SOIL Discuss.,
https://doi.org/10.5194/soil-2017-9-RC2, 2017

Interactive comment on "Opportunities and limitations related to the application of plant-derived lipid molecular proxies in soil science" *by* Boris Jansen and Guido L. B.

Anonymous Referee #2

Received and published: 11 June 2017

A report for "Opportunities and limitations related to the application of plant-derived lipid molecular proxies in soil science"

Abstract

In general I think that the abstract is valid to be read in isolation although, as the subsequent review text, is excessively centered in alkyl compounds, whereas most main groups of cyclic biomarkers (terpenoids steroids,. . .) are neglected to large extent. In the same way, the importance of biodegradation and microbial synthesis in my opinion is overemphasized as regards: i) abiotic diagenetic transformations and ii) changes in the speciation status of extractable lipid molecules.

Printer-friendly version

Discussion paper

Line 15 and below: “Molecules used include extractable and ester-bound lipids as well as their carbon or hydrogen isotopic composition” – I would write more eclectically and prudently as regards the non extractable lipids. In fact, most of them are incorporated as esters, but the ‘fixation’ or ‘immobilization’ of lipids in the soil organo-mineral matrix or in the complex three-dimensional structure of soil organic matter include more or less efficient mechanisms (mainly in the case of compounds lacking reactive groups e.g., alkanes) such as hydrophobic bonding, diffusion intro microporous structures, solid solution, chemisorption not depending on esters but on reactive unsaturated double bonds, etc.

Line 19 and below (i, ii, iii) – I would perhaps extend this short list of “constraining factors” with additional points, or perhaps expanding point iii) “transformation and/or (selective) degradation of (some of) the molecules once present in the soil”. . . This would include the generic changes in solubility associated with the “speciation status” of formerly extractable lipid molecules. This in not included strictly into the term “transformation”. Most lipids are subjected to a complex dynamic (to large extent abiotic) of polymerization and condensation together other organic and inorganic soil components. In most cases ,lipids turn into non-extractable compounds (polymerization of terpenes into macromolecular resins, photo-oxygenation and condensation or unsaturated aliphatic chains, etc) which are favored by soil desiccation and reactive colloidal minerals, and these nonextractable lipids may be stabilized in soil even in nonhydrolyzable forms.

In some cases it may be ‘erroneously’ considered that the lipids are biodegraded whereas the molecule remain intact in the soil a constituent of humic-type macromolecules, or encapsulated or entrapped into soil microcompartments where enzyme diffusion is largely hampered. On the other hand, changes in soil management or drastic environmental perturbation may lead to the release of lipid compounds (including pollutants) which were immobilized in the soil. The balance between the above processes may be responsible for a large proportion of the total variance in the composition of the molecular assemblages of lipid compounds in soil.

Apart from this, most of the research on (plant, soil) lipids has been based in GC/MS and a considerable amount of extractable lipid may consist on nonvolatile (high MW, oligomer) materials which could readily incorporate free lipids as a dynamic mechanism with a substantial bearing on the concentration and selective 'visibility' of lipid molecular proxies in soils (e.g., Soil Sci. 2001, 166(3), 186–196).

Other detail as regards the abstract and the whole review is that natural fires represent a frequent factor modifying the composition and the speciation status or lipid molecules, and some mention on these effects could be introduced in the review, which in my opinion is focused on biochemical processes, whereas abiotic reactions are also very active mainly in semiarid environments and soils under continental climate, where processes depending on the alternance of dry and wet seasons are crucial to explain lipid biogeochemical cycles.

Minor:

Page 1, line 16. I would rewrite "as well as" (I think that the subject of the sentence is "The molecules included" instead of e.g., "The information discussed...".

Page 2, line 15; page 12, line 16: It is often said that "parameter" is a misused word in English, that ought to been changed by "variable", "constraint", "factor", "index", measure", "characteristic"...

