

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.

Philippe Cattan et al.

philippe.cattan@cirad.fr

Received and published: 26 October 2018

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

General comments:

1) The word "residence time" is somewhat vague. Please specify at first mention what is exactly meant (e.g. mean transit time).

C1

Response: the groundwater residence time refers to the water age in aquifers defined as the mean transit time by Maloszewski and Zuber (1992). It would be addressed in the revised version of the manuscript.

Change in manuscript: L70 "Moreover, at depth, contrasting residence times of water (the water age in aquifers defined as the mean transit time (Małoszewski and Zuber, 1982)) in aquifers of several years to several decades partly account for the variability in GW contamination by CLD (Gourcy et al., 2009)"

2) You mention in I. 432 that the 5bCLD/CLD ratio in the commercial product Curlone was 0.0011. How was the ratio in the product Kepone that was applied before? Was the 5bCLD/CLD ratio in the commercial products constant over time, or did it vary between batches of the same product?

Response: according to Devault et al. (2016), Kepone and Curlone products had very similar ratio characterized by values of 0.00077. In our text, we specified a value form Clostre et al (2015). We propose to change to Devault et al. (2016) for consistency. Notice that Devault et al. also compared three different batches of Curlone without significant difference. Equally, we modified paragraph 3.1 according to your comment $N^{\circ}18$

Change in manuscript: L430 "This was hypothesized by observing the distribution of 5bCLD / CLD ratios in water (median of 0.03; 1st centile of 0.006) with a far higher median and first centile value than in the commercial products Kepone[®] and Curlone[®] used in FWI (mean ratio of 0.00077 \pm 0.00027(Devault et al., 2016)).

3) Can your findings / model be extrapolated to other CLD-contaminated areas in the Antilles, notably the island of Guadeloupe?

Response: indeed, our conceptual model could be generalized to Guadeloupe archipelago, where chlordecone was also applied intensively in banana plantations.

Change in manuscript : L441 end of §"Our results in Martinique island could indeed

be extrapolated to other CLD-contaminated areas as in Guadeloupe archipelago (FWI) where CLD was also intensively applied in banana plantations."

Specific comments: Abstract: 4) p. 1, l. 28: "old geology": I know what you mean, but maybe "old geological substrates" or "old geological formations" would be more appropriate?

Response: we agree with comment and "old geological formations" is indeed more appropriate in the abstract. In the revised version,

Change in manuscript : L28 and L373

5) p. 1, I.29: "theoretical leaching model": maybe "conceptual leaching model" (as in the manuscript title)

Responses: We agree. Change OK

Introduction: 6) p. 2, l. 64-65: "acute" and "environmental" are not opposites; better use "chronic" instead of "environmental" (exposure via the environment can be acute or chronic)

Response: We agree. Change OK

7) p. 2, l. 69: "partitioning coefficient (Koc) between the sorbed part on soil organic matter": not comprehensible ! needs to be rephrased

Response: OK. We propose to rephrase as follows, just giving the name of the coefficient: "soil organic carbon-water partitioning coefficient (Koc)"

8) p. 2, I. 71: "contrasting residence times": What residence times: of water or of CLD?

Responses: it refers to residence time of water and it will be addressed in the revised version.

Change in manuscript L70 See our response to comme 1) where we propose to add the following sentence: "...constrating residence times (the water age in aquifers defined

C3

as the mean transit time (Małoszewski and Zuber, 1982)) in aquifers of..."

Materials and Methods: 9) p. 3, l. 111-112: "ferralitic soils (latosols) ! ferralsols": What is the difference between the two? The WRB system contains the reference soil groups ferralsols and plinthosols, but not "ferralitic soil (latosols)".

Response: It is a mistake. The climate sequence described in Comet-Daage et al, 1965 is latosols -> ferrisols -> vertisols. A correspondence with the WRB system is given by Delvaux and Brahy (2014) and is ferralsol -> nitisol -> vertisol. We corrected.

Change in manuscript : L112-112

10) p. 6, l. 213: "measurable": maybe more precisely quantifiable", since it refers to the LOQ

Response: We agree. Change OK

11) p. 6, l. 215: "data item" (or data point): How is this defined? Unique combination of water sample and compound?

Response: OK. We propose to specify in the text "data item (i.e. water samples analyzed for CLD and 5bCLD)"

12) p. 6, l. 230: eq. 1: explain the indices (i, j, k, l, m, t)

Response: There is a mistake in the text. We corrected and specified in the text:

Change in manuscript: L 233 end of §". Indices i, j, t, k, I represent factors respectively for factors soil x geology, hydrological sector, date, sampling point, sample replication"

13) p. 6, l. 234: "totally correlated": express more precisely

Response: because of a limited number of sites for groundwaters, there is not a so high spatial variability of geology and soil as observed for surface water data set. Thus, for groundwater data set (model 2), geology and soil are correlated: Andosol on recent geological formations, and ferralsols on old geological formations. To get clearer, we

modified the sentence as follows:

Change in manuscript: L234 "Soil and geological factors were closely linked for the GW data set (andosols were always associated with recent geological formations and ferralsols with old geological formations)..."

