
225 circulating in the sandy podzol horizons, when the water-table was in high-level conditions  
226 and attained the A horizons. The "Spring" point was situated at the very beginning of a spring  
227 flowing from the center of the podzolic campinarana area. The spring always flowed during  
228 the sampling periods, with higher outflow immediately after rains. The samples corresponded  
229 thus to the upper part of the water-table circulating in the sandy podzol horizons. The "W2-  
230 150" point was situated 150 cm in depth within the white sand E horizon, 50 cm over the Bh  
231 horizon. The "S1-240" point was situated at 240 cm in depth within the sandy-clay Bhs  
232 horizons, where accumulates OM transferred from the soil surface. The remaining points were  
233 chosen along the line of greatest slope in order to obtain a sequence of samples describing  
234 changes in the groundwater properties when it passes in depth from the Bh horizons to the  
235 kaolin horizons, where occur bleaching and likely kaolinite precipitation, then flows laterally  
236 downslope (points S1-510, S2-490, S3-380, S4-400, S5-380, S6-300) in horizons where  
237 occurs gibbsite and iron oxides precipitation. More shallow sampling points (S2-160,  
238 SMVB-15, S3-160) were chosen in order to sample groundwater from a perched water-table  
239 likely circulating in the Ef ferralsol horizon and expected to overflow in micro-valley.

### 240 **2.2.3. Sampling periods and analysis**

241  
242 Groundwater was sampled during three periods indicated on Fig. 4. The first one (27 to  
243 30/07/2007) was typical of low rainfall periods, the second one (29/01 to 04/02/2008) was  
244 intermediate and the third one (19 to 25/05/2008), typical of high rainfall periods, allowed  
245 sampling high-level water-tables. The 10-days cumulated rainfalls before the sampling  
246 periods were 53, 88 and 178 mm for the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> sampling periods, respectively.  
247 Complementary sampling for acid-base microtitration and DOC characterization was realized  
248 on 09/02/2009 for points Spring, W2-150, S1-240, S1-510, S3-380 and S4-400.

249 Sampling was done by applying a continuous suction of 25 mmHg to the lysimeters. The  
250 first 20mL of each sampling was discarded in order to avoid dead volume and to rinse the  
251 sampling equipment. Groundwater was then sampled until 250 mL was reached or air was

252 entering the system. pH and  $E_H$  were measured immediately after sampling with a Eutech  
253 pH310 instrument after stabilization with gentle shake (calibration of the pH electrode was  
254 done every day). Each sample was then filtered using an inline 0.22 $\mu$ m cellulose membrane  
255 filter (Nalgene surfactant-free cellulose acetate) and separated in four aliquots for immediate  
256 analysis of dissolved  $H_4SiO_4$ ,  $Al^{3+}$ ,  $Fe^{2+}$  and  $Fe^{3+}$ , separately. A fifth aliquot was filtered using  
257 a 0.7 $\mu$ m fiber glass filter, poisoned with sodium azide, stored in 10 mL vacuum glass flasks  
258 (Vacutainer) then kept at low temperature (around 4°C) for laboratory analysis of DOC and  
259 other dissolved species.

260 Analysis of dissolved  $H_4SiO_4$ ,  $Al^{3+}$  and  $Fe^{2+}/Fe^{3+}$  were performed within one hour after  
261 sampling by colorimetry using a Lange DR 2800 Spectrophotometer with analytical kits  
262 LCK301, LCW028 and LCK320, respectively. The measurement ranges were 0.01-0.60  
263 mg.L<sup>-1</sup>, 0.005-1.000 mg.L<sup>-1</sup> and 0.05-6.0 mg.L<sup>-1</sup> and the absorbencies measured at 620 nm,  
264 695 nm and 485 nm for  $Al^{3+}$ ,  $H_4SiO_4$  and  $Fe^{2+}$ , respectively. The colorimetric method was  
265 chosen because it allowed measurements immediately after sampling and because it measures  
266 the free or displaceable species able to participate to solution-minerals equilibria. To ensure  
267 that no oxidation of  $Fe^{2+}$  was occurring between sampling and analysis,  $Fe^{2+}$  measurements  
268 were performed 10 minutes and 6 hours after water sampling. No significant differences  
269 between the results were observed. As the coloured DOM absorbency exponentially decrease  
270 from 220 to 650 nm (Schwartz et al., 2002), DOM contribution is low for  $Al^{3+}$  and  $H_4SiO_4$   
271 measurements realized at 620 and 695 nm, respectively, but can be significant for  $Fe^{2+}$   
272 measurement at 485 nm. In order to limit possible interferences due to the natural DOM color  
273 of the samples, absorbance of the filtered sample before any reagent addition was subtracted  
274 from absorbance of the final measurement.

275 Laboratory analyses were performed between 10 and 45 days after sampling. DOC  
276 analyses were performed with a Shimadzu TOC-V Analyzer calibrated with a 10 ppm  
277 potassium phthalate standard solution. Blank signal for filtered ultra-pure MQ water was  
278 about 0.1 ppm.  $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $F^-$ ,  $Cl^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $PO_4^{2-}$ ,  $SO_4^{2-}$  ions were  
279 determined by ion chromatography (Dionex DX 120), using 9 mmol.L<sup>-1</sup>  $NaHCO_3$  for cation  
280 elution and 10 mmol.L<sup>-1</sup> methane sulfonic acid for anion elution.

281 Some authors (Menzies et al., 1992) observed that colorimetric methods discriminate  
282 against micro-particulates and do not measure all Al present as soluble organic forms and thus  
283 underestimate total soluble Al. In order to check if some metal species were so strongly  
284 bonded to DOM that they were not displaced during the in-site colorimetric analysis,  $Al^{3+}$ ,  
285  $Fe^{2+}$  and  $Fe^{3+}$  were measured for a selected set of samples, before and after UV-oxidation of  
286 the DOM (Patel-Sorrentino et al., 2004). Oxidation was performed in cylindrical quartz  
287 vessels using a 450 Watt Hanovia medium-pressure mercury lamp; complete DOM oxidation  
288 was checked by DOC determination after irradiation. Results gave no significant differences  
289 in concentrations before and after UV-oxidation of the DOM, so that we may conclude that  
290 the colorimetric method gave the sum of free plus OM-bonded species for Al and Fe.

291 During data modeling, the pH values seemed underestimated in comparison to field  
292 observations, so that a special attention was paid to pH measurements. pH electrode  
293 calibration at field was realized with a standard electrode and standard reference solutions  
294 having a ionic strength high when compared to the studied solutions, which can give a  
295 measurements error. To test this hypothesis, pH measurement were achieved on seven  
296 selected samples, using the same electrode and adjusting the ionic strength (I) to 10<sup>-4</sup>, 10<sup>-3</sup> and  
297 10<sup>-2</sup> M with KCl. The pH increased with increasing ionic strength, an asymptote being  
298 reached when I = 10<sup>-2</sup> M (Supplementary Fig. S1). The difference  $\Delta$ pH between pH measured  
299 before adjustment and pH measured at I = 10<sup>-2</sup> M was dependent on the DOC content, which  
300 indicates that the DOM is actually charged and participates to the ionic strength. The pH were  
301 then corrected by using the empirical relationship [ $\Delta$ pH = 0.508 - 0.0047\*DOC] where DOC

302 is expressed in  $\text{mg L}^{-1}$ . In most cases  $\Delta\text{pH}$  was between 0.3 and 0.5 pH units; correction was  
303 however necessary for modeling. For example, as three  $\text{H}^+$  are exchanged during gibbsite  
304 hydrolysis, if pH increases 0.5 units the saturation index with regard to gibbsite will increase  
305 1.5.

306 In order to evaluate the behaviour of the studied solutions with regard to  $\text{H}^+$ , acid-base  
307 logarithmic scale microtitrations of selected samples were performed using the procedure  
308 describe by Garnier et al. (2004a). Briefly, sample solutions were acidified by  $0.2 \text{ mol l}^{-1}$   
309  $\text{HNO}_3$  additions until pH 2.5,  $\text{N}_2$  purged, and then titrated using  $0.1 \text{ mol l}^{-1}$  KOH until pH  
310 11.5. Acid-base titrations were performed using two Titrino 716 apparatus controlled by a  
311 Tinet 2.4 software (Metrohm). The combined pH-micro-electrode used (Mettler, Inlab422,  
312 reference:  $\text{Ag/AgCl/KCl } 3.0 \text{ mol l}^{-1}$ ) was calibrated daily by the titration of a  $\text{HNO}_3$   $0.01 \text{ mol}$   
313  $\text{l}^{-1}$  solution followed by theoretical fitting of the titration curve.

314 Small carboxylic acids were identified and quantified in selected samples by ionic  
315 chromatography (Dionex ICS 3000) using AG11-HC guard column, a IonPac ICE-AS11  
316 column, for elution NaOH with a gradient from 1 to  $5 \text{ mmol.L}^{-1}$  and a CD25 pulse  
317 electrochemical detector. On the same samples the  $\text{SUVA}_{254}$  index was measured using a  
318 Shimadzu UV-1800 spectrophotometer. This index is calculated as the ratio of UV  
319 absorbance at 254 nm to the product of DOC and UV cell path length; it is considered as  
320 characteristic of the hydrophobicity and aromaticity of the considered DOC (Chin et al.,  
321 1994).

322 Thermodynamic modeling of the solution-minerals interactions was performed by own  
323 calculation and checked using the PHREEQ-C (2.11) software with the Wateq-4f database  
324 (Ball and Nordstrom, 1991).