Introduction

Page 2, line 25 and below: A frequent feature included in the definition of biomarker compounds is that they are produced exclusively by biosynthesis, and cannot be formed by abiotic reactions. This is often the most important feature in studies on extraterrestrial organic matter or in molecular paleontology studying Precambrian kerogens formed before the origin of Life.

Page 2, line 29 (and throughout the text) – Use "en"-dash for numeric ranges

Page 3, Line 26 and below: "...of the publications using molecular proxies in soil science have been published in the last ten years (2006-2015). On average (± SEM) 59 ± 4 % of the publications with the respective keyword selections have been published in the last decade" – In fact, but depending on the searching strategy used by the authors, this could only be an affect of the fact that recent authors use 'new terms' to refer old subjects. This is also the case with, e.g., the so-called black carbon. There is a lot of classical (old) literature about this material, but the term was first used about 1982, and extensively used ca. 1993 (25 docs). Then, Scopus shows an increasing number of papers about this subject. In the same way, there is a lot of, in my opinion, interesting pioneer papers of soil lipid biomarkers which are not included in this review which, also in my opinion, include several recent papers not representing major contribution to classical studies . For instance, for this or similar paragraphs, I often cite the classical 1982 paper in Atmospheric Environment 16, 2139–159. There is also a specific paper of signature lipids in soil (not referred to as 'molecular proxies) in Eur. J. Soil Sci. 1996, 47, 183–196.

Page 4 (itemized list) : In general, I think that it is interesting to differentiate two main branches in the research lines on soil lipids: i) lipids as a source of biogeochemical information and, ii) lipids as active agents in soil processes reflected in soil quality; soil productivity, soil health...

Concerning the first line, there are several studies on the impact of forest fires on soil lipids. In fact, this is the environmental perturbation causing the major immediate and lasting effect on soil lipids; reviewed in e.g., (2004). Environment International (2004), 30: 855-870 or SJSS (2012), 2(2), 8-33 and references therein. In particular changes in diterpene resin acids and in RLC and CPI of alkanes are typical in fire-affected soils.

In general, and regarding the importance of biomarker compounds, or molecular tracers, or even lipid molecular fossils, there is large classical literature on the chemotaxonomic value of specific molecules in plants. I remember extensive use in the past of the classical series by e.g., Hegnauer, R. 1966. Chemotaxonomie der Pflanzen Bd.4.

Birkhauser Verlag. Basel und Stuttgart. Most important information in these old books (still?) cannot be retrieved readily using the ‘modern’ search in internet.

Concerning the effects of lipid on soils, there is extensive literature on the presumptive effect of lipid fractions in soil water repellency e.g., Geoderma (2010),155, 242-248 and Geoderma (2013) 206: 75-84, and references therein.

I would also include some paragraphs on the importance of several lipids compounds with an effect which may be allelopathic, antimicrobial, nematicidal, etc, and this have large importance in the soil organic matter transformation processes. There is many literature on the effect of resin acids (mono, di-sesquiterpenes. . .) from conifer plants as well as on the effect of several triterpenes in roots of angiosperms (amyrins, friedelans. . ..). All these compounds are also very important biomarkers, and in my opinion some paragraphs should highlight its importance.

Page 5, line 13: As suggested above, the polymerization and fixation of soil lipids would be an important natural phenomenon that cannot be considered included sensu stricto into the terms “transformation”.

Page 6, lines 5–6. I consider that the mention to lignin is not necessary (it is not a major source of typical volatile lipid compounds).

Page 7.

I think that Botanists are changing too frequently names of classical plant taxa, and perhaps the most recent names ought to be used, for instance using Poaceae instead of Gramineae, Fabaceae instead of Leguminosae, etc.

Line 20: Brassicaceae instead of Cruciferae. Line 21: Scrophulariaceae instead of Scrophylariaceae. Line 21: Solaneaceae instead of Lolaneaceae (????). Line 32: Styracaceae instead of Styracacea.

Page 7. Note that in the list of taxons in lines 20–21 you combine plant families with plant orders (e.g., Pinales, the only family of this order being Pinaceae).

