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 g-1, respectively (PP225225)” 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 than 1/4 of this OM could return 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:** H$_4$SiO$_4$, Al$^{3+}$, Fe$^{2+}$ and 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$^{th}$ §.

**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 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 Al$^{3+}$ and H$_4$SiO$_4$ measurements realized at 620 and 695 nm, respectively, but can be significant for 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⁺ 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⁺, 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⁻¹ HNO₃ additions until pH 2.5, N₂ purged, and then titrated using 0.1 mol l⁻¹ 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⁻¹) was calibrated daily by the titration of a HNO₃ 0.01 mol l⁻¹ 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⁻¹).

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 2nd § 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 $^{14}$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 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 Fe2+ 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 deposit 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 pedogentic 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 SUVA254 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 R² (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 pathways 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 suggest 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 LT expressed in 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 ^14C 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.
Biogeochemistry of an Amazonian Podzol-Ferralsol Soil System with White Kaolin

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Abstract

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

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

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

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

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

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

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

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

2 Material and methods

2.1 Description of the Studied Area

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

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

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

The podzols have a typical vertical succession of horizons: O, A1, E, Bh, Bhs. The organic O horizons are peat-like, with a thickness varying from a few centimetres to more
than 50. The more waterlogged the topsoil throughout the year, i.e. far from the plateau slopes, the thicker the O horizons. The humic A1 horizons are well-developed; they consist of clean white quartz sand and organic matter particles. The eluviated sandy Es horizons have thin (1-2 mm), dark-grey micro-horizons coloured by organic matter particles; they have traces of kaolinite and gibbsite and high porosity and hydraulic conductivity. The transition between Es horizons and the underlying kaolin shows the vertical following sequence: (1) Bh - the sandy Es horizon turns progressively darker, due to an increase of organic matter content; (2) Bhs - there is an irregular, finger-like transition towards a hardened, sandy-clay horizon, brown coloured (10YR 5/2) (colors are given according to Munsell, 1990) with dark brown (7.5YR 5/6) features formed by organic matter and Fe-oxides accumulation in cracks and tubular pores, the gibbsite content is higher, the quartz sand content diminishes quickly in depth, together with the increase of kaolinite and the hydraulic conductivity turns lower. The kaolin K1 and K2 horizons consist mainly of kaolinite, with gibbsite content around 8% at the upper part of K1 and decreasing in depth to be lower than 2% at the lower part of K2 (Fig. 3). The upper part of the kaolin is a clayey, whitish material with some orange-coloured coatings in tubular pores (K1 horizon). These coatings progressively diminish in depth, giving place to a homogeneous, white, clayey, butter-like material (K2 horizon). In depth, the C1 horizon is a silt-clay saprolite having muscovite and weathered feldspar.

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

2.2 Water Sampling and Analysis

2.2.1 Lysimeters

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

Regarding groundwater, thirteen zero-tension lysimeters were installed inside drilling holes at different depths, 2 points (W1-20 and W2-150) within the podzolic campinarana area (Fig. 1) and 11 points along the soil catena (Fig. 2). After installing the lysimeters, each
drilling hole was tamped by filling with the previously extracted soil material at the corresponding depth. Each lysimeter was made of a 50 mL polypropylene bottle bored with 5 mm diameter holes all around. A 2 mm diameter capillary PTFE tube was inserted through the bottle cap in order to permit extracting water from the topsoil with a manual vacuum pump. To prevent clogging of the capillary tube by soil particles, a cylindrical filter made of a SeFar Nitex 64µm polyamide open mesh was put inside the bottle. All lysimeters were acid-washed prior to installation.

2.2.2 Sampling points

The studies already conducted on Amazonian podzol-ferralsol systems (see introduction) have shown that 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. As in many old, deeply weathered soil covers soil variations are spatially explicit and depend on soil forming processes, closely related to water pathway and residence time (Boulet et al., 1982). In such a context, sampling points were selected based on the morphology of the soil cover and on the water pathways that could be inferred from soil patterns and topography; the continuity and consistency of observed variations along the water pathways will determine the validity of the data.