325

### 326 **3 Results**

327

#### 328 **3.1 Water pathways along the catena**

329

330 During the 1<sup>st</sup> sampling period, no samples were available in the S2-160 and S3-160 points,  
331 because of the lack of perched water-table in the Ef horizon due to insufficient rainfall.  
332 During the 2<sup>nd</sup> sampling period, the point S2-160 gave sample only one sampling day  
333 (31/01/08) when the S3-160 point gave sample three sampling days (29/01/08, 31/01/08 and  
334 02/02/08). During the 3<sup>rd</sup> sampling period, both S2-160 and S3-160 points gave samples every  
335 sampling day. This behaviour of the sampling points attests the fast level changes of the  
336 perched water table after heavy rains. When sufficiently high, a water table perched over the  
337 podzolic Bhs horizon laterally overflows towards the Ef horizon, then percolates downslope  
338 along this horizon or flows out in the flat-bottomed micro-valleys. The SMVB-15 point was  
339 situated at the bottom of a small micro-valley, at an altitude roughly corresponding to those of  
340 the S2-160 point, and allowed sampling the overflow of the perched water-table in the micro-  
341 valleys. Such overflow allows a direct exportation of the groundwater down to the streams  
342 and rivers, beside other pathways such as the usual overflowing of the groundwater in the  
343 lower parts of the landscape or pipes as observed elsewhere (Lucas et al. 1996). The water  
344 sampled at the SMVB-15 point during the 1<sup>st</sup> sampling period came necessarily from recent  
345 rainfall percolating the topsoil horizons, because of the lack of perched water table, when  
346 during the 2<sup>nd</sup> and 3<sup>rd</sup> sampling the waters could come from both recent rainfalls percolating  
347 topsoil horizons and overflowing of the perched water table. Except point S3-380 and  
348 downslope point S6-80, other sampling points of the catena gave samples every sampling day.

349 Two water pathways can thus be defined along the catena (Fig. 2). A deep, permanent  
350 water table flows more than two meters deep within the kaolin horizons. The lateral flow of  
351 its upper part corresponds to pathway n°1 and is described by the following succession of

352 samples: S1-510 – S2-490 – S3-380 – S4-400 – S5-380 – S6-300. A temporary, closer to the  
353 surface water table circulates in the Es and Ef horizons only after heavy rainfalls and can  
354 overflow in the micro-valleys. It corresponds to pathway n°2 and is described by the  
355 following succession of samples: S1-240 – S2-160 – S3-160.

356

### 357 **3.2 Composition of the Percolating Waters**

358

359 The composition of the groundwater from each sampling point and for each sampling day for  
360 dissolved Si, Al<sup>3+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, pH, E<sub>H</sub> and DOC is given in Supplementary Table S1 and  
361 summary from these data is given in Table 2. Some key points, representing the different  
362 kinds of circulating waters (Spring, W1-20, W2-150, S1-240, S1-510, S2-490, S4-400 and  
363 S6-300), were chosen for analysing other solutes (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>,  
364 SO<sub>4</sub><sup>2-</sup>, S<sup>2-</sup> and F<sup>-</sup>). Results are given in Table 3, except for S<sup>2-</sup> and F<sup>-</sup> which remained  
365 negligible.

366 The chemistry of the collected waters is hereafter described and discussed following the  
367 two pathways of the circulating waters, pathway n°1 for the deep water-table and pathway n°2  
368 for the perched water table. Overall average compositions of circulating waters are given in  
369 Fig. 5 for both pathways. Additional information can be found in Fig. S2 and S3 that give  
370 average by sampling periods for pathway n°1 and n°2, respectively. For most sampling  
371 points, the chemistry of the collected waters showed low variations within a sampling period  
372 as well as between sampling periods, as shown by the standard deviations in Fig 5, S2 and S3.

373

#### 374 **3.2.1. From the Podzolic Sands Downslope Following the Deep Water Table (Pathway** 375 **n°1).**

376

377 *pH.* The pH was acidic for all samples, ranging from 3.4 to 5.5. The minimum values were  
378 observed for the waters circulating in the white sand (points W1-20 and W2-150) and in the  
379 underlying Bhs (point S1-240). Those waters were also the more acidic on the average (4.1),  
380 and their maximum values did not exceeded 4.5. Regarding the deep water table, the pH  
381 progressively increased downslope from point S1-510 (average 4.5) to point S6-300 (average  
382 5.0). The pH slightly changed from one sampling period to the other, but considering each  
383 sampling period individually, the pH increase in the downslope direction was always  
384 progressive and significant (Fig. S3): T-test values of the difference between points separated  
385 by at least 2 other points in the sequence were all but two higher than 2. pH values over 5.2  
386 were only observed for the three points situated at the lower part of the slope (S4-400,  
387 S5-380, S6-300).

388 *DOC concentrations.* The waters from the upper horizons of the podzolic area (W1-20)  
389 had high DOC concentrations; the averages were 46, 36 and 27 mg.L<sup>-1</sup> for the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup>  
390 periods, respectively. The decrease from a period to the other was likely a dilution effect due  
391 to higher rainfall. The water sampled at 150cm in depth in the white sand (W2-150) had a  
392 more buffered composition throughout the three periods (37, 37 and 43 mg.L<sup>-1</sup>, respectively).  
393 In the Bhs horizon (S1-240), the DOC concentration varied from 12 to 19 mg.L<sup>-1</sup>, 15 mg.L<sup>-1</sup>  
394 on average. In the deep clayed horizons (points S1-510 to S6-300), the DOC concentrations  
395 were lower but no negligible, varying from 1.5 to 9.7 mg.L<sup>-1</sup>, 4.0 mg.L<sup>-1</sup> on average, without  
396 significant variations along the catena.

397 *Si and Al concentrations.* The waters from the upper horizons of the podzolic area (W1-  
398 20) always had very low Si and Al concentrations. The maximum values for Si and Al were  
399 0.1 and 0.14 mg.L<sup>-1</sup>, respectively, and the average values were 0.05 and 0.03 mg.L<sup>-1</sup>,  
400 respectively. On the other hand, the waters from the Bhs horizon (point S1-240) had the  
401 highest Si and Al values observed during the three sampling periods: Si ranged from 0.29 to



402 0.59 mg.L<sup>-1</sup> and Al ranged from 0.37 to 0.63 mg.L<sup>-1</sup>. At every sampling day the Si and Al  
403 values were close together (Fig. S2) and their averages over the three sampling periods were  
404 0.48 mg.L<sup>-1</sup> for both. The waters from point W2-150 had values intermediate between those  
405 of points W1-20 and S1-240. From the Bhs horizon down to the kaolin horizon, i.e. from  
406 point S1-240 to point S1-510, the Si concentrations underwent a decrease by more than half,  
407 down to 0.13 mg.L<sup>-1</sup> on average, when the Al values suffered a slighter decrease, down to  
408 0.37 mg.L<sup>-1</sup> on average. Going downslope from point S1-510, the Si values progressively  
409 increased again up to values around 0.5 mg.L<sup>-1</sup>. The Al values continued decreasing  
410 progressively.

411 *Fe concentrations and E<sub>H</sub>*. For all points except S3-380, Fe<sup>2+</sup> concentrations were higher  
412 than Fe<sup>3+</sup> concentrations. The Fe<sup>3+</sup> and Fe<sup>2+</sup> concentrations exhibited, however, a close  
413 behaviour along the whole catena except the last downslope point, i.e. from point W1-20 to  
414 point S5-380. For these points, Fe<sup>3+</sup> and Fe<sup>2+</sup> concentrations were frequently below the  
415 quantification limit and no individual samplings exceeded 0.20 and 0.46 mg.L<sup>-1</sup> for Fe<sup>3+</sup> and  
416 Fe<sup>2+</sup>, respectively. The points situated upslope in the white sand (W1-20 and W2-150) and in  
417 the Bhs horizon (S1-240) had values more variable and higher than the points situated  
418 midslope in the deep kaolin (S2-490 to S4-400). Those Fe<sup>3+</sup> and Fe<sup>2+</sup> values corresponded to  
419 E<sub>H</sub> values varying from 410 to 575 mV, without significant correlation between these  
420 variables. Downslope, the behaviours of Fe<sup>3+</sup> and Fe<sup>2+</sup> concentrations diverged: when the Fe<sup>3+</sup>  
421 concentrations remained low, the Fe<sup>2+</sup> concentrations increased slightly on point S5-380 then  
422 drastically on point S6-300 with a 0.57 mg.L<sup>-1</sup> average value. The increase of the Fe<sup>2+</sup>  
423 concentrations on the last downslope point is closely related to a decrease of the E<sub>H</sub>. The E<sub>H</sub>  
424 remained between 410 and 575 mV along the whole catena except the last downslope point  
425 where it was between 209 and 253 mV.

426 The waters from the Spring point had pH and chemical characteristics very similar to  
427 those observed for the W1-20 point, except regarding the E<sub>H</sub> which was higher (521±15  
428 versus 473±17 mV).

429

### 430 **3.2.2. From the Podzolic Sands Downslope Following the Perched Water Table** 431 **(Pathway n°2).**

432

433 *pH and DOC concentrations*. The transition from the point S1-240 to the points S2-160 then  
434 S3-160 came with a pH increase between 0.5 to 1 pH unit (4.1, 4.6 and 4.9 on average,  
435 respectively) and a progressive decrease of the DOC concentrations, from 15 to 5 then 4  
436 mg.L<sup>-1</sup> on average, respectively. The point SMVB-15 had pH values similar to those of points  
437 S2-160 and S3-160 (4.6 on average), but DOC values always higher than 27 mg.L<sup>-1</sup>  
438 (32 mg.L<sup>-1</sup> on average).

