Nanoclays from allophanic and non-allophanic soils: their implications on carbon sequestration potential

Recent studies indicate that global warming is partially caused by the increased emission into the atmosphere of greenhouse gases from the burning of fossil fuels, decomposition of carbon-rich materials and intensive deforestation. Carbon stabilization and sequestration is one of the ways to mitigate the greenhouse effect. It has been suggested that nanoparticles, could be highly effective in carbon sequestration, due to their large surface volume ratio (Khedr et al., 2006). Nanoparticles occur widely in the natural environment, especially in soil. Andisols, soils derived from volcanic ash contains different inorganic nanoparticles, among which allophane is the most abundant (Parfitt et al., 1983; Wada, 1987; Calabi-Floody et al., 2009). This mineral is a non-crystalline aluminosilicate, as nano-ball with an outer diameter of 3.5–5.0 nm, with defects in the wall structure give rise to perforations of ~ 0.3 nm in diameter. The association of soil organic matter (SOM) with inorganic nanoparticles, has been found to increase their stability (Monreal et al., 2010; Calabi-Floody et al., 2011) and may therefore contribute to the long-term storage of carbon in soil. In previous research we focus attention on extracting nanoparticles from soil to assess their potential for carbon sequestration. We found that the extracted aggregates of nanoparticles retain a significant amount of carbon (11.8 %) against intensive peroxide treatment (Calabi-Floody et al., 2011). Also we showed that the stabilized organic compounds in the nanoclay fraction may be characterized by pyrolysis-GC/MS (previous visit to the BIOEMCO).

The objectives of the present project are to continue our work concerning the characterization of organic matter stabilized by nanoclays on a molecular basis, in order to determine the carbon sequestration potential. In particular we aims are i) to evaluate the changes in chemical composition when SOM is stabilized by nanoclays, compared to other soil fractions (silt, clay and nanoclay) from an Andisol of the Southern Chile, and ii) to extract nanoclay fraction from French soils, in order to investigate the molecules associated to the nanoclay fraction in non-allophanic soils.

To reach these aims, we need to isolate the different fraction from bulk of soils (silt, clay and nanoclay). One part of these soil fractions will be treated with 30% hydrogen peroxide to remove the organic matter not intimately associated with the mineral phase, in order to study the carbon retention in different inorganic fraction (silt, clay and nanoclay) and evaluate the effect of fraction size. The analysis of organic matter will consider a molecular characterization of carbon compound associated to nanoclay fraction by means of pyrolysis GC/MS, and wet chemical analysis for plant litter compounds. The Laboratoire de Biogéochimie et Ecologie des Milieux Continentaux (BIOEMCO) Centre INRA Versailles-Grignon, France, has expertise scientist in these analysis and data interpretation. Such an expertise will be combined with my own expertise on nanoclay extraction and characterization and therefore lead scientifically productive and personally rewarding stay.

Description of the work carried out during the visit

In this internship we worked with tow type of soil one Andisol (allphanic soil from Chile) and one Cambisol (non allophanic soil from France)

2.1. Soil preparation and clay extraction

The soils used were an Andisol of the Piedras Negras Series in Southern Chile (UFRO experimental site, Laguna Azul) as allophanic soil, and a Cambisol from Versailles France (INRA experimental site, les Closeaux) as non-allophanic soil. The Andisol was collected in 2004 at 0-20 cm depth and in March 2011 at tow depth 0-20 and 20-40 cm. The Cambisol was sampled in April 2002 at 0-25 cm depth on tow plot i) only wheat cultivated (P26 as control) and ii) 0 to 9 years of maize cropping after wheat (P07). The samples were pooled, passed through a 2 mm mesh sieve, and dried in air (2–3 days at room temperature). Then 100 g of each soil samples were used for clay extraction. Briefly, deionized water (180 ml) was added to 50 g of air-dried bulk soil, and shaken overnight with 20 glass beads (diameter 5 mm). The fraction > 50 μm were collected by wet sieving. The fraction < 50 μm was sonified applying 7500 J g^{-1}, using a Sonics Vibra Cell model VC 550 equipment, the ratio soil mass (g) water (ml) was 1:10. Then around 14 g of soil suspension was placed in a one-liter measuring cylinder, from which the clay fraction (< 2 μm equivalent spherical diameter), was obtained by sedimentation under gravity, following Stokes' law. The separated clay suspension was concentrated by sedimentation overnight changing the ionic force achieved 1.8 M with NaCl.