Printer-friendly version

Discussion paper

Page 9 line 21. Check: Crassulaceae instead of Crassulacea. Note that Latin names of families should not be italicized, as a difference with genus and species names.

Page 9, line 17: I think that most of the flavonoids are water-soluble compounds.

Page 9, Line 25: 2.2.2 Cutin and suberin monomers – Some authors prefer terms such as "structural units" or "units", in the case of macromolecules, and 'monomers' in the case of typical polymers.

Page 10, lines 7–12: Some mention could be done to the typical iso- and anteiso-branched fatty acids (and alkanes) mainly C15 and C17, for instance Microbiological Reviews (1991), 55, 288–302. Despite these branched chains have also been described in the uropygial gland of birds, they are frequently considered indicators of bacterial metabolism in soil.

Page 10, line 14 and below: I would improve (clairify) this important section on the effect of temperature: i) specifying better the paragraph about the effect of environmental temperature on lipid-synthesizing organisms and ii) the effect of T on the fate of lipids in the soil.

On the other hand, I would discuss more extensively the studies as regards effects of environmental temperature in the degree of saturation of the fatty acids, i.e., the fact that unsaturated FAs increase cell-membrane fluidity, and cell division, favoring the growing of organisms living in very cold environments.

Finally, and as indicated above, it would be interesting to explain some effects of extreme temperatures, i.e., the case with forest fires or controlled burning. I think that typical changes in diterpene resin acids and in alkyl series are were first reported in Geoderma, (1988). 42, 115 127.

Page 11, line 9: Do not capitalize the name of the species in "Gossypium hirsutum L.". I would not include the initial of Linnaeus due to it is not done in the case of the other species names in the Chapter.

Printer-friendly version

Discussion paper

Page 12, line 14: I would specify e.g., “cauliflower” in addition to “Brassica oleracea” (if this were the case). Depending on the variety, this species include very different plants (subspecies) with very different chemistry, e.g. broccoli, Brussels sprout, etc.

Page 12, line 23. Italicize Pinus. Page 12, line 18. I would add “the Poaceae”, or “the graminaceous species”, or “perennial grass” ” before Chionochloa. Page 12, line 25. I would add “the lichen” before Xanthoria.

Page 15, line 20 and throughout the text: Leave blank space between numbers and units symbols

Page 17: I think this section is suitable to include some mention to brached fatty acids and alkanes, as the above indicated iso-and anteiso- chains. But also of chlorophyll-derived isoprenoids (phytane, pristane. . .) and other unusual in-chain branched alkenes typical of cyanobacteria.

Page 19: I think this section is suitable to include additional information on typical cyclic alkanes indicative of fossil organic matter or contamination with fossil fuels . This would be the case of hopanoids, but also of the classical chromatographic ‘hump’ of cyclic and branched alkanes generated by e.g., geothermal processes.

Page 20, subheading “Transformations and turnover in soil”

I think this would be a suitable section to be extended with additional subjects such as the “translocation of lipids” (amongst different soil microcompartments), a typical affect of forest fires, remember the classical studies in Proceedings. Soil Science Society of America (1970) 34:130âĂŤ133.

It is also important the “speciation of lipids” in studies on factors involved in soil water repellence (Geoderma (2010) 155: 242–248) or in soils treated with urban wastes, biosolids, or sewage sludges (e.g., Waste Management & Research (2004) 22: 23–24) which systematically lead to a increase of extractable lipids in native soil organic matter, which is progressively incorporated and ‘fixed’ at different organizational levels

Printer-friendly version

Discussion paper

of the soil humic colloidal matrix.

Page 21, line 1: Amblès

Page 21, lines 2–4: Similarly, it is possible to take advantage of the seco- acids as markers of the impact of fire or thermal treatments in soils under pine vegetation, as suggested by classical literature e.g., The Journal of Organic Chemistry 1968., 33: 3718 3722, and Journal of the American Oil Chemists' Society, 1969. 46, 633 634.