439 *Si and Al concentrations*. The Si concentrations slightly decreased when passing from  
440 point S1-240 (average 0.48 mg.L<sup>-1</sup>) to point S2-160 (average 0.46 mg.L<sup>-1</sup>), then decreased  
441 markedly on point S3-160 (average 0.30 mg.L<sup>-1</sup>). Al concentrations already decreased  
442 markedly when passing from point S1-240 (average 0.48 mg.L<sup>-1</sup>) to point S2-160 (average  
443 0.30 mg.L<sup>-1</sup>), then continued decreasing on point S3-160 (average 0.06 mg.L<sup>-1</sup>). The different  
444 behaviour of Si and Al resulted in a progressive increase of the Si/Al molar ratio based on  
445 average values: 1.0 at point S1-240, 2.3 at point S2-160 and 4.8 at point S3-160. The waters  
446 sampled from point SMVB-15 were characterized by high Si and Al concentrations when  
447 compared to the other sampling points, on average 1.86 and 0.68 mg.L<sup>-1</sup> for Si and Al,  
448 respectively, with a Si/Al molar ratio varying between 1.8 and 4.1 (2.7 for the average of  
449 ratios).

450 *Fe<sup>2+</sup>, Fe<sup>3+</sup> concentrations and E<sub>H</sub>*. The Fe<sup>2+</sup> concentrations increased when passing from  
451 point S1-240 (0.10 mg.L<sup>-1</sup> on average) to point S2-160 (0.21 mg.L<sup>-1</sup> on average) (except on

452 the 19/05/08), then decreased on point S3-160 (0.05 mg.L<sup>-1</sup> on average). The Fe<sup>2+</sup>  
453 concentrations on point S2-160 exhibited, however, a high variability, with a standard  
454 deviation (0.24) higher than the average value. The high Fe<sup>2+</sup> concentrations were always  
455 related to lower E<sub>H</sub> values, which reflect on the average values of E<sub>H</sub>: 501, 399 and 482 mV  
456 for points S1-240, S2-160 and S3-160, respectively. There is no, however, correlation  
457 between the bulk of Fe<sup>2+</sup> and E<sub>H</sub> values (R<sup>2</sup>=0.23). The Fe<sup>3+</sup> concentrations remained always  
458 lower than 0.08 mg.L<sup>-1</sup> for both S2-160 and S3-160 points. The waters sampled at point  
459 SMVB-15 had high Fe<sup>2+</sup> and Fe<sup>3+</sup> concentrations (on average 1.58 and 0.79 mg.L<sup>-1</sup>,  
460 respectively) when compared to any other sampling point, and relatively low E<sub>H</sub> values  
461 (372 mV on average).

462

### 463 3.3. DOM characterization

464

465 Microtitrations were achieved on samples collected at Spring and W2-150 points. An example  
466 of microtitration curve is given on Fig. 6. Three repetitions were made for each sample. The  
467 acid-base properties of the DOC were evaluated by fitting these results with the PROSECE  
468 software (Garnier et al. 2004a,b). This model consider a discrete distribution of acidic sites  
469 whose acidic constants pK<sub>a*i*</sub> and site densities L<sub>T,*i*</sub> are determined by fitting the experimental  
470 curves. The optimal number of acidic sites is defined as the simplest combination which  
471 conduces to the minimal fitting bias value (sum of the absolute differences between  
472 experimental and calculated pH values). Accordingly, a distribution of 4 acidic sites was  
473 sufficient to allow a correct fitting of experimental curves. The results are given on Table 4.  
474 The total calculated site densities were 40.2±6.1 and 27.2±3.6 meq.gC<sup>-1</sup> for the Spring and the  
475 W2-150 samples, respectively.

476 Small carboxylic acids identification and quantification for samples collected at points  
477 Spring, W2-150, S1-510, S3-380 and S4-400 are given in Table 5. With regard to the total of  
478 the identified small carboxylic acids, acetic acid represented between 38 and 61%, formic,  
479 succinic, oxalic and citric acids between 4 and 27% and lactic acid remained lower than 4%.  
480 The sum of small carboxylic acids was higher than 2 mg L<sup>-1</sup> and lower than 1 mg L<sup>-1</sup> in the  
481 DOC-poor samples. The proportion of small carboxylic acids in the DOC, however, was  
482 lower than 10% in the DOC-rich samples (Spring and W2-150) and higher than 47% for the  
483 other samples. The SUVA<sub>254</sub> index (Table 5) values are in accordance with these results. The  
484 two DOC-rich samples exhibited a SUVA<sub>254</sub> index more than two fold higher than those of  
485 the DOC-poor samples which indicate that the former contain much more humic substances  
486 than the latter.

487

## 488 4 Discussion

489

### 490 4.1 Evolution of the Percolating Waters along the Catena

491

#### 492 4.1.1 Waters in the Podzolic Area

493

494 The spring water and the water circulating in the upper part of the white sands (CA-020  
495 point) had similar characteristics: the highest DOC and the lower pH and Si values compared  
496 to all other samples and very low Al, Fe<sup>2+</sup> and Fe<sup>3+</sup> values (0.05, 0.02 and lower than 0.01  
497 mg.L<sup>-1</sup> on average for dissolved Si, Al and Fe, respectively). These values, as well of the  
498 values observed for other elements, are in the range of values observed by Cornu et al. (1997;  
499 1998) in a similar podzolic area – similar soil and vegetation – situated near Manaus.  
500 Dissolved Si, Al and Fe found here can come from canopy leaching, litter mineralization and  
501 dissolution of quartz and trace minerals (Table 2). This water is thus quite aggressive with

502 regard to clay or iron minerals, due to acidity and to complexing capacity of the DOC which  
503 greatly enhances the weathering rates (Robert and Berthelin, 1986). When it reaches the  
504 transition between white sands and kaolin horizon, in the Bh horizons, it dissolves kaolinite  
505 and Fe- or Al-oxides so that the concentrations of Si, Al and Fe in the percolating water  
506 increase, as observed at point S1-240. The molar values of dissolved Si and Al at point S1-  
507 240 were very close one to the other, which is in accordance with the hypothesis of a  
508 congruent dissolution of kaolinite in the Bh horizons. The up and down movements of the  
509 water-table perched over the Bh favour the upward dispersion of solutes, which explains that  
510 concentrations at point W2-150 are intermediate between concentrations at the topsoil and  
511 concentrations within the Bh. The decrease of DOC concentration when water passes from the  
512 white sand to the Bh is due to the DOC adsorption on kaolinite or Fe-oxides and gibbsite  
513 surfaces (Davis, 1982; Kaiser et Zech, 2000). Such adsorption was observed in Amazonian  
514 podzols everywhere a DOC-rich water-table circulating in a quite sandy material passes  
515 through a material having some clay or oxides (Chauvel et al., 1987; Bardy et al., 2008;  
516 Fritsch et al. 2009).

517

#### 518 **4.1.2 Waters in the Kaolin Horizons (Pathway n°1)**

519

520 Passing from the Bh (point S1-240) to the underlying deep kaolin (point S1-510), the water  
521 exhibited a slight pH increase, a drastic decrease of DOC, a decrease of Si and a slight  
522 decrease of Al and Fe. The DOC decrease can be explained by adsorption of humic  
523 substances on clay and Fe mineral surfaces of the Bh. The DOC observed in the water  
524 percolating in the deep kaolin horizons, however, shows that a small proportion of DOM was  
525 not retained in the Bh and is able to migrate through a clayey material.

526 Si, Al and Fe variations in percolating waters as well as the higher content of gibbsite and  
527 Fe-oxides at the upper part of the kaolin horizons can be explained by the following  
528 considerations. The DOM which migrates through the sandy horizons is carrying complexed  
529 Al and Fe (Benedetti et al., 2003; Fritsch et al., 2009). Most organo-metallic complexes  
530 adsorb on mineral surfaces in the Bh-Bhs, but do not accumulate indefinitely and most of  
531 them will eventually be mineralized, releasing Al and Fe in the soil solution. The assumption  
532 of a relatively rapid turn-over of the OM is strengthened by the young apparent  $^{14}\text{C}$  ages  
533 (<3000 y) measured for a NOM from a similar deep Bh in the Manaus area (Montes et al.,  
534 2011). Fe precipitates as Fe-oxides (likely goethite and lepidocrocite) and Al precipitates as  
535 kaolinite, resulting in the decrease of Si concentration. Al in excess precipitates as gibbsite,  
536 giving high gibbsite content in the horizons immediately beneath the Bh (Fig. 3).

537 Going downslope in the deep kaolin horizons, the pH increase is more related to an  
538 increase of the sum of charges of major ions than to a decrease of the charges due to the DOM  
539 (Table 6). The increase of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations when going downslope is  
540 likely due to higher content in weatherable minerals closer to the soil surface. The pH  
541 increase could explain the precipitation of Al as gibbsite nodules (Fig. 2) and the consecutive  
542 decrease of Al concentration in the soil solution (Fig. 5).

543

#### 544 **4.1.3 Waters in the Perched Water Table (Pathway n°2)**

545

546 When flowing from the white sand to the non-podzolic leached horizon Ef, passing the Bh,  
547 the groundwater lost most of its DOC, but remained with DOC concentrations higher than 5  
548  $\text{mg L}^{-1}$  thus aggressive with regard to secondary minerals. It can therefore favour the clay  
549 impoverishment of the Ef horizon with a positive feedback due to higher water flow after clay  
550 impoverishment. The increase of the Si/Al molar ratio can be explained by precipitation of Al  
551 as gibbsite as observed downslope along the pathway n°1. In the micro-valley bottom, at point

552 SMVB-15, Si, Al and Fe values are exceptionally high with regard to the high rainfall climate;  
 553 Si values for example may approach the quartz solubility (2.9 mg L<sup>-1</sup>). This may be due to the  
 554 fact that the water sampled at this point added dissolved elements brought by the overflowing  
 555 groundwater and elements locally produced by the litter degradation. It has indeed been  
 556 shown that the forest recycles a great amount of Si through litterfall and that litter dissolution  
 557 in the topsoil can increase groundwater Si concentration up to saturation with kaolinite  
 558 (Lucas, 2001).