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

2.2.3. Sampling periods and analysis

Groundwater was sampled during three periods indicated on Fig. 4. The first one (27 to 30/07/2007) was typical of low rainfall periods, the second one (29/01 to 04/02/2008) was intermediate and the third one (19 to 25/05/2008), typical of high rainfall periods, allowed sampling high-level water-tables. The 10-days cumulated rainfalls before the sampling periods were 53, 88 and 178 mm for the 1st, 2nd and 3rd sampling periods, respectively. Complementary sampling for acid-base microtitration and DOC characterization was realized on 09/02/2009 for points Spring, W2-150, S1-240, S1-510, S3-380 and S4-400. Sampling was done by applying a continuous suction of 25 mmHg to the lysimeters. The first 20mL of each sampling was discarded in order to avoid dead volume and to rinse the sampling equipment. Groundwater was then sampled until 250 mL was reached or air was
entering the system. pH and E\textsubscript{H} were measured immediately after sampling with a Eutech pH310 instrument after stabilization with gentle shake (calibration of the pH electrode was done every day). Each sample was then filtered using an inline 0.22\(\mu\)m cellulose membrane filter (Nalgene surfactant-free cellulose acetate) and separated in four aliquots for immediate analysis of dissolved H\textsubscript{4}SiO\textsubscript{4}, Al\textsuperscript{3+}, Fe\textsuperscript{2+} and Fe\textsuperscript{3+}, separately. A fifth aliquot was filtered using a 0.7\(\mu\)m fiber glass filter, poisoned with sodium azide, stored in 10 mL vacuum glass flasks (Vacutainer) then kept at low temperature (around 4°C) for laboratory analysis of DOC and other dissolved species.

Analysis of dissolved H\textsubscript{4}SiO\textsubscript{4}, Al\textsuperscript{3+} and Fe\textsuperscript{2+}/Fe\textsuperscript{3+} were performed within one hour after sampling by colorimetry using a Lange DR 2800 Spectrophotometer with analytical kits LCK301, LCW028 and LCK320, respectively. The measurement ranges were 0.01-0.60 mg.L\textsuperscript{-1}, 0.005-1.000 mg.L\textsuperscript{-1} and 0.05-6.0 mg.L\textsuperscript{-1} and the absorbencies measured at 620 nm, 695 nm and 485 nm for Al\textsuperscript{3+}, H\textsubscript{4}SiO\textsubscript{4} and Fe\textsuperscript{2+}, respectively. The colorimetric method was chosen because it allowed measurements immediately after sampling and because it measures the free or displacable species able to participate to solution-minerals equilibria. To ensure that no oxidation of Fe\textsuperscript{2+} was occurring between sampling and analysis, Fe\textsuperscript{2+} measurements were performed 10 minutes and 6 hours after water sampling. No significant differences between the results were observed. As the coloured DOM absorbency exponentially decreases from 220 to 650 nm (Schwartz et al., 2002), DOM contribution is low for Al\textsuperscript{3+} and H\textsubscript{4}SiO\textsubscript{4} measurements realized at 620 and 695 nm, respectively, but can be significant for Fe\textsuperscript{2+} measurement at 485 nm. In order to limit possible interferences due to the natural DOM color of the samples, absorbance of the filtered sample before any reagent addition was subtracted from absorbance of the final measurement.

Laboratory analyses were performed between 10 and 45 days after sampling. DOC analyses were performed with a Shimadzu TOC-V Analyzer calibrated with a 10 ppm potassium phthalate standard solution. Blank signal for filtered ultra-pure MQ water was about 0.1 ppm. Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Cl\textsuperscript{−}, NO\textsubscript{2}\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, PO\textsubscript{4}\textsuperscript{2−}, SO\textsubscript{4}\textsuperscript{2−} ions were determined by ion chromatography (Dionex DX 120), using 9 mmol.L\textsuperscript{-1} NaHCO\textsubscript{3} for cation elution and 10 mmol.L\textsuperscript{-1} methane sulfonic acid for anion elution.

