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Hydrology and Earth System Sciences
Discussions

Interactive comment on "A conceptual model of organochlorine fate from a combined analysis of spatial and mid/long-term trends of surface and ground water contamination in tropical areas (FWI)" *by* Philippe Cattan et al.

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The response to the Referees is structured as follows: (1) comments from Referees, (2) author's response, (3) author's changes in manuscript in quotation marks

RC: First, using a transformation product (TPs) 5bCLD as a tracer of degradation extent and associated persistence is a valuable idea, but the degradation of the TP itself is never discussed. Similarly the model seems to consider as a perfect tracer 5bCLD, i.e. without degradation. This main assumption can significantly alter the assessment of

persistence done and this point is never discussed.

Response: We thank the reviewer for raising this important point. Degradation of the TP can be discussed adding a new calculation step in the model accounting for 5bCLD degradation. Eq (4) can be modified as follow: 5bCLD(t+1)=5bCLD(t)-5bCLD(t)×T_5bCLD-5bCLD(t)×C_5bdegrad+CLD(t)×C_degrad

Then, we test 3 values of C5bdegrad in a wide range surrounding the one of CLD (Cdegrad): C5bdegrad = 0, C5bdegrad= Cdegrad, C5bdegrad =10 x Cdegrad. Notice these values are highly speculative since there is no experimental value of C5bdegrad and that Cdegrad is the result of optimization process in our paper. Results are reported in the Figure "test" which shows the evolution of the 5bCLD lixiviation and of the ratio for the 3 tested values. The figure 1 shows similar dynamics of ratio evolution or of lixiviation evolution. The difference between the simulations remains weak, notably because the tested values are about 10 and 100 times lower than lixiviation rate (T5bCLD equals 0.1242 here while Cdegrad equals 0.0014)). Consequently, introducing a degradation coefficient does not alter here our first conclusions. Running optimization process with this new term we find T5bCLD = 0.1242 ; Cdegrad = 0.0014 ; C5bdegrad = 0.0010 Our assumptions are consistent with estimations of Dolfing et al. (2012) showing that the solubility is higher for transformation products of CLD.

Change in manuscript: So, to account for the reviewer comment, we propose 1) To complete the current model adding a degradation term for 5bCLD. 2) Given the lack of knowledge and the uncertainty about degradation rate, we propose to add the following comment in the text. "The values of degradation remain uncertain since we have no reference for comparison. In our case, the optimization process yield a far lower degradation rate compare to the lixiviation rate. Consequently, the model will be less sensitive to changes in degradation rate than in lixiviation rate that determine the ratio in water. Additionally, there is an uncertainty comparing degradation rates for 5bCLD and CLD. Optimization process yield degradation rates for 5bCLD and CLD of the same order of magnitude. Additional simulations show that setting C5bdegrad ten times higher than Cdegrad instead of zero reduce the ratio 5bCLD / CLD by 10 percent without changing the dynamic of ratio and of 5bCLD lixiviation (not shown). Knowing that transformation products of chlordecone are likely to be more mobile in the environment than their parent compound (Dolfing et al. 2012), we assume our model give sufficient bases for interpreting our results".

RC: Do you have access to CLD/5bCLD ratio in soil to have an idea of the initial signature over time to decipher soil degradation process to those associated to surface and groundwater flowpaths?

Response: Reference of ratio in soils are in the paper of Clostre et al (2015).The median value of 0.011 in nitisols and 0.017 in andosols were used in our paper to constrain our model (see section 3.4). This does not help to speculate about ratios in water since they depend on lixiviation rates of CLD and 5bCLD. In our article, data from Cabidoche et al (2009) were used to assess CLD lixiviation rate (TCLD) for andosols and nitisols. The 5bCLD lixiviation rate (T5bCLD) stemming from the optimization process appears higher than TCLD. This result is consistent with Devault et al (2016) who conclude for a higher mobility for 5bCLD than for CLD. Whatever, it is unlikely that CLD was leached while 5bCLD accumulated in soil profile due to the highest mobility of transformation products (Dolfing et al., 2012).