2.2. Nanoclay extraction

The nanoclay fraction was extracted using the methodology as described by Calabi-Floody et al., (2011) (Fig. 1). Briefly, 5 g of the clay was suspended in 100 mL of 1 M NaCl, ultrasonicated at 280 J mL^{-1} for 6 min, and centrifuged in a Sorvall Instrument RC-SB refrigerated superspeed centrifuge at 1351 g for 40 min and 25 °C. The centrifugation speed was the same as used by Li and Hu (2003). The average diameter of the particles was less than 100 nm when the first-round supernatant was discarded in order to remove mineral impurities. The pellet was suspended in 50 mL of deionized water with moderate stirring for 40 min and centrifuged again. The supernatant was collected, while the pellet was resuspended (in deionized water) and centrifuged. This procedure was repeated 11 more times. The collected supernatants, containing the nanoclay, were dialyzed (1000 kDa membrane) against deionized water until the conductivity of the water reached 0.5–0.8 μS cm^{-1}. The dialyzed material was freeze-dried to yield solid nanoclay.

100 mL NaCl 1M → Clays 5g → 6 min ultrasonication (214 JmL^{-1})

Centrifuge 3.000 rpm x 40 min ⤑ Discard supernatant

50 mL H_2O → Clay pellet

1 min ultrasonication (72 JmL^{-1})

Centrifuge 3.000 rpm x 40 min → Nanoclay suspensions

Nanoclay suspensions → Nanoclay concentration (1.8 M NaCl)
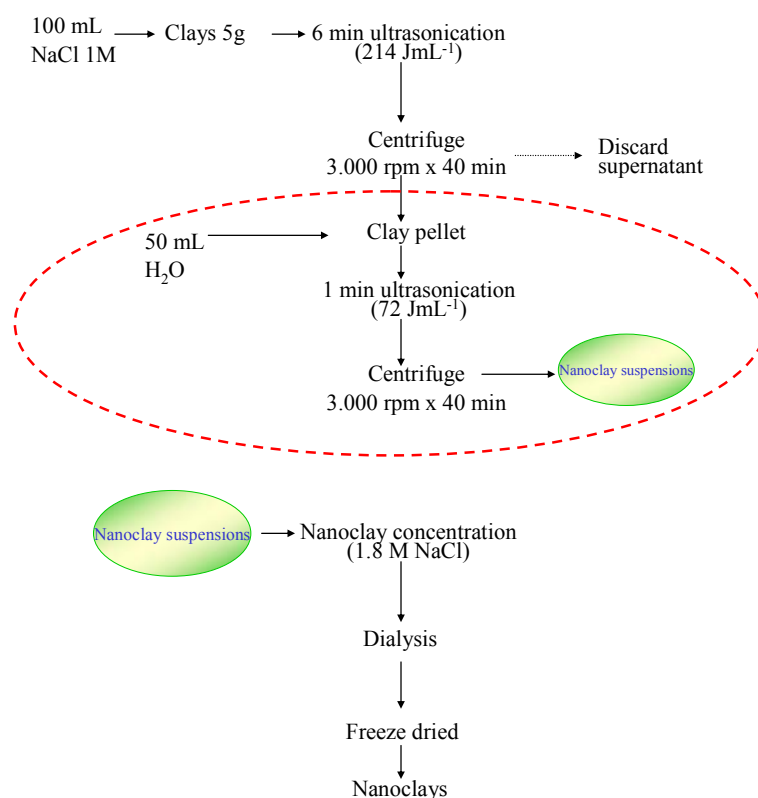
Dialysis

Freeze dried

Nanoclays

Figure 1. Scheme of nanoclay extraction

2.3 Transmission electron microscopy (TEM)

A drop of the clay or nanoclay suspension (1 μg mL^{-1}) was evaporated on a carbon-coated copper grid. TEM images were obtained with a Jeol-1200 EXII instrument operating at 120 kV, equipped with a Gatan 782 camera for image digitization. Electron diffraction (ED) was made at 60 cm from the focus.