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

During data modeling, the pH values seemed underestimated in comparison to field observations, so that a special attention was paid to pH measurements. pH electrode calibration at field was realized with a standard electrode and standard reference solutions having a ionic strength high when compared to the studied solutions, which can give a measurements error. To test this hypothesis, pH measurement were achieved on seven selected samples, using the same electrode and adjusting the ionic strength (I) to 10\textsuperscript{-4}, 10\textsuperscript{-3} and 10\textsuperscript{-2} M with KCl. The pH increased with increasing ionic strength, an asymptote being reached when I = 10\textsuperscript{-2} M (Supplementary Fig. S1). The difference \(\Delta\text{pH}\) between pH measured before adjustment and pH measured at I = 10\textsuperscript{-2} M was dependent on the DOC content, which indicates that the DOM is actually charged and participates to the ionic strength. The pH were then corrected by using the empirical relationship \(\Delta\text{pH} = 0.508 - 0.0047*\text{DOC}\) where DOC...
is expressed in mg L⁻¹. In most cases ΔpH was between 0.3 and 0.5 pH units; correction was however necessary for modeling. For example, as three H⁺ are exchanged during gibbsite hydrolysis, if pH increases 0.5 units the saturation index with regard to gibbsite will increase 1.5.

In order to evaluate the behaviour of the studied solutions with regard to H⁺, 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⁻¹ HNO₃ additions until pH 2.5, N₂ purged, and then titrated using 0.1 mol l⁻¹ KOH until pH 11.5. Acid-base titrations were performed using two Titrino 716 apparatus controlled by a Titin 2.4 software (Metrohm). The combined pH-micro-electrode used (Mettler, Inlab422, reference: Ag/AgCl/KCl 3.0 mol l⁻¹) was calibrated daily by the titration of a HNO₃ 0.01 mol l⁻¹ solution followed by theoretical fitting of the titration curve.

Small carboxylic acids were identified and quantified in selected samples by ionic chromatography ( Dionex ICS 3000) using AG11-HC guard column, a IonPac ICE-AS11 column, for elution NaOH with a gradient from 1 to 5 mmol.L⁻¹ and a CD25 pulse electrochemical detector. On the same samples the SUVA₂₅₄ index was measured using a Shimadzu UV-1800 spectrophotometer. This index is calculated as the ratio of UV absorbance at 254 nm to the product of DOC and UV cell path length; it is considered as characteristic of the hydrophobicity and aromaticity of the considered DOC (Chin et al., 1994). Thermodynamic modeling of the solution-minerals interactions was performed by own calculation and checked using the PHREEQ-C (2.11) software with the Wateq-4f database (Ball and Nordstrom, 1991).

3 Results

3.1 Water pathways along the catena

During the 1st sampling period, no samples were available in the S2-160 and S3-160 points, because of the lack of perched water-table in the Ef horizon due to insufficient rainfall. During the 2nd sampling period, the point S2-160 gave sample only one sampling day (31/01/08) when the S3-160 point gave sample three sampling days (29/01/08, 31/01/08 and 02/02/08). During the 3rd sampling period, both S2-160 and S3-160 points gave samples every sampling day. This behaviour of the sampling points attests the fast level changes of the perched water table after heavy rains. When sufficiently high, a water table perched over the podzolic Bhs horizon laterally overflows towards the Ef horizon, then percolates downslope along this horizon or flows out in the flat-bottomed micro-valleys. The SMVB-15 point was situated at the bottom of a small micro-valley, at an altitude roughly corresponding to those of the S2-160 point, and allowed sampling the overflow of the perched water-table in the micro-valleys. Such overflow allows a direct exportation of the groundwater down to the streams and rivers, beside other pathways such as the usual overflowing of the groundwater in the lower parts of the landscape or pipes as observed elsewhere (Lucas et al. 1996). The water sampled at the SMVB-15 point during the 1st sampling period came necessarily from recent rainfall percolating the topsoil horizons, because of the lack of perched water table, when during the 2nd and 3rd sampling the waters could come from both recent rainfalls percolating topsoil horizons and overflowing of the perched water table. Except point S3-380 and downslope point S6-80, other sampling points of the catena gave samples every sampling day. Two water pathways can thus be defined along the catena (Fig. 2). A deep, permanent water table flows more than two meters deep within the kaolin horizons. The lateral flow of its upper part corresponds to pathway n°1 and is described by the following succession of
samples: S1-510 – S2-490 – S3-380 – S4-400 – S5-380 – S6-300. A temporary, closer to the surface water table circulates in the Es and Ef horizons only after heavy rainfalls and can overflow in the micro-valleys. It corresponds to pathway n°2 and is described by the following succession of samples: S1-240 – S2-160 – S3-160.