Change in manuscript: We propose to add the following sentence section 3.4 L406: "... continuously without a plateau. This result is consistent with Devault et al (2016) who conclude for a higher mobility for 5bCLD than for CLD, and more generally with results of Dolfing et al. (2012) who shows that transformation products have a highest mobility than CLD."

RC: Second, residence time is used to explain the spatial variability of the ratio compounds/TPs. To support the discussion, the authors should provide existing reported information/simulation of these residence times: - to discuss spatially contrasted compounds/TPs ratio delivery by soil to ground water

Response: please see our response to the comment "19)" of the First referee

RC- to address the question of degradation of the TP itself (especially for long residence time)

Response: longer residence time does not mean that the TP degradation is higher. In fact degradation occurs in the soil, whereas residence time in the aquifer refers to transfers in depth (below soil cover) where the degradation (as well as the retention) is considered as null. Groundwater residence time is generally superior to several years (up to several decades – see Gourcy et al., 2009 for instance) that is widely superior to the residence time of the infiltrated water in the soil cover (several days or months).

RC: Third, if the sampling effort, statistical analyses and conceptual development provided a coherent approach for groundwater (slow flowpath), I have many questions on the surface water component.

Response: Global comment about flowpath. First, volcanic soils in Caribbean islands have a high infiltration capacity (saturated hydraulic conductivity superior to 60 mm/h (Cattan et al., 2006; Crabit et al, 2016). Then, despite high rainfall intensities and amounts, most of rainfall infiltrates (about 95% at the plot scale according to Cabidoche et al, (2009); more than 90% at the watershed scale according to Charlier et al., 2008; 2011) generating either subsurface or deep flows. So leaching is the main process in pesticide transport.

Second, usually, one reason to study separately pesticide transport by surface runoff is that the pesticide concentration in runoff water may vary highly according to time of pesticide application at the plot scale (Saison et al., 2008) as well as at the watershed scale (Charlier et al., 2009). It is not the case for CLD which have been applied long time ago: boundary conditions relative to pesticide concentration in soil are almost steady. Surely, during application period, agricultural practices may have affect 5bCLD/CLD ratio day by day. However our model aims to simulate the ratio evolution over a long time period. A second reason to consider separately runoff and infiltration water is that pesticide concentration in surface water at the plot scale may differ from infiltrated water. There are few references about this point for CLD. Cabidoche et al (2009) notice that CLD concentration in surface runoff was more than 3-fold lower than in drainage, while runoff volume was 10 times lower than drainage volume. They consequently neglected loads in runoff that represented less than 1/30 of those in drainage at the plot scale.

Given the previous consideration, we then chose to focus here on lixiviation process, which affect the ratio dynamic on the long term. The reviewer ask the question of the effect of event-driven process (storm event, surface runoff, erosion, application practices) on long term trends and how they can modify CLD concentration in water and the ratio. It is a difficult issue that would require getting spatial distribution of stormy event, and their contribution to river pollution. This lack of knowledge probably leads to minor CLD exportation. Indeed, most of the time (even in rainy regions), surface flow in the river is driven by baseflow from aquifer's drainage, originated from water infiltration. Knowing that groundwater concentrations are widely higher than in rivers, concentrations during storm events would led to generate diluted concentrations in surface waters.

We propose different changes relatively to the reviewer comments. We equally propose to add a §"main assumption about CLD transfer" in discussion section