559

#### 560 **4.2 The Properties of the Dissolved Organic Matter**

561

562 The remaining negative charges due to the DOM were calculated in order to calculate the  
 563 DOM acid site density. Table 6 reports the ion balance for the samples given on Table 3. The  
 564 remaining negative charge due to the DOM ( $Z_{\text{DOM}}$ ) expressed in meq.C<sup>-1</sup> was calculated from  
 565 the sum of charges of major ions  $\sum_i z_i$  expressed in  $\mu\text{eq.L}^{-1}$ , the pH and the dissolved organic  
 566 carbon concentration expressed in mg.L<sup>-1</sup>, using the following equation:  
 567

$$Z_{\text{DOM}} = \frac{(10^{-6\text{pH}} - \sum_i z_i)}{\text{DOC}}$$

568

569 The average DOM charge ranged from -6.2 to -6.5 meq.gC<sup>-1</sup> for the water circulating in  
 570 the sandy podzol horizons, whereas -11 meq.gC<sup>-1</sup> for the water in the deep Bhs and ranged  
 571 from -31 to -37 meq.gC<sup>-1</sup> for the waters circulating in the deep Bhs and in the deep kaolinitic  
 572 horizons. The DOM circulating in the kaolinitic horizons had therefore values much higher  
 573 than the DOM from the white sands. As all the waters were quite acidic, most of these  
 574 charges were due to carboxylic-type sites. The acid site density  $L_T$  expressed in meq.gC<sup>-1</sup> was  
 575 approximated by modelling for a single carboxylic-type ligand, considering various pKa from  
 576 3 to 4.5, using the following equation:  
 577

$$L_T = Z_{\text{DOM}}(1 + 10^{\text{pKa}-\text{pH}})$$

578

579 The results are given on Table 6. The calculated acid-site densities of the DOM  
 580 circulating in the white sands horizons range from 7 to 23 meq.gC<sup>-1</sup> when considering a pKa  
 581 ranging from 3 to 4.5. This is consistent with the values obtained by modelling the  
 582 microtitration curves for the Spring and W2-150 points (26.7±0.8 and 18.0±0.8 meq.gC<sup>-1</sup> for  
 583 carboxylic-type sites, respectively) (Table 4). Regarding carboxylic-type acid site densities,  
 584 we found no data for equatorial podzols or ferralsol groundwater available in the literature. In  
 585 comparison, Ravichandran et al. (1998) obtained a total of acid-site densities ranging from  
 586 1.45 to 3.8 meq.gC<sup>-1</sup> for various humic substances (AF and AH) coming from the Everglades  
 587 and from Suwanee River, i.e. lower values than reported here. Considering natural waters,  
 588 total carboxylic acid site density obtained in pristine boreal areas (Köhler et al., 1999; Cuss et  
 589 al., 2010) or springs from acid podzolic temperate zone (Hruska et al., 2003) were 8.6±1.6,  
 590 9.8±0.24 and 10.2±0.6 meq.gC<sup>-1</sup>, respectively. These values are in the range of those reported  
 591 here.

592 The DOM circulating in depth in the kaolinitic horizons was quite different. Considering  
 593 a pKa ranging from to 3 or 4.5, the calculated site densities are quite high, ranging from 31 to  
 594 67 meq.gC<sup>-1</sup> (in comparison, one site per carbon would give a site density equal to  
 595 83.3 meq.gC<sup>-1</sup>). This is consistent with the higher proportion of small carboxylic acids  
 596 observed in the DOC-poor groundwaters: site densities of formic, oxalic, acetic, citric,  
 597 succinic and lactic acids are 83.3, 83.3, 41.7, 41.7, 41.7 and 27.8 meq.gC<sup>-1</sup>, respectively. This

598 is also consistent with the low SUVA<sub>254</sub> values of the DOC-poor groundwaters indicating a  
599 low proportion of humic substances.

600 The dynamics of the DOC in the soil system can thus be described as follows. The  
601 groundwater circulating in the white sand is rich in DOM, this DOM having a high proportion  
602 of humic compounds and less than 10% of small carboxylic acids. When this groundwater  
603 passes through the Bh, most of its DOM is adsorbed, resulting in a more than 10-fold decrease  
604 of the DOC content. The dissolved humic substances are preferentially adsorbed, so that the  
605 proportion of small carboxylic acids increases up to around 50% of the total DOC. It is  
606 however impossible to determine if these small carboxylic acids are a fraction of the DOM  
607 which came from the white sands or if they were produced by microbial activity in the Bh-  
608 Bhs. The ability of small carboxylic compounds to percolate through a kaolinitic material can  
609 be explained by the fact that they are more hydrophilic than larger, humified components  
610 usually hydrophobic. It is also in accordance with results obtained by Kang and Xing (2007),  
611 which showed that the adsorption of carboxylic acids on clay surfaces is lower when the  
612 compounds are small and is lower on kaolinite than on 2:1 clays. Kaiser and Zech (2000)  
613 showed that the sorption of DOM on the clay fraction is sharply reduced when Fe-oxides and  
614 gibbsite are removed from the clay fraction. Indeed, the Fe-oxides and gibbsite contents are  
615 very low in the white kaolin horizon. When the solutions percolating in the white kaolin reach  
616 a material with a higher content in Fe-oxides and gibbsite, the DOM can be adsorbed, and  
617 then mineralized, resulting in the release of previously DOM-complexed Al or Fe and a  
618 positive feedback for Fe-oxides and gibbsite precipitation.

619

### 620 **4.3 Groundwater – minerals relationships**

621

#### 622 **4.3.1 The Si-Al system**

623

624 The positions of the average groundwaters in the Si-Al system are given in Fig. 7. The line  
625 “kaolinite 1” corresponds to the stability with kaolinite calculated with the Wateq-4f data  
626 base, which uses the same value ( $\text{Log}(K_{\text{sp}}) = 3.705$ ) than the one proposed by Tardy and  
627 Nahon (1985) after a critical analysis of the literature. However, as stressed by Grimaldi et al.  
628 (2004), kaolinite solubility is not well defined in most tropical soils because of iron  
629 substitution and variable crystallinity and these authors also used a lower value ( $\text{Log}(K_{\text{sp}}) =$   
630  $2.853$ ) that gave the line “kaolinite 2” in Fig. 7.

631

632 Even without considering complexation by DOM, the spring water and the groundwater  
633 circulating in the upper part of the white sands (Spring and W1-20) are far away from  
634 saturation with kaolinite or gibbsite. Except point S5-380, the groundwaters circulating in the  
635 kaolinitic horizons (from S1-510 to S6-300 along the pathway n°1 and from S3-160 to S2-160  
636 along the pathway n°2) are distributed between the two kaolinite lines, which indicate a  
637 control by kaolinite precipitation/dissolution. Their evolution downslope (white arrow), i.e.  
638 with increasing residence time, is thus driven by an increase of Si concentrations likely due to  
639 quartz dissolution. Most are supersaturated with regard to gibbsite, which is consistent with  
640 gibbsite precipitation in slope horizons (see envelope of centimetrical Al-nodules on Fig. 2)  
641 but may also indicate a higher gibbsite solubility or Al complexation with DOM. No  
642 explanation was found for the fact that the point S5-380 is far away from equilibrium due to  
643 the very low Al concentrations that have always been observed along the three sampling  
644 periods, although these low values are consistent with the gradual decrease of Al  
645 concentration in the groundwater along the slope. The micro-valley bottom groundwater  
646 (SMVB-15) is clearly oversaturated with regard to kaolinite because of very high Si  
647 concentrations likely due, as stressed before, to litter mineralization.

647

### 4.3.2 Iron, iron bearing minerals and bleaching of the kaolin

Measured  $\text{Fe}^{2+}$  values were almost always higher than  $\text{Fe}^{3+}$  values, indicating that iron in the soil system is mainly transported as  $\text{Fe}^{2+}$  even when  $E_H$  is relatively high, more than 450 mV. As seen in the Fe Pourbaix diagram (Fig. 8), the DOM-rich groundwaters from the white sands or the micro-valley bottom (circles) are well below the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  transition, which is explained by acidity for the white-sand groundwater and by lower  $E_H$  for micro-valley bottom (SMVB-15) where litter mineralization occurs. Except the S2-160 point, all DOM-poor groundwaters circulating in the kaolin as well as in the Ef horizons are close to the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  transition, most time slightly below, indicating that the mobility of iron in these horizons depends on small  $E_H$  variations which can be due to microbial pulses in upper horizons or Bh-Bhs organic matter mineralization (Montes et al., 2007). According to Cornell and Schwertmann (1969), the bright orange-coloured coatings in tubular pores observed immediately beneath the Bhs are characteristics of lepidocrocite, which forms by fast iron precipitation in soils submitted to rapid  $E_H$  changes. The position of the S2-160 point (Ef horizon) is characterized by a low  $E_H$  when compared to the upstream S1-240 or W2-150 points or the downstream S3-160 point. This may be due to the fact that the water sampled at this point has just flowed through the Bh-Bhs where organic matter oxidation may lower the  $E_H$ . Downslope, sulphide-smelling groundwaters of point S6-300 are typical of reduced conditions.