3.2 Composition of the Percolating Waters

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

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

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

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

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

Si and Al concentrations. The waters from the upper horizons of the podzolic area (W1-20) always had very low Si and Al concentrations. The maximum values for Si and Al were 0.1 and 0.14 mg L$^{-1}$, respectively, and the average values were 0.05 and 0.03 mg L$^{-1}$, respectively. On the other hand, the waters from the Bhs horizon (point S1-240) had the highest Si and Al values observed during the three sampling periods: Si ranged from 0.29 to
0.59 mg.L\(^{-1}\) and Al ranged from 0.37 to 0.63 mg.L\(^{-1}\). At every sampling day the Si and Al values were close together (Fig. S2) and their averages over the three sampling periods were 0.48 mg.L\(^{-1}\) for both. The waters from point W2-150 had values intermediate between those of points W1-20 and S1-240. From the Bhs horizon down to the kaolin horizon, i.e. from point S1-240 to point S1-510, the Si concentrations underwent a decrease by more than half, down to 0.13 mg.L\(^{-1}\) on average, when the Al values suffered a slighter decrease, down to 0.37 mg.L\(^{-1}\) on average. Going downslope from point S1-510, the Si values progressively increased again up to values around 0.5 mg.L\(^{-1}\). The Al values continued decreasing progressively.

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

The waters from the Spring point had pH and chemical characteristics very similar to those observed for the W1-20 point, except regarding the \(E_H\) which was higher (521±15 versus 473±17 mV).

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

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

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

**Fe\(^{2+}\), Fe\(^{3+}\) concentrations and \(E_H\).** The Fe\(^{2+}\) concentrations increased when passing from point S1-240 (0.10 mg.L\(^{-1}\) on average) to point S2-160 (0.21 mg.L\(^{-1}\) on average) (except on
the 19/05/08), then decreased on point S3-160 (0.05 mg.L\(^{-1}\) on average). The Fe\(^{2+}\) concentrations on point S2-160 exhibited, however, a high variability, with a standard deviation (0.24) higher than the average value. The high Fe\(^{2+}\) concentrations were always related to lower E\(_H\) values, which reflect on the average values of E\(_H\): 501, 399 and 482 mV for points S1-240, S2-160 and S3-160, respectively. There is no, however, correlation between the bulk of Fe\(^{2+}\) and E\(_H\) values (R\(^2\)=0.23). The Fe\(^{3+}\) concentrations remained always lower than 0.08 mg.L\(^{-1}\) for both S2-160 and S3-160 points. The waters sampled at point SMVB-15 had high Fe\(^{2+}\) and Fe\(^{3+}\) concentrations (on average 1.58 and 0.79 mg.L\(^{-1}\), respectively) when compared to any other sampling point, and relatively low E\(_H\) values (372 mV on average).

3.3. DOM characterization

Microtitrations were achieved on samples collected at Spring and W2-150 points. An example of microtitration curve is given on Fig. 6. Three repetitions were made for each sample. The acid-base properties of the DOC were evaluated by fitting these results with the PROSECE software (Garnier et al. 2004a,b). This model considers a discrete distribution of acidic sites whose acidic constants pK\(_a\) and site densities L\(_T,i\) are determined by fitting the experimental curves. 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. The results are given on Table 4. The total calculated site densities were 40.2±6.1 and 27.2±3.6 meq.gC\(^{-1}\) for the Spring and the W2-150 samples, respectively.