Change in the manuscript: L417 addition of the §"4.1 main assumption about CLD transfer. In our study we focused on long term trend of CLD and 5bCLD concentration in water and their ratio. We considered that the main process that determined pollutant concentrations in water was relative to the CLD desorption by water that infiltrates into the soil. We assumed this hypothesis for different reasons. First, water mainly infiltrates. In fact given the high soil infiltration rate (saturated hydraulic conductivity superior to 60 mm/h (Cattan et al. 2006; Crabit et al, 2016), most of rainfall infiltrates (about 95% at the plot scale according to Cabidoche et al, (2009); more than 90% at the watershed scale according to Charlier et al., 2008;2011) generating

either subsurface or deep flows. Consequently, transportation by surface runoff is low. Cabidoche et al (2009) notice that CLD concentration in surface runoff was more than 3-fold lower than in drainage, while runoff volume was 10 times lower than drainage volume. They consequently neglected loads in surface runoff that represented less than 1/30 of those in drainage at the plot scale Second soils have little erodibility: Cabidoche et al (2009) notice that "All the soil types in FWI are acidic, which prevents clay dispersion and sheet erosion. Hydric erosion appears to be due only to bad soil management practices, which concentrate runoff that then forms streams that are able to carry aggregates". So erosion from cultivated soils is probably not a major way of CLD transportation. Moreover, given the torrential type flow in rivers in FWI, the most likely future of eroded soil, is to sediment in the sea, with then a weak impact on river pollution. Finally, neglecting transport via surface runoff on plots and hillslopes, we probably underestimated pollutant exportation. But we expected that it should not have a great impact on the long-term dynamics of concentrations and ratio in rivers, which is one of the main topic of our paper".

RC: The representativeness of the sampling (low frequency mainly during based-flow, if I well understood the database characteristics) is not discussed taking into account percentage of Chlordecon exported during storm event associated to tropical climat.

Response: We propose to add the following sentence:

Change in manuscript: L438 "However, since sampling mainly occurred outside storm event periods, calculation with these data will lead to minor the estimate of CLD exportations."

RC: With a large Koc, the question of Chlordecon released from soil to river by erosion during runoff event is never discussed. How these pulses can contribute to spatial and temporal patterns of chlordecon in surface water?

Response: Some studies are underway on the subject. At the moment, Cabidoche et al (2009) notice that "All the soil types in FWI are acidic, which prevents clay dispersion and sheet erosion. Hydric erosion appears to be due only to bad soil management practices, which concentrate runoff that then forms streams that are able to carry aggregates". So erosion from cultivated soils is probably not a major way of CLD transportation. Second, it is difficult to speculate on the future of eroded contaminated soil and their impact on water contamination. Given the torrential type flow in rivers in FWI, the most likely future of eroded soil, is to sediment in the sea, with then weak impact on river pollution.

Change in manuscript: sea the new §4.1 above

RC: For surface water, it could be relevant to know if the CLD concentrations correspond only to the dissolved phase or if it is a "total" concentration.

Response: the CLD concentration is a total concentration

RC: Information on the filtration and purification steps are not provided in the M&M section.

Response: there was no purification nor filtration since the suspended matter content of samples was low (less than 250 mg L-1). Analyses were performed on raw water. We propose to add the following sentences section 2.2.2

Change in manuscript: L153 "Analyses were carried out on raw sampling water. Thus, the CLD and 5bCLD water contents correspond to the dissolved and particulate fractions. Note that the particulate fraction of the samples was low (< 250 mg L-1) due to sampling conducted mainly during periods of low flow."

RC: Can contaminated sediments in river potentially be remobilized by event and alter trend assessment in surface water?

Response: see our previous response

RC: In the conceptual model, the surface runoff and the surface water to groundwater seem not considered. The choice targeting mainly leaching and not the other off-site

transport is never discussed. The authors mentioned "hope for pollution mitigation" based on statistical model, but I wonder how fast flow in river can modify this assessment.

Response: see our previous response

Specific remarks: RC: L324 GW, as well as in SW fed by it. And vice et versa ?

Response: whereas infiltration from ditches towards aquifers is a likely process in such regions due to the high permeability of the shallow formations (Charlier, 2007), and even if some river infiltrations may contribute also to groundwater recharge (Charlier et al., 2011), we consider that the infiltration of surface water is a minor process of groundwater contamination at a global scale. In fact, in cultivated areas, surface water is generally widely less contaminated in CLD than groundwaters.

RC: L323 The age of the main geological units was used as an indicator of hydrogeology and notably residence time in the aquifers. Could you provide evidence ? Residence time assessment form others studies ?