Two processes are thus able to favour the bleaching of the kaolin associated with podzols areas. The first one, as hypothesized by Montes et al. (2007), is that solutions percolating in depth are able to reduce iron and that their reducing capacity can be enhanced by mineralization in depth of the organic matter transferred from the topsoil by podzolic processes. The second one is that small carboxylic compounds transferred from the podzolic horizons are able to migrate within the kaolin, enhancing the iron mobility by complexing  $\text{Fe}^{3+}$  and, as already observed in very oxidizing media (Kieber et al., 2005),  $\text{Fe}^{2+}$ . This latter process can also explain the lack of a good correlation between  $E_H$  and  $\text{Fe}^{2+}$ . The final result is a complete bleaching of kaolin horizons and it is likely that the deeper the permanent water-table, the deeper percolates the groundwater and the thicker the kaolin bleached horizons.

## 5 Conclusion

The groundwater produced by the hydromorphic podzols is acidic, around pH 4.1, and DOM-rich (DOC around  $37 \text{ mg L}^{-1}$ ). Its DOM has a high proportion of humic compounds and less than 10% of small carboxylic acids and its acid-site density ranges from 7 to  $23 \text{ meq gC}^{-1}$  when considering a pKa ranging from 3 to 4.5; these properties are similar to those observed in podzolic temperate areas. This DOM-rich groundwater circulates in the sandy podzol E horizons. It seeps and overflows in the lower parts of the podzolic areas and can also, after high rainfall events, drain through a specific network of micro-valleys at the podzol-ferralsol transition. These two pathways allow direct DOM exportation, feeding the black-water streams and rivers.

A part of this DOM-rich groundwater percolates in depth down to the kaolin or ferralsolic horizons. When passing the Bh, most of the DOM is adsorbed, feeding the Bh and allowing carbon storage in depth. It is likely that part of the adsorbed OM can suffer posterior mineralization. The rate of such a process, which determines the rate of carbon storage, has yet to be defined.

The adsorption of DOM when the groundwater passes the Bh results in a more than 10-fold decrease of the DOC content. The dissolved humic substances are preferentially adsorbed, so that the proportion of small carboxylic acids increases up to around 50% of the

698 total DOC. The resulting groundwater is DOM-poor (DOC around 37 mg L<sup>-1</sup>) with a high  
699 acid-sites density, ranging from 31 to 67 meq gC<sup>-1</sup> when considering a pKa ranging from 3 to  
700 4.5, due to the large proportion of small carboxylic acids. Significant amounts of small  
701 carboxylic compounds have thus the ability to percolate through kaolinitic materials.

702 With regard to the soil system dynamics, the aggressive DOM-rich groundwater  
703 circulating in the sandy podzol E horizons favours kaolinite and Fe- or Al-oxides dissolution  
704 and subsequent development of the sandy horizons at the expense of the clayey ones. In the  
705 deep groundwater circulating in the kaolin and in the kaolinitic ferralsolic horizons, Si and Al  
706 content is controlled by gibbsite and kaolinite precipitation/dissolution and by quartz  
707 dissolution. Fe is mainly transported as Fe<sup>2+</sup>, due to acidity and relatively low E<sub>H</sub>. Its mobility  
708 can be related to small E<sub>H</sub> variations for which microbial activity can be decisive and can also  
709 be enhanced by the significant concentration of small carboxylic acids. The long-term result  
710 of these processes is the bleaching of the kaolin, the precipitation of Al-nodules in slope  
711 horizons and of Fe-oxides in the upper downslope horizons. An accurate modelling of the  
712 minerals-solutions relationships will, however, need further investigation of the DOM acidity  
713 and complexing properties with regard Al and Fe.

714 As the bleaching of the kaolin is favoured by the deep percolation of white-sand issued  
715 solutions, kaolin is likely to occur where active giant podzols are close to a slope gradient  
716 sufficient to lower the water-table, which is a configuration easily identified by remote  
717 sensing.

718 With regard to methods, it must be noticed that usual pH measurement protocols are  
719 inadequate for low ionic strength groundwaters and that pH measurement must be adapted by  
720 using low ionic strength references, by adjusting the ionic strength during pH measurement or  
721 by using a corrective model.

722  
723 *Acknowledgments* — This work benefited from FAPESP funding n°07/02543-0, from ARCUS  
724 PACA-Brésil funding (French Ministry of Foreign Affairs MAE and Région  
725 Provence-Alpes-Côte d'Azur) and from CAPES-COFECUB bilateral cooperation  
726 funding.  
727

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880 **Tables**

881

882 **Table 1. Minerals identified in the soil material. Pits and horizon are located on Fig. 2.**

883

Horizon	Depth (m)	Texture	Mineralogy				Other minerals
			Quartz (%)	Kaolinite (%)	Gibbsite (%)	Muscovite (%)	
<i>Pit P1 - Podzol</i>							
O & A1	0.0-0.8	Sand	88-95	2-12	ε-5	0-ε	A, R, Go, H
Es	0.8-1.9	Sand	100	ε	ε	0-ε	A, R, Go, H
Bh-Bhs	1.9-2.3	Sandy loam	90-94	6-10	ε	ε	A, R, Go, H
K1	2.3-4.0	Silty clay loam	ε-3	92-96	8-4	ε-1	A, M, Go, H
K2	4.0-10.0	Silty clay loam	ε-3	96-97	4-2	ε-1	A, M, Go, H
<i>Pit P2 - Ferralsol</i>							
A	0.0-0.3	Sandy clay loam	59-70	18-26	2-3	ε	A, V, Go
B1	0.3-1.3	Sandy clay loam / Clay loam	36-68	14-66	1-3	ε	A, V, R, Go
Ef	1.3-1.6	Silty clay loam	37	60	3	ε-1	Go
K1	1.6-3.0	Silty loam	6	94	ε	3-4	A, R, Go, H
K2	3.0-6.6	Silty loam	10	90	ε	2-6	A, R, Go, H
<i>Pit P3 - Ferralsol</i>							
A	0.0-0.1	Sandy clay loam	62	34	4	ε-1	A, R, Go
B2	0.1-1.0	Sandy clay	8-65	32-86	3-6	ε-1	A, R, Go
K3	1.0-1.3	Clay	10	86	4	1	A, Go, H
K1	1.3-4.0	Clay	2-9	86-92	5-8	1-2	A, R, Go, H
K4	4.0-5.6	Clay / Silty clay	2	96	2	2-13	A, R, Mc, Mg, Go, H
<i>Pit S1 - Gleysol</i>							
A	0.0-0.1	Sandy loam	59	24	1	3	A, R, Go, H
B3	0.1-1.4	Sandy loam	60-71	9-13	ε-1	3-7	A, R, Mc, Go, H
K4	1.4-2.7	Loam	42	15	ε	15	A, V, R, Mc, I, Go, H

A: anatase, M: muscovite, V: vermiculite, Mc: microcline, Mg: magnetite, I: illite, R: rutile, Go: goethite, H: hematite, ε: very small amounts

884

885

886 **Table 2**

887 **Summary of the composition of the groundwater for each sampling point.**

888

	Si (mg L <sup>-1</sup> )			Al <sup>3+</sup> (mg L <sup>-1</sup> )			Fe <sup>3+</sup> (mg L <sup>-1</sup> )			Fe <sup>2+</sup> (mg L <sup>-1</sup> )		
	av	max	min	av	max	min	av	max	min	av	max	min
Spring	0.05	0.07	0.02	0.02	0.05	<0.01	0.01	0.05	0.00	<0.05	0.10	<0.05
W1-20	0.05	0.10	0.02	0.03	0.14	<0.01	0.03	0.07	0.00	0.06	0.13	<0.05
W2-150	0.27	0.48	0.19	0.18	0.24	0.14	0.04	0.15	0.00	0.10	0.38	<0.05
S1-240	0.48	0.59	0.29	0.48	0.63	0.37	0.06	0.15	0.00	0.10	0.19	<0.05
S1-510	0.13	0.20	0.10	0.37	0.41	0.33	0.02	0.03	0.00	0.07	0.20	<0.05
SMVB-15	1.86	2.44	1.19	0.68	0.81	0.57	0.79	1.65	0.39	1.58	2.52	0.42
S2-160	0.46	0.57	0.31	0.20	0.27	0.17	0.04	0.08	0.02	0.21	0.63	<0.05
S2-490	0.21	0.41	0.11	0.14	0.18	0.07	0.03	0.04	0.02	<0.05	0.09	<0.05
S3-160	0.30	0.40	0.21	0.06	0.09	0.04	0.01	0.04	0.00	0.05	0.15	<0.05
S3-380	0.19	0.24	0.12	0.07	0.14	0.01	0.02	0.05	0.00	<0.05	0.06	<0.05
S4-400	0.49	0.71	0.25	0.03	0.07	<0.01	0.07	0.46	0.01	<0.05	0.07	<0.05
S5-380	0.55	0.69	0.38	<0.01	0.01	<0.01	0.03	0.07	0.01	0.08	0.15	<0.05
S6-80	0.29	0.56	0.15	0.63	0.76	0.50	0.06	0.11	0.01	0.15	0.48	<0.05
S6-300	0.48	0.57	0.24	0.09	0.11	0.08	0.06	0.13	0.03	0.74	1.11	0.52
	pH			E <sub>H</sub> (mV)			DOC (mg L <sup>-1</sup> )					
	av	max	min	av	max	min	av	max	min			
Spring	4.0	4.3	3.4	521	542	503	37	45	29			
W1-20	4.1	4.5	3.6	473	495	451	34	55	24			
W2-150	4.2	4.5	3.9	512	563	472	40	52	35			
S1-240	4.1	4.4	3.5	501	567	410	15	19	12			
S1-510	4.5	5.1	3.8	514	575	468	2	3	2			
SMVB-15	4.6	5.1	4.0	372	415	325	32	38	27			
S2-160	4.6	5.1	3.8	399	484	296	7	9	6			
S2-490	4.6	5.1	3.9	499	543	444	4	7	2			
S3-160	4.9	5.2	4.7	482	519	448	5	10	4			
S3-380	4.9	5.2	4.6	494	532	467	4	6	2			
S4-400	4.8	5.3	4.1	494	520	482	5	9	2			
S5-380	4.9	5.4	4.3	460	478	437	3	5	2			
S6-80	4.5	5.1	4.1	456	510	365	16	19	13			
S6-300	5.0	5.5	4.4	172	191	147	5.4	9.7	3.5			