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

4 Discussion

4.1 Evolution of the Percolating Waters along the Catena

4.1.1 Waters in the Podzolic Area

The spring water and the water circulating in the upper part of the white sands (CA-020 point) had similar characteristics: the highest DOC and the lower pH and Si values compared to all other samples and very low Al, Fe\(^{2+}\) and Fe\(^{3+}\) values (0.05, 0.02 and lower than 0.01 mg.L\(^{-1}\) on average for dissolved Si, Al and Fe, respectively). These values, as well of the values observed for other elements, are in the range of values observed by Cornu et al. (1997; 1998) in a similar podzolic area – similar soil and vegetation – situated near Manaus. Dissolved Si, Al and Fe found here can come from canopy leaching, litter mineralization and dissolution of quartz and trace minerals (Table 2). This water is thus quite aggressive with
regard to clay or iron minerals, due to acidity and to complexing capacity of the DOC which greatly enhances the weathering rates (Robert and Berthelin, 1986). When it reaches the transition between white sands and kaolin horizon, in the Bhs horizons, it dissolves kaolinite and Fe- or Al-oxides so that the concentrations of Si, Al and Fe in the percolating water increase, as observed at point S1-240. The molar values of dissolved Si and Al at point S1-240 were very close one to the other, which is in accordance with the hypothesis of a congruent dissolution of kaolinite in the Bhs horizons. The up and down movements of the water-table perched over the Bh favour the upward dispersion of solutes, which explains that concentrations at point W2-150 are intermediate between concentrations at the topsoil and concentrations within the Bh. The decrease of DOC concentration when water passes from the white sand to the Bhs is due to the DOC adsorption on kaolinite or Fe-oxides and gibbsite surfaces (Davis, 1982; Kaiser et Zech, 2000). Such adsorption was observed in Amazonian podzols everywhere a DOC-rich water-table circulating in a quite sandy material passes through a material having some clay or oxides (Chauvel et al., 1987; Bardy et al., 2008; Fritsch et al. 2009).

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

Passing from the Bhs (point S1-240) to the underlying deep kaolin (point S1-510), the water exhibited a slight pH increase, a drastic decrease of DOC, a decrease of Si and a slight decrease of Al and Fe. The DOC decrease can be explained by adsorption of humic substances on clay and Fe mineral surfaces of the Bh. The 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. Si, Al and Fe variations in percolating waters as well as the higher content of gibbsite and Fe-oxides at the upper part of the kaolin horizons can be explained by the following considerations. The DOM which migrates through the sandy horizons is carrying complexed Al and Fe (Benedetti et al., 2003; Fritsch et al., 2009). Most organo-metallic complexes adsorb on mineral surfaces in the Bh-Bhs, but do not accumulate indefinitely and most of them will eventually be mineralized, releasing Al and Fe in the soil solution. The assumption of a relatively rapid turn-over of the OM is strengthened by the young apparent 14C ages (<3000 y) measured for a NOM from a similar deep Bh in the Manaus area (Montes et al., 2011). Fe precipitates as Fe-oxides (likely goethite and lepidocrocite) and Al precipitates as kaolinite, resulting in the decrease of Si concentration. Al in excess precipitates as gibbsite, giving high gibbsite content in the horizons immediately beneath the Bhs (Fig. 3).

Going downslope in the deep kaolin horizons, the pH increase is more related to an increase of the sum of charges of major ions than to a decrease of the charges due to the DOM (Table 6). The increase of Na⁺, K⁺, Ca²⁺ and Mg²⁺ concentrations when going downslope is likely due to higher content in weatherable minerals closer to the soil surface. The pH increase could explain the precipitation of Al as gibbsite nodules (Fig. 2) and the consecutive decrease of Al concentration in the soil solution (Fig. 5).

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

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 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. The increase of the Si/Al molar ratio can be explained by precipitation of Al as gibbsite as observed downslope along the pathway n°1. In the micro-valley bottom, at point
SMVB-15, Si, Al and Fe values are exceptionally high with regard to the high rainfall climate; Si values for example may approach the quartz solubility (2.9 mg L\(^{-1}\)). This may be due to the fact that the water sampled at this point added dissolved elements brought by the overflowing groundwater and elements locally produced by the litter degradation. 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).