Response: please see our response to the comment "19)" of the first referee

RC: L57 and L60, 1993 or 1992, I guess banned in 1992 but used until 1993. Please explain.

Response: Yes there was exemption until 1993. We propose

Changes in the manuscript: L60 "…ban in 1992 (there was exemption in FWI until 1993)"

RC: L121 "they are intergrades" ?

Response: Intergrades are defined by Colmet-Daage relative to the climatic sequence ferralsols -> vertisols for soils that are "intermediate". Since Colmet-Daage classification is specific, we propose to suppress the last part of the sentence which is unclear "and they are intergrades resulting from the alteration of ferralitic soils)"

RC: L134 unweathered formations, to several decades for old weathered formations (provide range for "Old")

Change in manuscript: "between a few years for recent unweathered formations (<0.5-1My), to several decades for old weathered formations (> 1My)"

RC: L139 routine basis with CLD. For (double space before For)

Response: OK

RC: L150 5bCLD is the main CLD co- and alteration product of CLD: what do you mean by alteration product ? Transformation / degradation product ? Please clarify ?

Response: In fact, 5bCLD can be considered both as a co-product and as a degradation product. Consulting biochemists, the word "alteration" seemed more convenient. We propose the following change:

Change in manuscript: "5bCLD is the main alteration product of CLD (the term "alteration" here means that 5b is both a co-product and a degradation product)for which . . ."

RC: L151 "Reference standards for CLD and 5bCLD were purchased" : provide purity degree

Change in manuscript: "with a purity degree of 96.7%."

RC: L149 Between sampling and analysis, no information is provided on the filtration (raw water/filtrated water?) , purification ?, please add

Response: OK analyses were performed on raw water

RC: L181 was not detected (i.e. 0.001 for LDA26 or 0.003 μg L-1 for BRGM), and an intermediate value of 0.006 μg.L-1 : why is different of value provided in L177 0.003 μg.L-1 ? Please clarify

Response: 0.003 line 177 refers to the limit of detection; 0.006 is an intermediate

value between the limit of detection 0.003 and the limit of quantification 0.01 when the compound was detected but not measurable. We propose to change "measurable" by "quantifiable"

RC: L184 double space the 5bCLD

Response: OK

RC: L183 Factors. Not clear for me, how heterogeneity of upstream catchment for SW or drainage area for GW were integrated in metrics ?

Response: factors refer to global descriptors that don't integrate such spatial heterogeneity at a local scale. Apart soil (as it is explained in the text), each site is associated with the factor value at the sampling point.

RC L204. For GW, double space

Response: OK

RC Fig. 1. I suggest to modify this figure to add sampling point distribution (the different zoom levels can be significantly reduced)

Response: sampling distribution are presented in figure 3

RC: L248 Kendall (MK) test. We calculated Sen trends, Sen trend ? Not defined, Instead to use Sen trend in the text, I suggest to explain the information underlined by this metric (to improve understanding for the reader)

Response: OK, please see our response to the first Referee. We propose the following change

Change in manuscript: L248 "We calculated Sen trends(namely Sen's slope estimator, (Gilbert, 1987)) for each variable (CLD, 5bCLD and ratio) in order to compare dynamics for the two compounds. The Sen trends of a set of two-dimensional points (xi,yi) is the median m of the slopes (yj $-$ yi)/(xj $-$ xi) determined by all pairs of sample points. The

Sen's slope estimator is more robust than the least-squares estimator because it is much less sensitive to outliers"

RC: The section 3.2.1. looks like a figure caption (modify and interpret directly in this section)

Response: Section 3.2.1 aims to present Figure 3 and the distribution of pollution

RC: L300 "areas since 1970, i.e. during CLD application. Surprisingly, SW and GW contamination occurred outside these banana areas" Explanation ? other dissipation Processes ? Are the contaminated areas are downstream of banana areas ?

Response: we suggest CLD misuse L304

RC: Fig3. Legend can not be read (too small).