2.4 Chemical characterization of soil organic matter

The molecular composition of the SOM associated with the clay and nanoclay fractions were determined by analytical pyrolysis, using samples that had been freeze-dried and ground to a fine powder. Curiepoint pyrolysis was carried out by heating to the Curie temperature of 650°C. The pyrolysis products were analysed by GC/MS, carried out with a pyrolysis unit (GSG Curiepoint Pyrolyser 1040 PSC) coupled to a gas chromatograph (Hewlett Packard HP 5890) and a mass spectrometer (Hewlett Packard HP 5889; electron energy 70 eV).

3 Results and discussion

3.1 Clay extraction from 100 g of soil

The theoretical clay content in Chilean Andisols is around 30 % bulk of soil. We extracted 7.7 g from Andisol 0-20 cm depth (26 % of the theoretical clay content) and 12.8 g of clay from Andisol 20-

40 cm depth (43 %). The low clay extaction was due to high organic matter content in the Chilean Andisol ~ 25 % w/w (Escudey et al.,2001). Which generate strong interaction between allophane content and organic matter, increasing clay sedimentation. The French Cambisol had easier clay extracton than Andisol, due to lower organic mater content than Chileand Andisol. The clay extraction was around 95 % of the total theoretical clay content ~ 17 %, obtaining 16.5 g of clay from P26 and 16.2 g from P07.

3.2 Nanoclay extraction

The transmission electron microscopy (TEM) showed that the methodology proposed by Calabi-Floody et al. (2011) was useful for nanoclay extractions from a Cambisol, obtaining crystalline nanoparticles (Fig. 2a) with hexagonal morphology (Fig. 2b) and mainly size ~ 50 nm of external diameter (Fig. 3). The nanoclay extraction on the Chilean Andisol follows the same pattern that was showed in Calabi-Floody et al. (2011). After 12 washed, nanoclay suspension was obtained. The French Cambisol showed a rapid process of nanoclay extraction, after 5 washed was obtained the nanoclay suspension. This difference in the nanoclay extraction could be interesting for nanotechnological applications because the nanoclay extraction in the French Cambisol is faster than in Chilean Andisol. However, the nanoparticles from French Cambisol are completely different than the Chilean Andisol. Andisol are mainly constituted by allophane, a non-crystalline ('short-range order') aluminosilicate as hollow spherule with an outer diameter of 3.5-5.0 nm (Parfitt, 1990). The extracted nanoclay from Andisol Piedras Negras series by Calabi-Floody et al. (2011) consists of spherical aggregates of allophane with a diameter of about 100 nm and an average height of 3–5.5 nm.
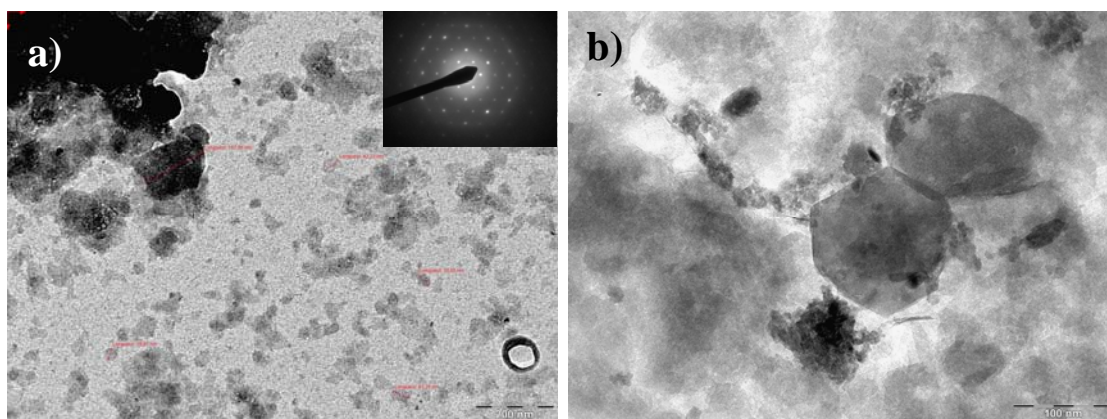