4.2 The Properties of the Dissolved Organic Matter

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

\[
Z_{\text{DOM}} = \frac{(10^{-6\text{pH}} - \sum z_i)}{\text{DOC}}
\]

The average DOM charge ranged from -6.2 to -6.5 meq.gC\(^{-1}\) for the water circulating in the sandy podzol horizons, whereas -11 meq.gC\(^{-1}\) for the water in the deep Bhs and ranged from -31 to -37 meq.gC\(^{-1}\) for the waters circulating in the deep Bhs and in the deep kaolinitic horizons. The DOM circulating in the kaolinitic horizons had therefore values much higher than the DOM from the white sands. As all the waters were quite acidic, most of these charges were due to carboxylic-type sites. The acid site density \(L_T\) expressed in meq.gC\(^{-1}\) was approximated by modelling for a single carboxylic-type ligand, considering various pKa from 3 to 4.5, using the following equation:

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

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

The DOM circulating in depth in the kaolinitic horizons was quite different. Considering a pKa ranging from 3 to 4.5, the calculated site densities are quite high, ranging from 31 to 67 meq.gC\(^{-1}\) (in comparison, one site per carbon would give a site density equal to 83.3 meq.gC\(^{-1}\)). This is consistent with the higher proportion of small carboxylic acids observed in the DOC-poor groundwaters: site densities of formic, oxalic, acetic, citric, succinic and lactic acids are 83.3, 83.3, 41.7, 41.7, 41.7 and 27.8 meq.gC\(^{-1}\), respectively. This
is also consistent with the low SUVA_{254} values of the DOC-poor groundwaters indicating a low proportion of humic substances.

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

4.3 Groundwater – minerals relationships

4.3.1 The Si-Al system

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

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

Measured Fe$^{2+}$ values were almost always higher than Fe$^{3+}$ values, indicating that iron in the soil system is mainly transported as 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 Fe$^{2+}$/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 Fe$^{2+}$/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 Fe$^{3+}$ and, as already observed in very oxidizing media (Kieber et al., 2005), Fe$^{2+}$. This latter process can also explain the lack of a good correlation between E$_H$ and Fe$^{2+}$. The final result is a complete bleaching of kaolin horizons and it is likely that the deeper the permanent watertable, 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 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 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
The resulting groundwater is DOM-poor (DOC around 37 mg L\(^{-1}\)) with a high acid-sites density, ranging from 31 to 67 meq gC\(^{-1}\) when considering a pKa ranging from 3 to 4.5, due to the large proportion of small carboxylic acids. Significant amounts of small carboxylic compounds have thus the ability to percolate through kaolinitic materials.

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

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

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

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

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (m)</th>
<th>Texture</th>
<th>Quartz (%)</th>
<th>Kaolinite (%)</th>
<th>Gibbsite (%)</th>
<th>Muscovite (%)</th>
<th>Other minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pit P1 - Podzol</td>
<td>O &amp; A1</td>
<td>0.0-0.8</td>
<td>Sand</td>
<td>88-95</td>
<td>2-12</td>
<td>ε</td>
<td>5</td>
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<tr>
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<td>Es</td>
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<td>Sand</td>
<td>100</td>
<td>ε</td>
<td>ε</td>
<td>0-ε</td>
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<td>Bs-Bhs</td>
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<td>6-10</td>
<td>ε</td>
<td>ε</td>
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<td>K1</td>
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<td>Silty clay loam</td>
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<td>92-96</td>
<td>8-4</td>
<td>ε</td>
<td>1</td>
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<tr>
<td>K2</td>
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<td>96-97</td>
<td>4-2</td>
<td>ε</td>
<td>1</td>
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<tr>
<td>Pit P2 - Ferralsol</td>
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<td>59-70</td>
<td>18-26</td>
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</tr>
<tr>
<td>B1</td>
<td>0.3-1.3</td>
<td>Sandy clay loam / Clay loam</td>
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<td>14-66</td>
<td>1-3</td>
<td>ε</td>
<td>A, V, Go</td>
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<td>Ef</td>
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<td>60</td>
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<td>A, Go</td>
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<td>K1</td>
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<td>Silty loam</td>
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<td>94</td>
<td>ε</td>
<td>3-4</td>
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<td>A, R, Go, H</td>
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### Table 2