Response: We propose a new Figure with larger legend

RC: Fig4. two small, I suggest to merge some of them or provide in SI

Response: there are two comments for Figure 4. Perhaps this comment is relative to Fig3 ? or Fig6. We propose a new Figure 6

RC: L308 contamination level. For example, the CLD content of hydrographic subsector 1 (see Figure 3 left for locations) was different from hydrographic subsector 2 even though the points in each zone had the same contamination level. It is very descriptive, please provide explanaton

Response: We propose to rephrase L308-309

Change in manuscript: "For example, although sample points of subsector 1 and 2 are very close, they do not have the same contamination level. In contrast, all sample points of subsector 1 have the same contamination level (same for subsector 2). This suggest that the hydrographic sector, i.e. the water flows within a same hydrological unit, mainly determined contamination level of sample points rather than the geograph-

ical closeness of these points."

RC: L 320 "This statistically confirmed"/ Missing word ?

Response: We propose to rephrase: "This is a statistical confirmation of the result mapped in Figure 3. . ."

RC: Figure 4. provide full name under the figure Ferr_And, Nit_And. . .

Response: OK

RC: L375 : "duration of pollution": persistance of pollution ?

Change in manuscript: "persistence of pollution"

RC: Fig 7. Legend is hidding some point: modify. I suggest to redesign the figure 7 to improve understanding of key message for the reader (add sectors/types and assessment indicator) ???

Response: We propose to keep the legend of the figures in the middle and to suppress the legend of figures on the left and right sides where points are hidden. Sen trends for others factors (hydrographic sectors and historical banana area) are not represented due to the absence of relationships.

Change in manuscript: redesign of figure 7 whith and a new caption: "Sen trends of CLD vs. mean log content of CLD, 5bCLD, and 5bCLD / CLD ratio (from left to right – natural logarithm) in SW, according to a) soil, and b) geology (for soil and geology, see legend in the middle figure).

RC Fig 8. time unit ? Years. . . As discussed in the main comments, all the model predictions seem to be dependant of persistence of the 5bCLD, how the results could be altered by considering TPs degradation.

Response: see response above

RC: L437 0.1 μg L-1 437 during baseflow periods (flood flow periods being rarely sampled) given a current concentration of 0.5 μg L-1 438 on average. I don't understand your assumption?

Response: baseflow periods refers to periods without flood flows (or storm flows). Please see also our response to your comment "34)"

RC: L499 "catchment scale", you used watershed during all the manuscript why changed now? "The residence time - estimated by the water apparent age: not discussed or characterized before?

Response: catchment is replaced by watershed. Regarding the residence time, it was discussed in L452-458 of the submitted version

RC: L388 "they should lie": sentence ?

Response: the ratios should lie

Additional references

Cattan, P., Y.-M. Cabidoche, J.-G. Lacas, and M. Voltz. 2006. Effects of tillage and mulching on runoff under banana (Musa spp.) on a tropical Andosol. Soil Tillage Res. 86:38–51.

Charlier, J.-B. 2007. Fonctionnement et modélisation hydrologique d'un petit bassin versant cultivé en milieu volcanique tropical. Ph.D. diss. Université des Sciences et Techniques du Languedoc, Montpellier II.

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Saison, C., P. Cattan, X. Louchart, and M. Voltz. 2008. Eff ect of spatial heterogeneities of water fl uxes and application pattern on cadusafos fate on banana cultivated andosols. J. Agric. Food Chem. 56:11947–11955.