Figure 2. Transmission electron micrographs of nanoclays from Cambisol (P07): a) electron diffraction patterns and b) close-up.

The nanoclay yield from French Cambisol was ~ 9.8 %, whilst for Chilean Andisol 0-20 cm depht was ~ 0.5 %. The strong interactions between organic matter and allophane in Andisol (Mora and Canales, 1995), might difficult the disaggregation of nanoclay decreasing the nanoclay yield. These results are agreed with low clay extraction in these Andisol due to the high organic mater content. Low nanoclay yields, contitute a problem for future applications in nanotechnological. The high allophane content ~ 11% of clay fraction (Vistoso et al., 2009; Matus et al., 2008; Mora and Barrow, 1996; Mora and Canales, 1995) and morphology of allophanic nanoclays is interesting for technological applications. Thus, improvements are required in the nanoclay extractions from soils with high organic matter content.
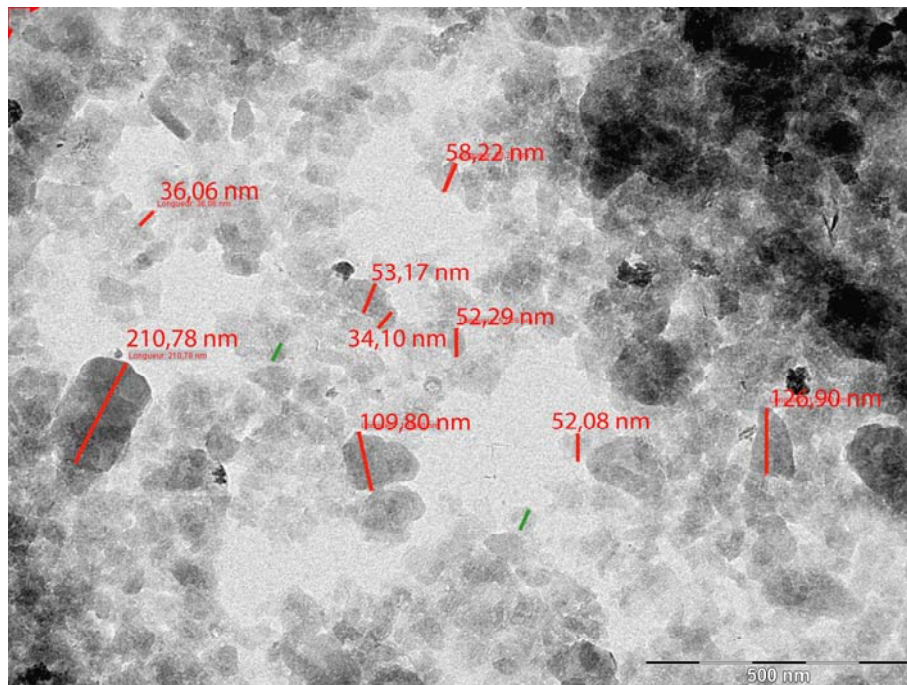
Figure 3. Transmission electron micrographs of nanoclays from Cambisol (P07) with size of particles.

3.3 Nanoclay characterization

3.3.1 Analitical pyrolysis

Organo-mineral complexes were studied by Pyrolysis carried out for clay and nanoclay fractions from Cambisol and Andisol. The Andisol contain more organic matter than Cambisol, this was confirmed for the higher pyrolysis products in the Andisol fractions than the Cambisol fractions. One representative pyrogram for each fraction is presented in Fig. 4 and 5. The identified pyrolysis products are listed in the Table 1 (Andisol fractions) and 2 (Cambisol fractions) see in appendix.