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

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<tr>
<th>Sampling Point</th>
<th>Si (mg L⁻¹)</th>
<th>Al³⁺ (mg L⁻¹)</th>
<th>Fe³⁺ (mg L⁻¹)</th>
<th>Fe²⁺ (mg L⁻¹)</th>
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<td>Spring</td>
<td>avg</td>
<td>max</td>
<td>min</td>
<td>avg</td>
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<td>0.02</td>
<td>0.02</td>
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<tr>
<td>W2-150</td>
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<td>0.19</td>
<td>0.18</td>
</tr>
<tr>
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<td>0.20</td>
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<td>0.37</td>
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<td>0.57</td>
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<td>191</td>
<td>147</td>
<td>5.4</td>
<td>9.7</td>
<td>3.5</td>
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Table 3
Major ions charge, DOC and pH (average±standard deviation).

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<tr>
<th>Sampling point</th>
<th>Number of samples</th>
<th>Major ions charge</th>
<th>FeIII (&lt;em&gt;a&lt;/em&gt;) (&lt;em&gt;µ&lt;/em&gt;eq.L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Cl- (&lt;em&gt;µ&lt;/em&gt;eq.L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>NO&lt;sub&gt;2&lt;/sub&gt;- (&lt;em&gt;µ&lt;/em&gt;eq.L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>NO&lt;sub&gt;3&lt;/sub&gt;- (&lt;em&gt;µ&lt;/em&gt;eq.L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>SO&lt;sub&gt;4&lt;/sub&gt;²- (&lt;em&gt;µ&lt;/em&gt;eq.L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>pH&lt;sup&gt;b&lt;/sup&gt;</th>
<th>DOC (&lt;em&gt;mg&lt;/em&gt;.L&lt;sup&gt;-1&lt;/sup&gt;)</th>
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<td>S1-240 4</td>
<td>30.2±13.7</td>
<td>13.4±19.1</td>
<td>19.7±15.5</td>
<td>7.8±2.7</td>
<td>46.4±15.6</td>
<td>52.8±4.5</td>
<td>3.6±3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1-510 4</td>
<td>14.8±2.1</td>
<td>4.8±6.1</td>
<td>5.0±1.3</td>
<td>4.7±1.4</td>
<td>34.7±8.5</td>
<td>39.6±3.4</td>
<td>2.2±1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2-490 4</td>
<td>27.6±13.2</td>
<td>33.6±28.2</td>
<td>8.7±6.9</td>
<td>3.9±1.4</td>
<td>53.2±12.7</td>
<td>15.0±5.5</td>
<td>1.4±0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S4-400 4</td>
<td>36.9±10.4</td>
<td>31.4±19.4</td>
<td>43.2±6.6</td>
<td>9.9±1.4</td>
<td>73.9±12.4</td>
<td>3.3±2.3</td>
<td>1.4±0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S6-300 4</td>
<td>18.1±2.7</td>
<td>16.4±10.0</td>
<td>30.4±1.7</td>
<td>4.9±0.5</td>
<td>61.6±8.4</td>
<td>9.0±5.2</td>
<td>26.4±14.3</td>
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<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated for the sum of Al or FeIII species, respectively.
<sup>b</sup> Values after correction, see text.

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

<table>
<thead>
<tr>
<th>Spring</th>
<th>pKa</th>
<th>&lt;em&gt;L&lt;/em&gt;&lt;sub&gt;T&lt;/sub&gt; (meq.gC&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>&lt;em&gt;L&lt;/em&gt;&lt;sub&gt;T&lt;/sub&gt; (meq.gC&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.5±0.6</td>
<td>17.2±0.4</td>
<td>4.1±0.3</td>
</tr>
<tr>
<td>&lt;em&gt;W&lt;/em&gt;2-150</td>
<td>4.7±0.4</td>
<td>9.5±0.4</td>
<td>5.2±0.1</td>
</tr>
<tr>
<td>pKa</td>
<td>6.9±2.6</td>
<td>8.1±2.3</td>
<td>8.7±0.1</td>
</tr>
<tr>
<td>&lt;em&gt;L&lt;/em&gt;&lt;sub&gt;T&lt;/sub&gt; (meq.gC&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>9.3±1.5</td>
<td>5.4±5.6</td>
<td>10.6±0.1</td>
</tr>
</tbody>
</table>

Table 5
DOC characterization.