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890

891 Table 3  
 892 Major ions charge, DOC and pH (average±standard deviation).  
 893

Sampling point	Number of samples	Major ions charge						
		Na <sup>+</sup> (µeq.L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (µeq.L <sup>-1</sup> )	K <sup>+</sup> (µeq.L <sup>-1</sup> )	Mg <sup>2+</sup> (µeq.L <sup>-1</sup> )	Ca <sup>2+</sup> (µeq.L <sup>-1</sup> )	Al <sup>a</sup> (µeq.L <sup>-1</sup> )	Fe <sup>2+</sup> (µeq.L <sup>-1</sup> )
Spring	4	24.7±2.5	9.7±4.5	8.9±2.0	10.3±3.0	103.0±26.4	2.2±2.6	1.0±0.5
W1-20	1	26.4	3.8	36.5	12.6	82.8	3.3	2.2
W2-150	1	34.2	64.5	35.1	15.8	88.6	19.5	3.6
S1-240	4	30.2±13.7	13.4±19.1	19.7±15.5	7.8±2.7	46.4±15.6	52.8±4.5	3.6±3.8
S1-510	4	14.8±2.1	4.8±6.1	5.0±1.3	4.7±1.4	34.7±8.5	39.6±3.4	2.2±1.1
S2-490	4	27.6±13.2	33.6±28.2	8.7±6.9	3.9±1.4	53.2±12.7	15.0±5.5	1.4±0.8
S4-400	4	36.9±10.4	31.4±19.4	43.2±6.6	9.9±1.4	73.9±12.4	3.3±2.3	1.4±0.9
S6-300	4	18.1±2.7	16.4±10.0	30.4±1.7	4.9±0.5	61.6±8.4	9.0±5.2	26.4±14.3
		Fe <sup>III</sup> <sup>a</sup> (µeq.L <sup>-1</sup> )	Cl <sup>-</sup> (µeq.L <sup>-1</sup> )	NO <sub>2</sub> <sup>-</sup> (µeq.L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (µeq.L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (µeq.L <sup>-1</sup> )	pH <sup>b</sup>	DOC (mg.L <sup>-1</sup> )
Spring	4	0.6±0.2	11.5±4.1	0.0±0.0	3.6±6.2	11.1±1.2	4.0±0.08	37.4±1.9
W1-20	1	1.5	8.2	4.1	8.6	8.6	4.1	34.4
W2-150	1	2.1	19.7	32.3	8.9	35.1	4.2	40.2
S1-240	4	3.9±2.6	16.6±9.9	0.0±0.0	74.6±10.8	24.2±9.4	4.0±0.09	15.2±0.7
S1-510	4	1.2±0.5	11.2±2.8	2.0±2.0	41.8±7.2	17.4±6.2	4.6±0.08	2.3±0.4
S2-490	4	1.5±0.6	13.3±9.7	0.0±0.0	11.2±5.1	22.8±7.1	4.6±0.13	4.0±1.6
S4-400	4	3.9±1.8	32.5±18.1	3.9±3.9	23.4±10.4	34.7±14.1	4.8±0.07	4.9±2.0
S6-300	4	3.3±0.9	12.5±1.1	0.0±0.0	6.5±4.6	15.0±4.3	5.1±0.17	5.4±0.9

894 <sup>a</sup> Calculated for the sum of Al or Fe<sup>III</sup> species, respectively.

895 <sup>b</sup> Values after correction, see text.

896  
 897 Table 4  
 898 Result of modelling the microtitration curves by 4 discrete acidic site – pKa and site density L<sub>T</sub>.  
 899

<i>Spring</i>				
pKa	3.5±0.6	4.7±0.4	6.9±2.6	9.3±1.5
L <sub>T</sub> (meq.gC <sup>-1</sup> )	17.2±0.4	9.5±0.4	8.1±2.3	5.4±5.6
<i>W2-150</i>				
pKa	4.1±0.3	5.2±0.1	8.7±0.1	10.6±0.1
L <sub>T</sub> (meq.gC <sup>-1</sup> )	10.9±0.3	7.1±0.5	2.6±0.3	6.6±3.5

900  
 901 Table 5  
 902 DOC characterization.  
 903

	Spring	W2-150	S1-510	S3-380	S4-400
<i>DOC and small carboxylic acids (mgC L<sup>-1</sup>)</i>					
DOC	35.6	38.3	1.3	1.7	2.1
Lactic acid	0.05	0.05	0.02	0.04	0.02
Acetic acid	0.28	0.17	0.10	0.17	0.24
Formic acid	1.18	1.10	0.44	0.62	0.60
Succinic acid	0.64	0.56	0.11	n.a.	n.a.
Oxalic acid	0.26	0.19	0.09	0.04	n.a.
Citric acid	0.72	n.a.	0.07	0.12	0.13
<i>SUVA<sub>254</sub> index (L mg<sup>-1</sup> m<sup>-1</sup>)</i>					
	5.8	4.9	1.5	1.3	2.1

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Table 6  
Calculated charge due to DOM and acid site density for various pKa.

Sampling point	Number of samples	Sum of charges of major ions $\sum_i Z_i$ ( $\mu\text{eq}\cdot\text{L}^{-1}$ )	pH	DOC ( $\text{mg}\cdot\text{L}^{-1}$ )	Charge due to DOM $Z_{\text{DOM}}$ ( $\text{meq}\cdot\text{gC}^{-1}$ )	Acid-site density $L_T$ ( $\text{meq}\cdot\text{gC}^{-1}$ )			
						pKa			
						3.0	3.5	4.0	4.5
Spring	4	134± 28	4.0±0.08	37.4 ± 2.9	-6.3 ± 1.8	7 ± 2	8 ± 3	13 ± 5	26 ± 11
W1-20	1	142	4.1	34.4	-6.5	7	8	12	23
W2-150	1	184	4.2	40.2	-6.2	7	7	10	19
S1-240	4	59± 36	4.0±0.09	15.2±0.7	-11 ± 4	12 ± 4	14 ± 6	22 ± 10	46 ± 22
S1-510	4	33± 3	4.6±0.08	2.3±0.4	-31 ± 4	31 ± 4	33 ± 5	38 ± 7	55 ± 12
S2-490	4	98 ± 39	4.6±0.13	4.0±0.7	-37 ± 13	38 ± 14	40 ± 15	47 ± 18	67 ± 29
S4-400	4	109± 29	4.8±0.07	4.9±2.0	-32 ± 8	33 ± 8	34 ± 9	37 ± 10	48 ± 15
S6-300	4	135± 27	5.1±0.17	5.4±0.9	-32 ± 5	32 ± 5	33 ± 5	34 ± 6	40 ± 8

908  
909

910 **Figure Captions**

911

912 Fig. 1. Situation of the studied sequence and extension of highly podzolic areas (in grey) in  
913 the Rio Negro basin. Compilation of highly podzolic areas was realized from digitalized soil  
914 maps of Amazonia (IBGE, 2009). The detailed view of the studied area is issued from  
915 IKONOS imagery, the darker forested area corresponds to closed, low forest over  
916 hydromorphic podzols. E2 and E1 are sampling points outside the sequence.

917

918 Fig. 2. View of the soil system along the catena. Capital letters of horizon names refer to  
919 FAO, 1993. O: organic, peat-like horizon; A1: organic-rich, dark brown horizon; A: horizons  
920 brown-coloured by organic matter; Es: podzolic eluviated horizons; B1: oxic B horizons  
921 varying from sandy upslope to sandy-clayey downslope; B2: oxic sandy-clay B horizons; B3:  
922 pseudogley B horizons; K: kaolin horizons; Bh-Bhs: horizons with organic matter and Al-Fe  
923 accumulation; Ef: non podzolic leached horizon; C1 and C2: saprolitic horizons. P1 to P4:  
924 situation of mineralogical data given in Table 1.

925

926 Fig. 3. Solid soil phase: kaolinite, gibbsite and total organic carbon (TOC) in the podzol from  
927 the upper part of the catena (Pit 1). Horizontal axis is in % for kaolinite and gibbsite and in ‰  
928 for TOC.

929

930 Fig. 4. Daily rainfall in the area. Grey vertical bars indicate the sampling periods.

931

932 Fig. 5. Average composition of the sampled waters along the pathways n°1 and n°2. Vertical  
933 bars give the calculated standard deviation for each set of data.

934

935 Fig. 6. Microtitration curves of DOM-rich groundwaters and result of modelling with the  
936 PROCESE software.

937

938 Fig. 7. Position of the groundwaters in the Si-Al system calculated from the average  
939 compositions without considering complexation by DOM. Red and green symbols indicate  
940 groundwaters following pathway n°1 and n°2, respectively, triangular symbols indicate  
941 groundwaters supposed to be controlled by kaolinite dissolution/precipitation and circles  
942 indicate groundwaters with high DOC.

943

944 Fig. 8. Position of the groundwaters in the iron Pourbaix diagram drawn for low  
945 Fe-concentrated waters ( $<10^6$  M). Symbols are the same that in Fig. 7.