Analysis of pyrograms showed that nanoclay from Cambisol had the highest relative contribution of N-containing (N) pyrolysis products, whilst the highest contribution of Polysaccharide-derived compound (PS) was from Andisol clay and nanoclay fractions (Fig. 6). The relative contribution of compounds of unspecific origin (U) was higher in clay than nanoclay fractions (Fig. 6) and the highest proportion of contaminant derived from siloxanes (S) was observed in nanoclay fraction from Andisol, this could suggest that nanoclay fraction play a stabilization role of this contaminant in the Chilean Andisol. The black carbon content in Andisol fractions had higher relative contribution than Cambisol fractions between 41 to 12 % (Fig. 7). These results could be due to Chilean Andisol had ~ 25% w/w of organic matter in the bulk of soil (Escudey et al., 2001). We expected more stable carbon on Andisol nanoclay fraction due to high allophane content (Calabi-Floody et al., 2011), which have strong organo-mineral interactions (Mora and Canales, 1995; Calabi-Floody et al., 2011). However, was observed 41% more black carbon in clay from Andisol than nanoclay from Cambisol and 24% more than clay from Cambisol. The nanoclay fraction from Andisol showed less relative contribution than clay from Andisol

but was higher than nanoclay (27%) and clay (12%) from Cambisol. This difference could be attributed at Siloxane contaminant group which represent 11% of the relative abundance of Andisol nanoclay fraction, which was not detected in clay fraction. If this group is not considerate from the relative abundance of nanoclay. The black carbon abundance is the same for clay and nanoclay, suggesting that allophane content has the stabilizing effect in this soil.
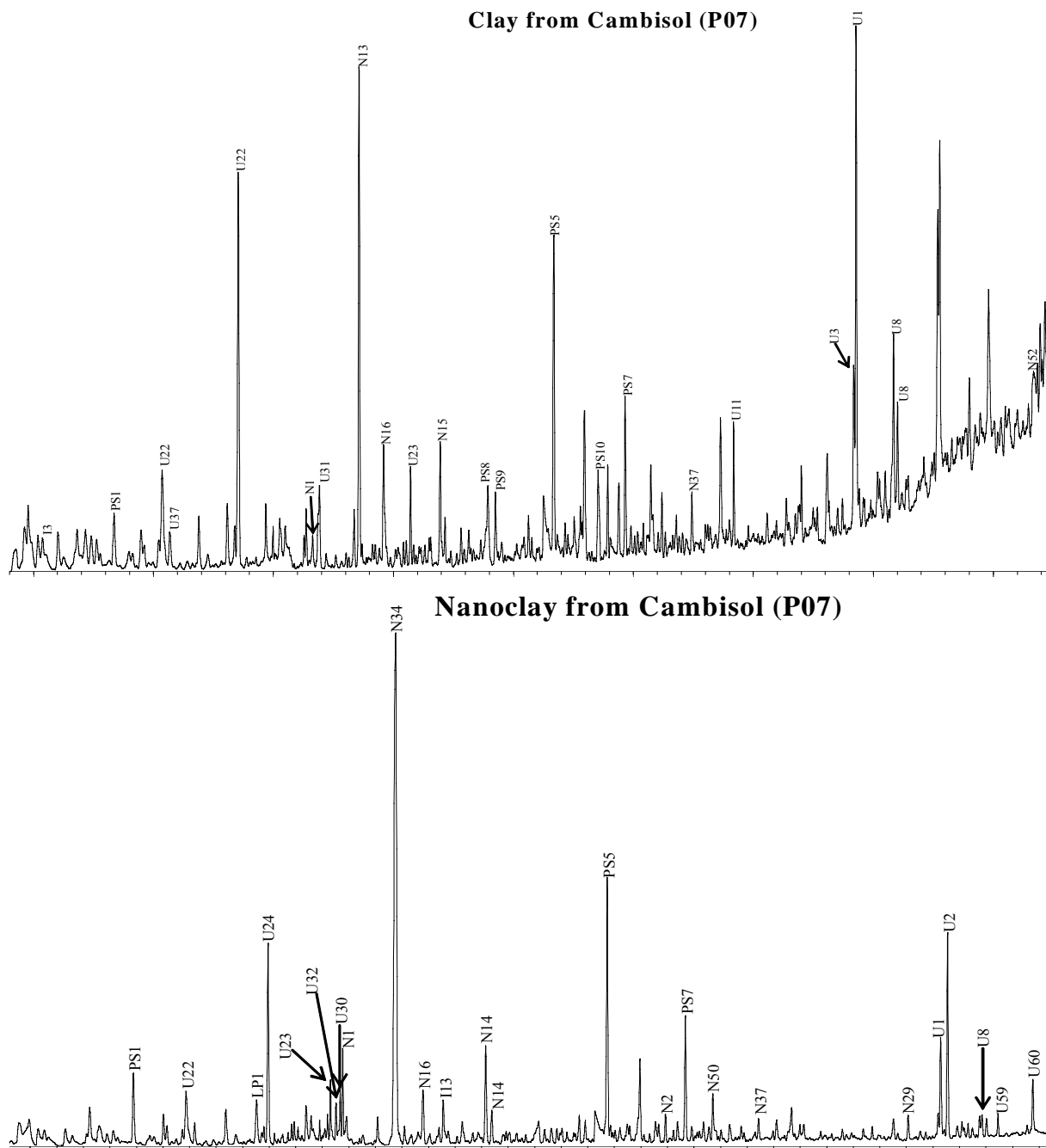