<table>
<thead>
<tr>
<th>Spring</th>
<th>W2-150</th>
<th>S1-510</th>
<th>S3-380</th>
<th>S4-400</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg.C.L&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>35.6</td>
<td>38.3</td>
<td>1.3</td>
<td>1.7</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>0.05</td>
<td>0.05</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.28</td>
<td>0.17</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>Formic acid</td>
<td>1.18</td>
<td>1.10</td>
<td>0.44</td>
<td>0.62</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>0.64</td>
<td>0.56</td>
<td>0.11</td>
<td>n.a.</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>0.26</td>
<td>0.19</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.72</td>
<td>n.a.</td>
<td>0.07</td>
<td>0.12</td>
</tr>
</tbody>
</table>

SUVA<sub>254</sub> index (L mg<sup>-1</sup>.m<sup>-1</sup>)

<table>
<thead>
<tr>
<th></th>
<th>Spring</th>
<th>W2-150</th>
<th>S1-510</th>
<th>S3-380</th>
<th>S4-400</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.8</td>
<td>4.9</td>
<td>1.5</td>
<td>1.3</td>
<td>2.1</td>
<td></td>
</tr>
</tbody>
</table>
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 $\sum z_i$ (μeq L⁻¹) | pH | DOC (mg L⁻¹) | Charge due to DOM $Z_{\text{DOM}}$ (meq gC⁻¹) | Acid-site density $L_T$ (meq gC⁻¹) | pKa
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>4</td>
<td>134±28</td>
<td>4.0±0.08</td>
<td>37.4±2.9</td>
<td>-6.3±1.8</td>
<td>7±2</td>
<td>8±3</td>
</tr>
<tr>
<td>W1-20</td>
<td>1</td>
<td>142</td>
<td>4.1</td>
<td>34.4</td>
<td>-6.5</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>W2-150</td>
<td>1</td>
<td>184</td>
<td>4.2</td>
<td>40.2</td>
<td>-6.2</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>S1-240</td>
<td>4</td>
<td>59±36</td>
<td>4.0±0.09</td>
<td>15.2±0.7</td>
<td>-11±4</td>
<td>12±4</td>
<td>14±6</td>
</tr>
<tr>
<td>S1-510</td>
<td>4</td>
<td>33±3</td>
<td>4.6±0.08</td>
<td>2.3±0.4</td>
<td>-31±4</td>
<td>31±4</td>
<td>33±5</td>
</tr>
<tr>
<td>S2-400</td>
<td>4</td>
<td>98±39</td>
<td>4.6±0.13</td>
<td>4.0±0.7</td>
<td>-37±13</td>
<td>38±14</td>
<td>40±15</td>
</tr>
<tr>
<td>S4-400</td>
<td>4</td>
<td>109±29</td>
<td>4.8±0.07</td>
<td>4.9±2.0</td>
<td>-32±8</td>
<td>33±8</td>
<td>34±9</td>
</tr>
<tr>
<td>S6-300</td>
<td>4</td>
<td>135±27</td>
<td>5.1±0.17</td>
<td>5.4±0.9</td>
<td>-32±5</td>
<td>32±5</td>
<td>33±5</td>
</tr>
</tbody>
</table>
Figure Captions

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

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

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

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

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

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

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

Fig. 8. Position of the groundwaters in the iron Pourbaix diagram drawn for low Fe-concentrated waters (<10⁶ M). Symbols are the same that in Fig. 7.
Fig. 1
Fig. 2

- Tension-free lysimeters
- Observation pit
- Observation borehole
- Centimetre Al-nodules
- Fe-red spots
- Water-table (02-2006)
- Water pathway n°1
- Water pathway n°2

Situation of flat-bottomed microvalley

Water-pathway n°1
Water-pathway n°2

Observation borehole
Observation pit

Centimetre Al-nodules
Fe-red spots

Tension-free lysimeters
Fig. 5
Fig. 7
Fig. 8
Fig. S1
Fig. S3