14) p. 6, l. 241: "dispersion indices": How can this quantity be interpreted? and 15) p. 6, l. 242: "confidence coefficient": What is this?

Response: dispersion indices can be interpreted like standard deviation. From the log values ln(x), we determined a confidence interval [lninf, lnsup] (with lninf = ln(x)-sd, lnsup = ln(x)+sd, sd the standard deviation of log value). That is real values are included in the interval [exp(lninf), exp(lnsup)]. Because exp(sd) is not convenient, we defined a new dispersion index: [exp(lnsup)-exp-ln(inf)]/2, i.e. "half the difference between the limits of the confidence interval".

Change in manuscript: In fact, since we no more used these dispersion indices in the current version of the article, we propose to suppress L241 and 242.

16) p. 6, l. 248: "Sen trends": What are Sen trends, and what do they mean statistically? (Explain in 1 or 2 sentences.) Response: OK. We propose the following change

Change in manuscript: L248 "We calculated Sen trends (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"

17) p. 8, I. 258-262: What are the dimension and unit of the lixiviation rates TCLD and T5bCLD? This does not become entirely clear from eq.6 because of the various unit conversion factors. I end up with the unit 1/year. Responses: Tcld and T5bcld are

C5

mass ratio. We propose to add a comment for that in the text:

Change in manuscript: L258 "TCLD and T5bCLD are the rates of lixiviation for CLD and 5bCLD (i.e. the ratio of lixiviated mass of CLD or 5bCLD to their respective mass in soil)..."

Additionally we propose to modify Eq. (6) for consistency with regard to the dimensions Eq. (6): $T_CLD = (R \times S)/(Koc \times (C/1000) \times D \times (d \times S))$ where Koc (L kg-1) is the partitioning coefficient between the sorbed part on soil organic matter and the dissolved part in water, D (kg dm-3) the bulk density, C (g kg-1) the soil carbon content, and R (dm) the annual amount of rainfall, S the soil surface (dm²) et d the soil depth (dm).

Results: 18) p. 8, I. 279-281: It should be mentioned here how high the ratio 5bCLD/CLD was in the commercial products that were applied, and whether it was constant over time.

Response: We propose to add the following text at the end of the paragraph:

Change in manuscript: L281 end of §"According to Devault et al. (2016), these differences cannot stem from the use of different commercial products or different batches of a same product. Indeed, these authors found no significant statistical difference between the ratio of the commercial products Kepone[®] and Curlone[®] used in FWI, no more than between samples from different batches of Curlone[®]. They found a mean ratio in commercial products of 0.00077 \pm 0.00027, i.e. ten times lower than our observation in river."

19) p. 9, I. 324-325: "shorter residence times were observed for more recent formations": (Are you referring to GW only or also to SW?) This is interesting. I would rather have expected the opposite. Can you briefly explain why hydraulic residence times (mean transit times?) are shorter in the younger geological formations of Martinique than in the older ones?

Response: We refer to groundwaters (knowing that groundwaters are the main contrib-

utor of contamination of surface waters). We propose to add the following text in the 2.1 Section:

Change in manuscript: L134 after "old weathered formations". "Knowing that weathering of geological formations increases with their age, it is the main cause of a global decrease of the aquifer permeability, notably in volcanic regions (Lachassagne et al., 2014). Indeed, clayey alteration products by weathering constrain soils physical and hydrodynamic properties by reducing the porosity and consequently the permeability (Adelinet et al., 2008)."

Response: Thus, as we observe higher 5b/CLD ratio on younger geological formations (i.e. unweathered formations), we hypothesis that this was related to a shorter residence time. We propose to modify the sentence as follows: L324 Change in manuscript: "Thereby, shorter residence times were observed for aquifers located in more recent and unweathered geological formations"

20) p. 10, l. 344: "water CLD contents below the detection limit appeared less frequently": meaning not entirely clear ! rephrase

Response: We propose the following text:

Change in manuscript: L343 "For the two sites showing a decrease in water CLD content, the number of samples with 5bCLD contents below the detection limit decrease over time, and equaled zero in the case of the Source Morne Figue site after 2011"

21) p. 10, l. 384: unit for bulk density is missing

Response: We corrected (kg dm-3)

22) p. 13, l. 457: "unweathered formations favour rapid transfers"; Why is that? (cf. comment on I. 324-325)

Response: please see our response to comment "19)"

23) p. 13, p. 468: "we cannot assess it": Assess what?

C7

Response: the effect of soil on degradation process. We modified the text accordingly.

Conclusions: 24) p. 13, 507-508: "This led to implications regarding where and how to act to reduce impacts": Can you elaborate on this further? Is there really anything that can be done except waiting for CLD to degrade and leach from the system?

Response: We propose some examples:

Change in manuscript: L508 "(e.g. choice of crops according to pollution levels since some plants are less sensitive to contamination than others (Clostre et al., 2015), constraints on water use like irrigation, choice of priority areas to test decontamination processes, setting up compensation plans according to the risk...)"