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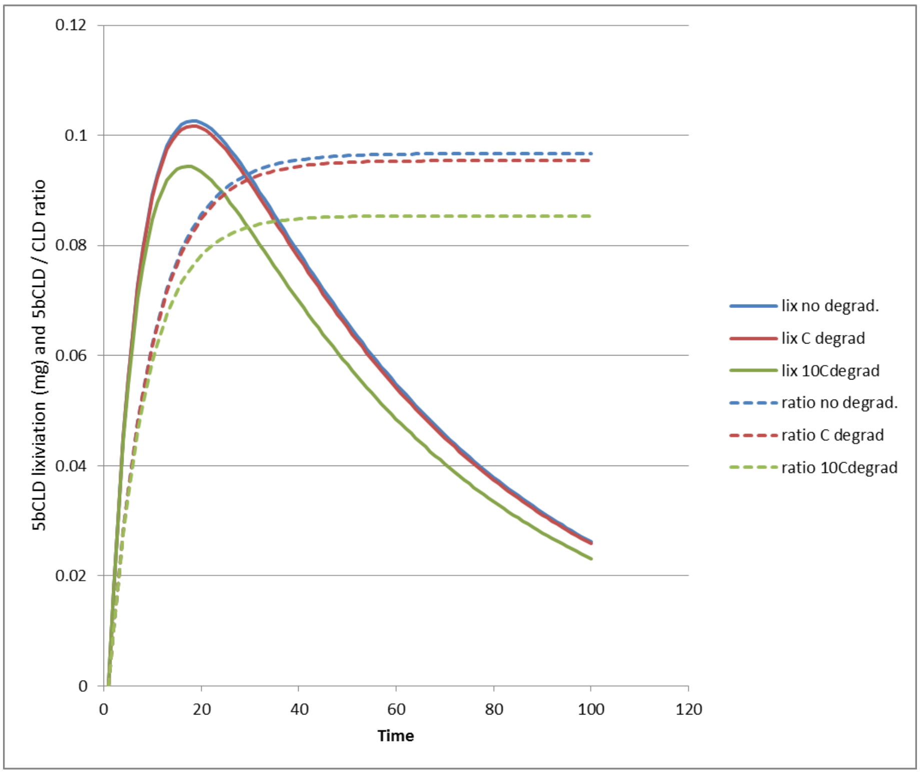

Fig. 1. test

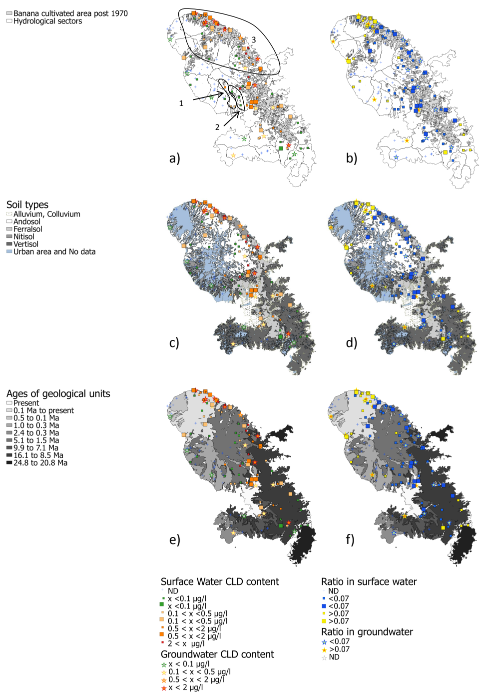

Fig. 2. Distribution of water CLD content (a, c, e) and 5bCLD / CLD ratio (b, d, f) for SW (square) and GW (star), according to banana cultivated areas and hydrological sectors (a and b), soils (c and d) adap

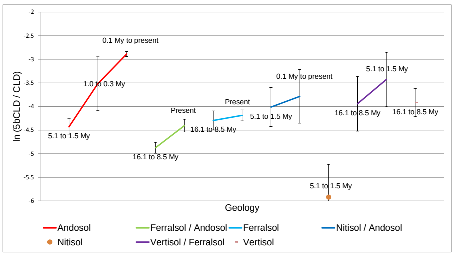

Fig. 3. Mean 5bCLD / CLD ratio (natural logarithm) according to soil types and to the age of the geological formations. Ferr_And, Nit_And and Vert_Ferr account for watersheds with two main types of soil, name