946

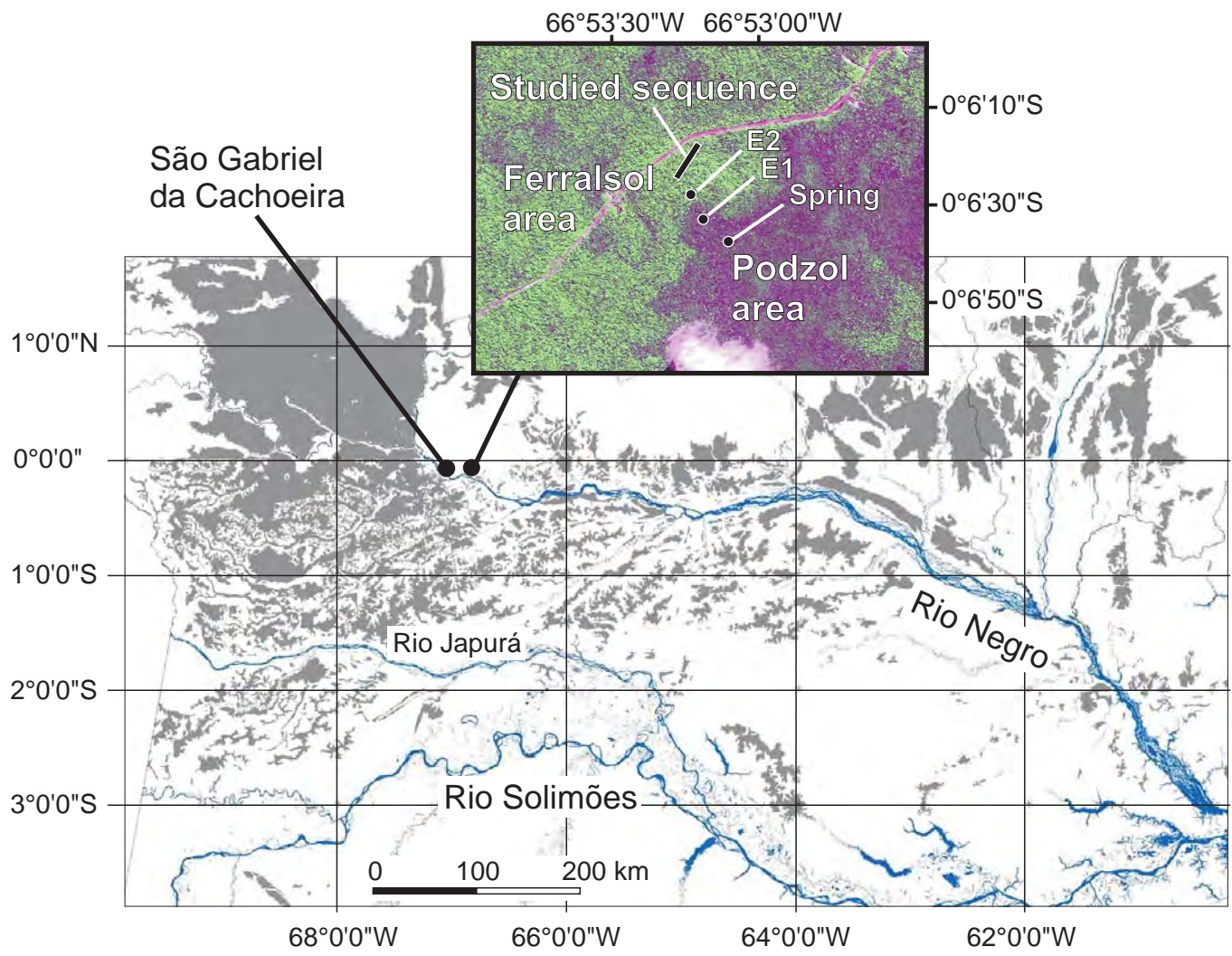


Fig. 1



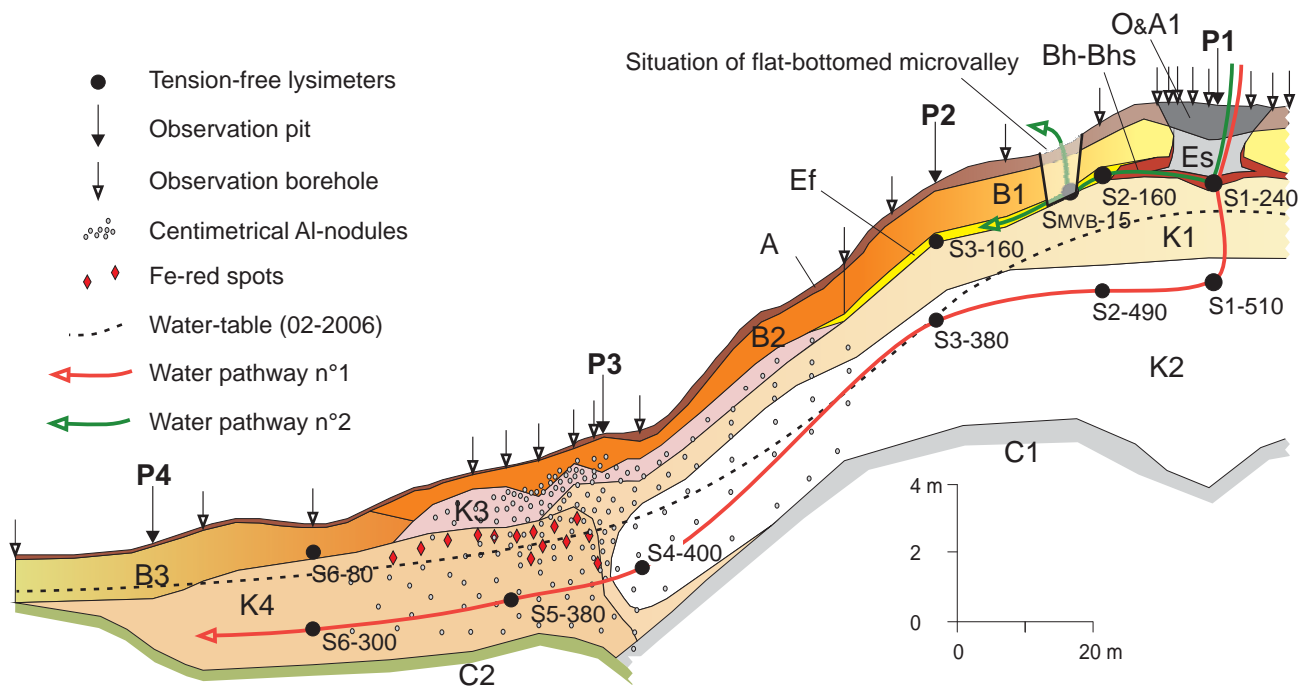


Fig. 2

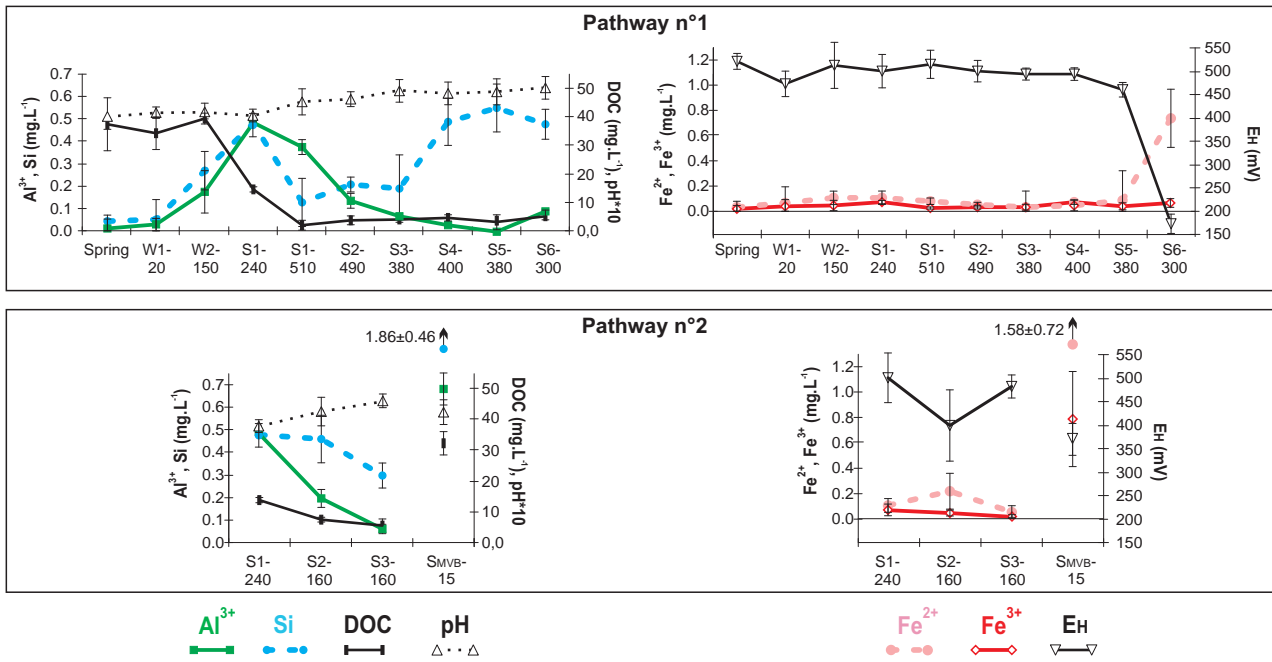


Fig. 5

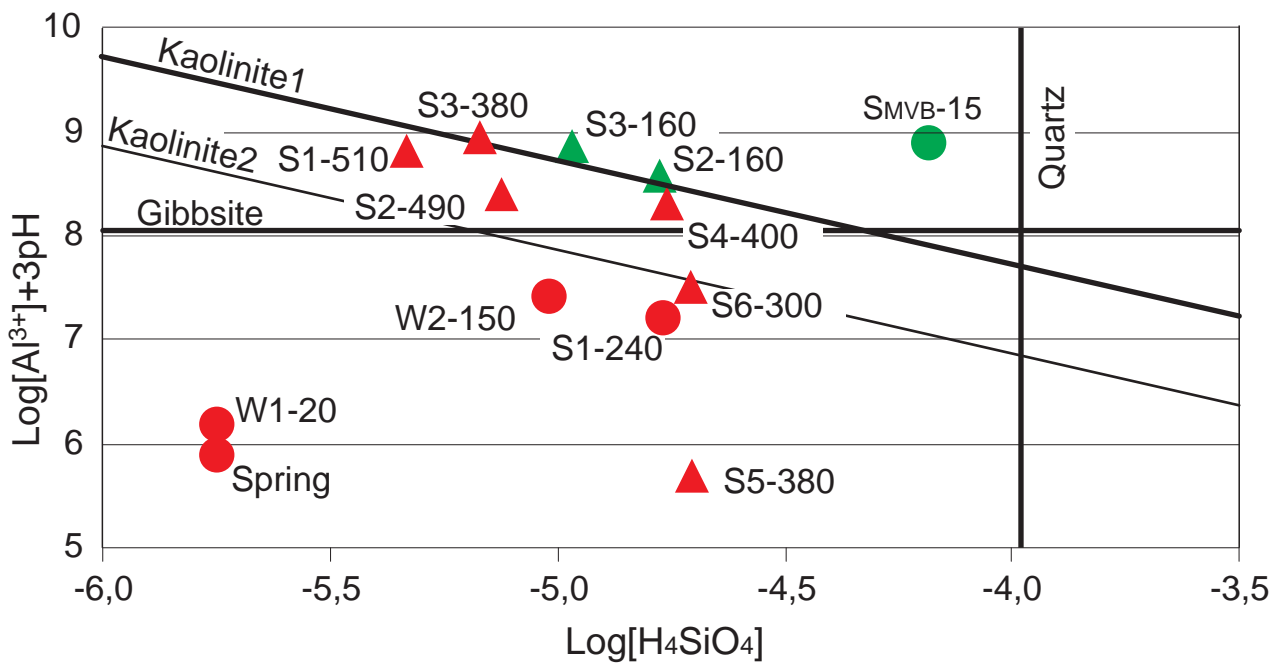