Figures: 25) Figure 3: The figure is neat, but too small for reading the legend or for identifying much on the map. ! upscale

Response: We propose a new Figure

Change in manuscript: change of Figure 3 and relative caption: "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) adapted from Colmet Daage (1965), and geology (e and f) adapted from Germa et al. (2011). Large squares are relative to sample points having more than ten sampling dates and small squares having fewer than ten sampling dates

26) Figure 4: y-axis: The numbers are difficult to interpret. Try lg or non-logarithmised numbers instead of ln.

Response: As specified in material and methods, data were log transformed for all analysis. For Figure 4 we worked with log-transformed data. We propose to complete the caption Figure 4 specifying the correspondence between log and non-log values:

Change in manuscript: "The y values of -6, -4 and -2 correspond to ratio values of 0.002, 0.018 and 0.135 respectively."

27) Figure 4: give the unit of formation age (million years) directly in the figure (e.g. 1.0-0.3 Ma)

Response: This is done

28) Figure 6: too small, needs upscaling (if it takes too much space after upscaling, consider shifting it to a SI section).

Response: We propose a new Figure

29) Figure 7: If one doesn't know what Sen trends are, the figure is not understandable.

Response: This is now explain in the text accordingly to the response to your comment $N^{\circ}16$

Tables: 30) Table 2: Table header needs to be rephrased to improve understandability.

Response: We propose the following headers that matches terms in the caption and the text:

Change in manuscript: Simulation , target value, fixed parameter

Best regards, Stefan Reichenberger

References:

Adelinet M., J. Fortin, N. d'Ozouville, S. Violette, 2008. The relationship between hydrodynamic properties and weathering of soils derived from volcanic rocks, Galapagos Islands (Ecuador). Environ Geol (2008) 56:45–58, DOI 10.1007/s00254-007-1138-3.

Clostre, Florence, Philippe Cattan, Jean-Marie Gaude, Céline Carles, Philippe Letourmy, and Magalie Lesueur-Jannoyer. 2015. "Comparative Fate of an Organochlorine, Chlordecone, and a Related Compound, Chlordecone-5b-Hydro, in Soils and Plants." Science of The Total Environment 532 (November): 292–300. https://doi.org/10.1016/j.scitotenv.2015.06.026.

Delvaux, B.; Brahy, V. "Mineral Soils conditioned by a Wet (Sub)Tropical Climate". FAO.

C9

Retrieved 14 June 2014.

Devault, D. A., Laplanche, C., Pascaline, H., Bristeau, S., Mouvet, C. and Macarie, H. 2016. Natural transformation of chlordecone into 5b-hydrochlordecone in French West Indies soils: statistical evidence for investigating long term persistence of organic pollutants, Environ. Sci. Pollut. Res., 23(1), 81–97, doi:10.1007/s11356-015-4865-0.

Gilbert, Richard O. 1987. Statistical Methods for Environmental Pollution Monitoring. New York: Wiley.

Lachassagne P., B. Aunay, N. Frissant, M. Guilbert, and A. Malard, 2014. Highresolution conceptual hydrogeological model of complex basaltic volcanic islands: a Mayotte, Comoros, case study. Terra Nova, 26, 307–321, doi: 10.1111/ter.12102.

Maloszewski, P., Zuber, A., 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers: I. : Models and their applicability, J. Hydrol., 57, 207-231.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-377, 2018.

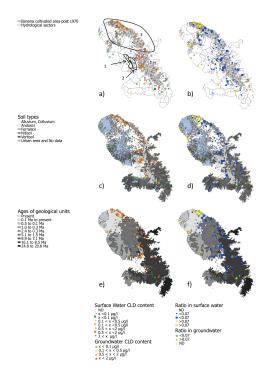


Fig. 1.

C11

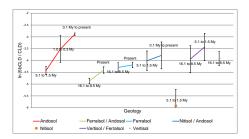


Fig. 2.

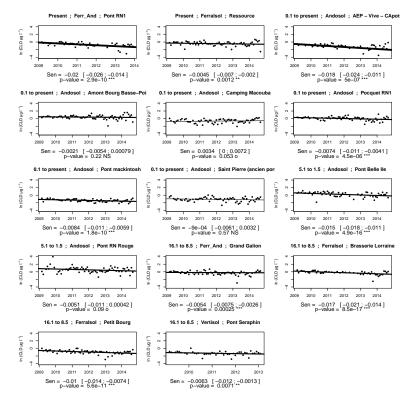


Fig. 3.

C13

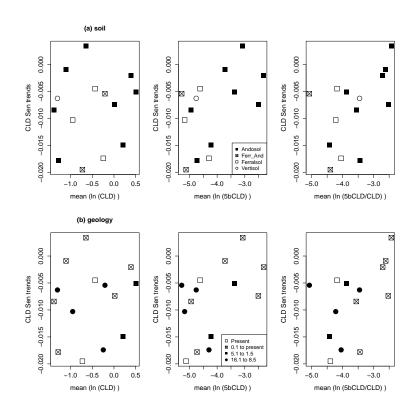


Fig. 4.