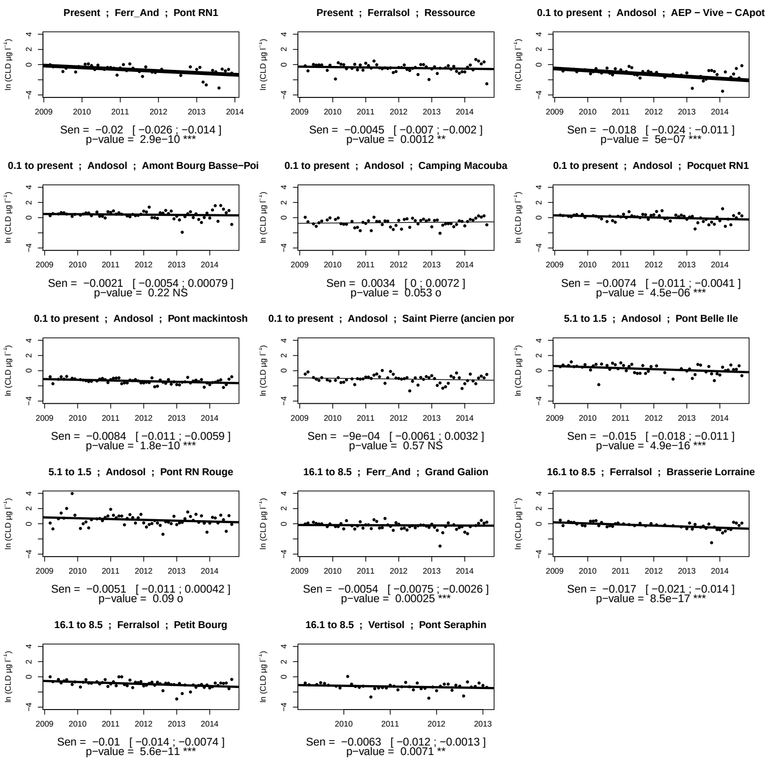

Fig. 4. CLD (natural logarithm) trends in SW according to geology and soil type. Sen trend and confidence interval; p value of the Modified Mann-Kendall test for serially correlated data using the Yue and Wan

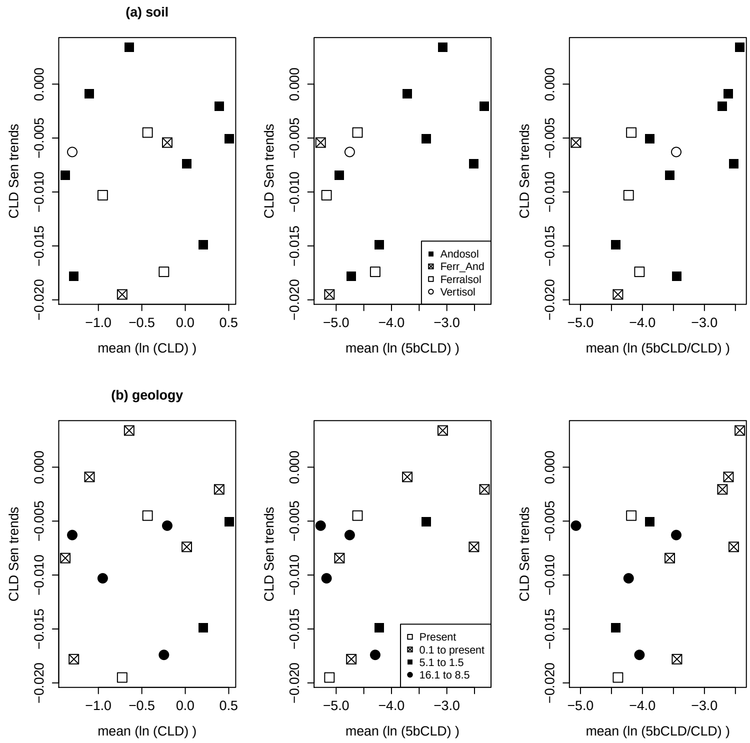

Fig. 5. Sen trends of CLD vs. mean log content of CLD, 5bCLD, and 5bCLD / CLD ratio (from left to right – natural logarithm) in SW, according to a) soil, and b) geology (for soil and geology, see legend in th