In any case, I think that the pioneer booklet by Zinkel et al., (1971) ought to be indicated in the reviews (Diterpene Resin Acids. USDA, Forest Service. Forest Products Laboratory. Madison, Wisconsin.)

Page 22. Differences between different soil compartments

This section would be suitable to introduce some mention to 'lipid speciation' suggested in previous paragraphs. In particular the mechanisms leading to 'fixation' or 'immobilization" of lipids with the humic-type substances are extremely complex and effective, considering that compounds lacking reactive functional groups such as paraffins may be incorporated into condensed forms of organic matter, and require drastic chemical degradation methods for its release (e.g., Soil Biol. Biochem., (1987) 19(5): 513–520). Mechanisms not including encapsulation ("at a molecular level", line 20) but diffusion into microporous structures, or chemisorption in the case of unsaturated chains, fatty acids, etc, may be typical processes.

Note that not only "different soil compartments" but also "different plant compartments" are relevant as regards the distribution of lipids. The same alkane or fatty acid molecule may be present in extractive forms as an epicuticular plant wax. Or can be entrapped as nonhydrolyzable ester, or as sterically blocked alkyl chain in cutans, or in complex polyalkyl macromolecules of unknown structure presumptively existing in plants and soils, e.g., Naturwissenschaften (1986) 73: 579–585.

In the case of humic-type fractions, it has been indicated that condensation or polymerization of lipid may be an active abiotic mechanism (Naturwissenschaften (1991), 78: 359–362). Nevertheless, the pioneer studies were probably those from Australian soils (Aust. J. Soil Res. (1987) 25;71–82) suggesting a preferential incorporation of alkyl components in soil microaggregates (phenomenon which was also indicated in more recent papers cited in line 30).

Page 22, line 21. I prefer humic macromolecules or humic substances instead of 'polymers'. Page 23, line 1. I prefer alkyl rather than aliphatic (e.g., sugar is aliphatic).

Page 24, line 26. I would change 'biopolymers' (?) by alternative terms such as lipids, biomolecules, homologous series of-, etc (?).

Page 25, lines 1–11: As regards factors determining the presence or the lack of individual molecules in soils, please consider my above suggestions of not overemphasizing selective biodegradation of the lipid compounds, but also immobilization, condensation, insolubilization, fixation or encapsulation as molecules in 'recalcitrant', 'entrapped', 'fixed', or condensed forms, etc. . .

Page 28: General conclusions: I would discuss some of the above processes in the general conclusions

Line 20: I would change terms such as 'microbial degradation' by more general ones such as "microbial reworking". This will compensate the (relatively) ill-posed problem about the fate of lipids described in this chapter. Microorganims: i) degrade soil lipids, ii) synthesize alternative lipids which are released to soils, iii) contribute to the biodegradation of the organic matter with an affect of releasing its 'building blocks' and iv) modify the reactivity of organic matter by oxidative processes leading to e.g., increased titrable acidity (both carboxyl and phenolic hydroxyl groups), then humic-type organic matter have increased potential to retain, incorporates or insolubilize lipids into nonextractable forms.

References

Check the style of all references and abbreviations of Journals (e.g., page 30, line 20; page 31, line 9).

Italicize genus (Latin names), as in page 29, lines 23 and 29; page 32, line 12: page 40, line 8; page 42, line 7; page 45, line 2.

Page 30, line 2:italicize n- in n-alkanes. The same in page 31, line 5; page 32, line 28; page 33, line 9; page 39, line 19; page 43, line 11.

Page 31, line 6: Do not capitalize unnecessarily "isotopic". The same in some Title words in page 44, line 33.

Page 34. line 21. Subscript in CO2.

Page 41, line 34: Spectrom.

Page 44, line 5: Annu Rev Earth Planetary Sci.

Interactive comment on SOIL Discuss., https://doi.org/10.5194/soil-2017-9, 2017.