Fig. 7

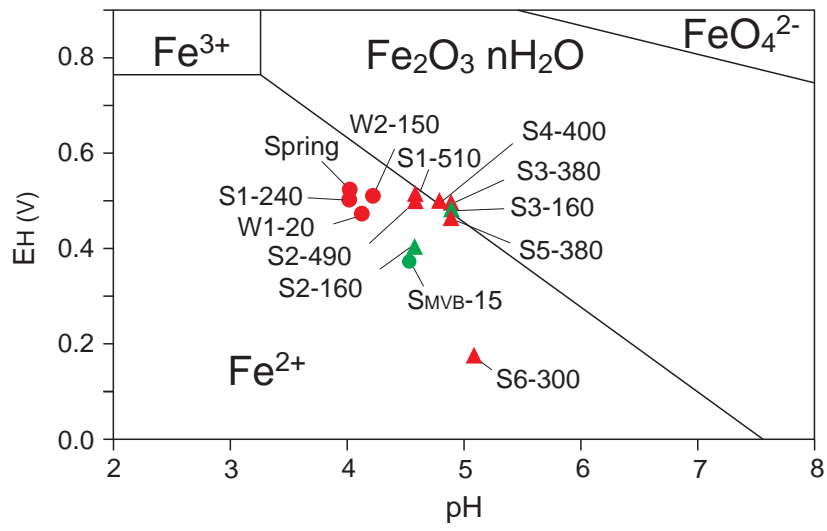


Fig. 8

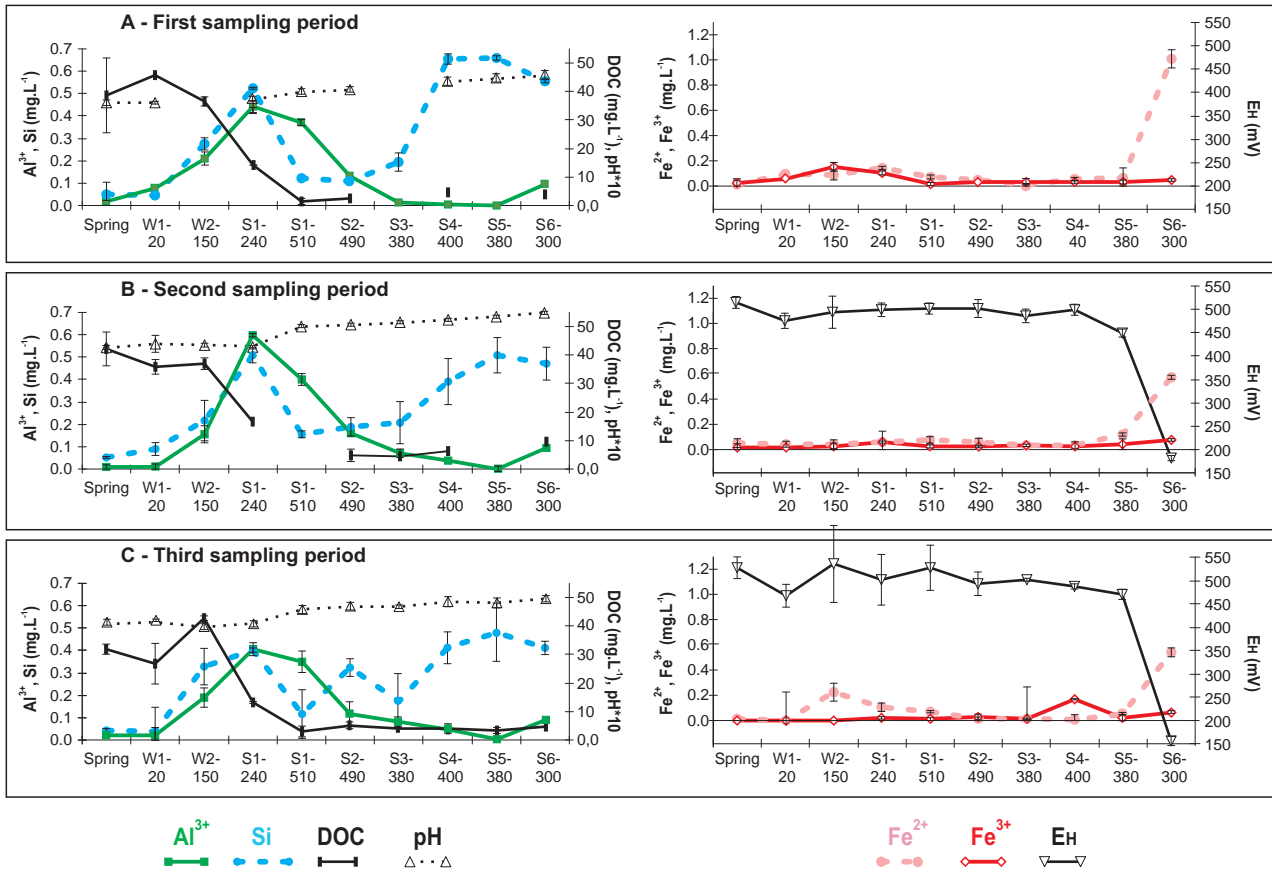


Fig. S1

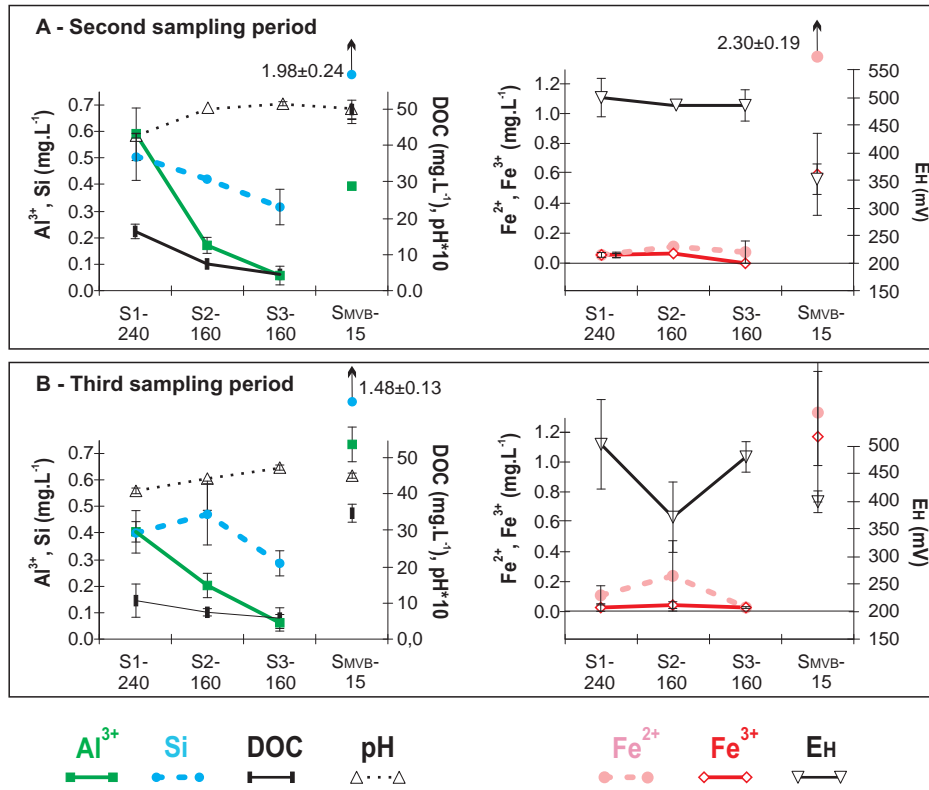


Fig. S3