Figure 4. Pyrogram from Cambisol fractions. Peak labels refer to Table 1 for Andisol and 2 for Cambisol
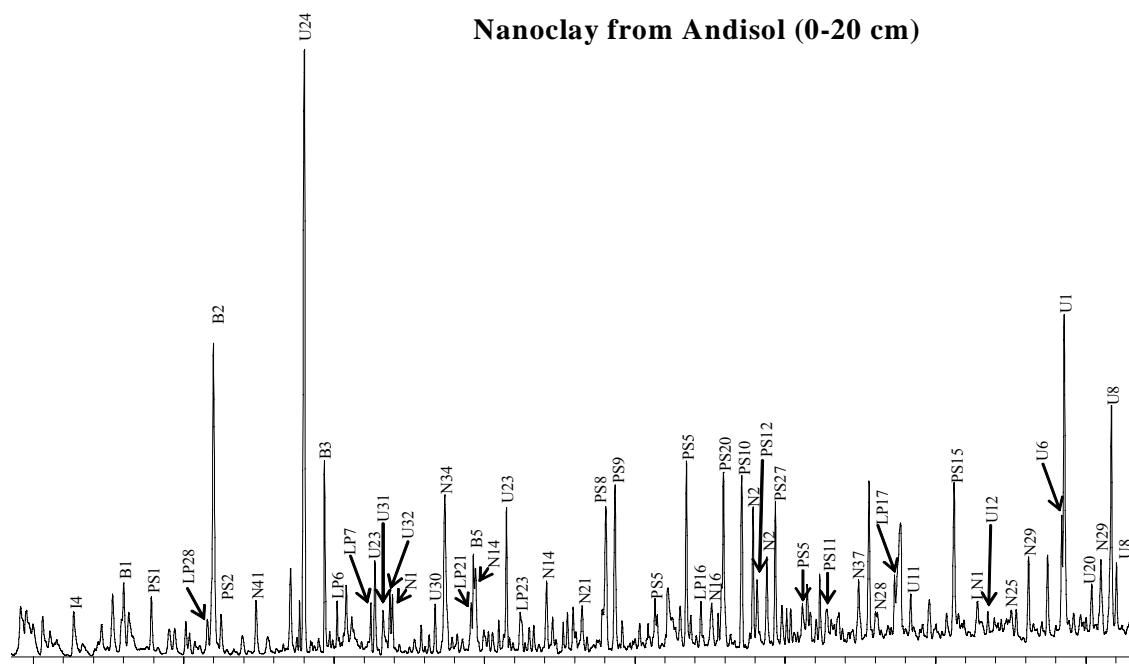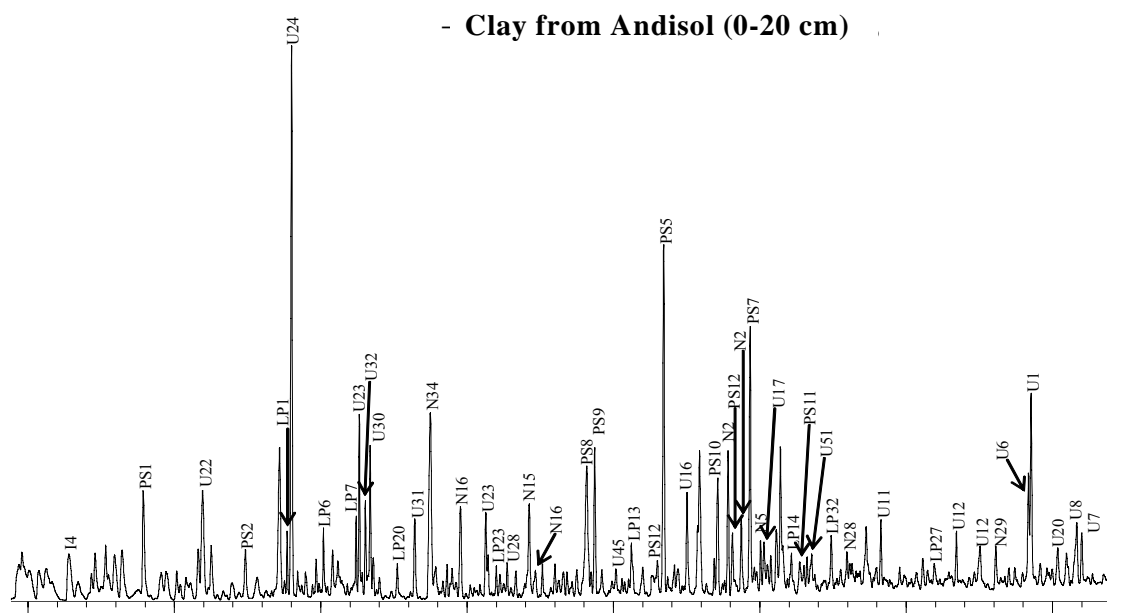
Figure 5. Pyrogram from Andisol fractions. Peak labels refer to Table 1 for Andisol and 2 for Cambisol
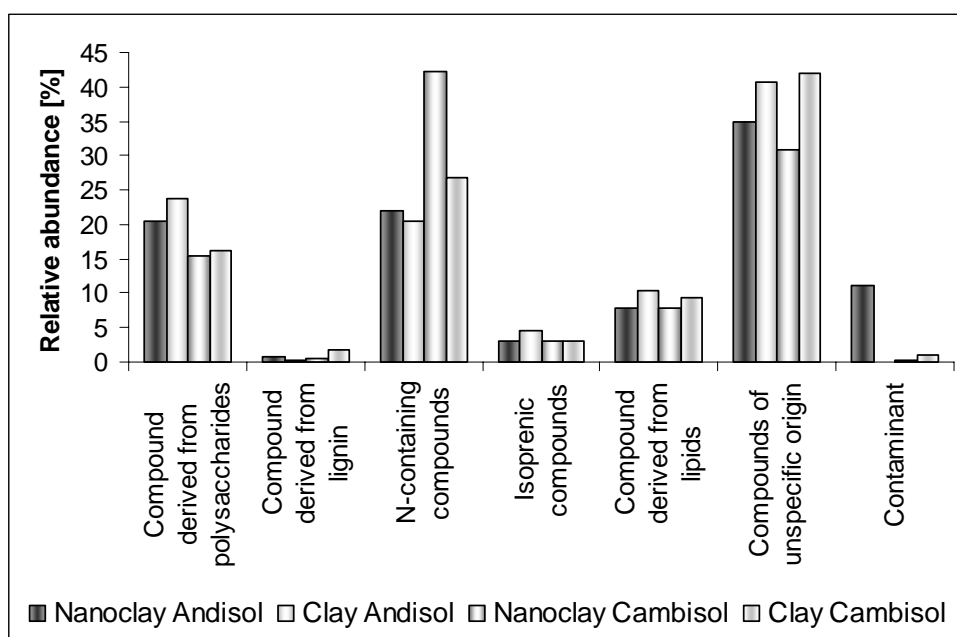
Figure 6. Relative abundance of different classes of identified pyrolysis products on the different soil fractions
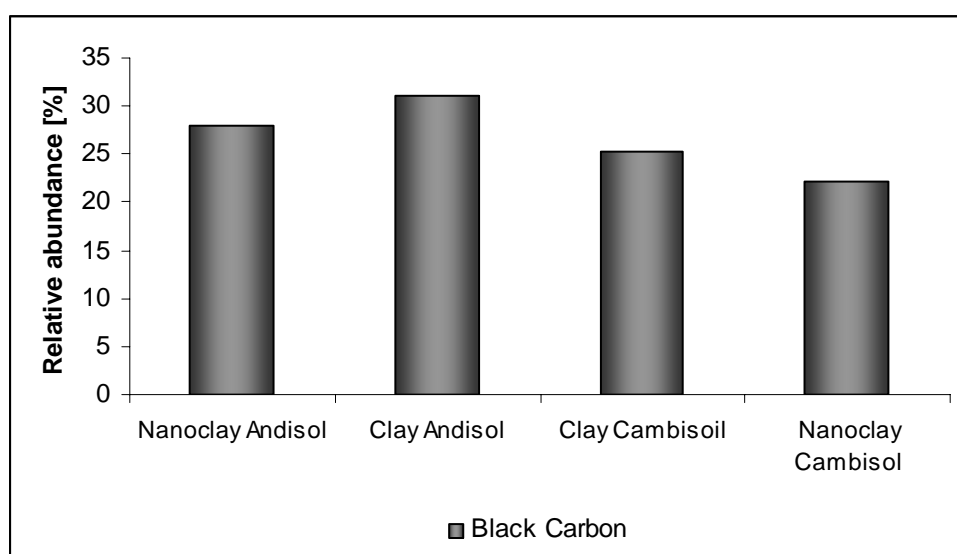
Figure 7. Relative contribution of black carbon on the different soil fractions

The study of nanoclay fraction (Fig. 8) from two type of soils (Andisol and Cambisol) showed more relatively abundant of the PS, LN, I, U and S pyrolysis products in Andsisol (Fig. 8). The main differences on the pyrolysis compound detected on nanoclay fractions were in S 11-fold more in Andisol than Cambisol, N were 93 % more abundant in Cambisol than Andisol and 58% of LN more contribution in Andisol than Cambisol. The analysis of the clay fractions (Fig. 9) from Andisol and Cambisol presented major relative abundance on LN, N, U and S of the pyrolysis products in Cambisol. The highest difference was in S which was not detected in Andisol clay. Cambisol clay showed 392 % more LN than Andisol and 56 % more I were observed in Andisol clay than Cambisol. More results and analysis are in process to give more explanations of this study.

Figure 8. Comparison of the pyrolysis products found on nanoclay fractions extracted from Cambisol and Andisol.

Figure 9. Comparison of the pyrolysis products finding on clay fractions extracted from Cambisol and Andisol.

Preliminary Conclusions

- The nanoclay extraction in French Cambisol is faster and easier than in Chilean Andisols, this could be attributed to the high organic matter content in the Chilean soils.

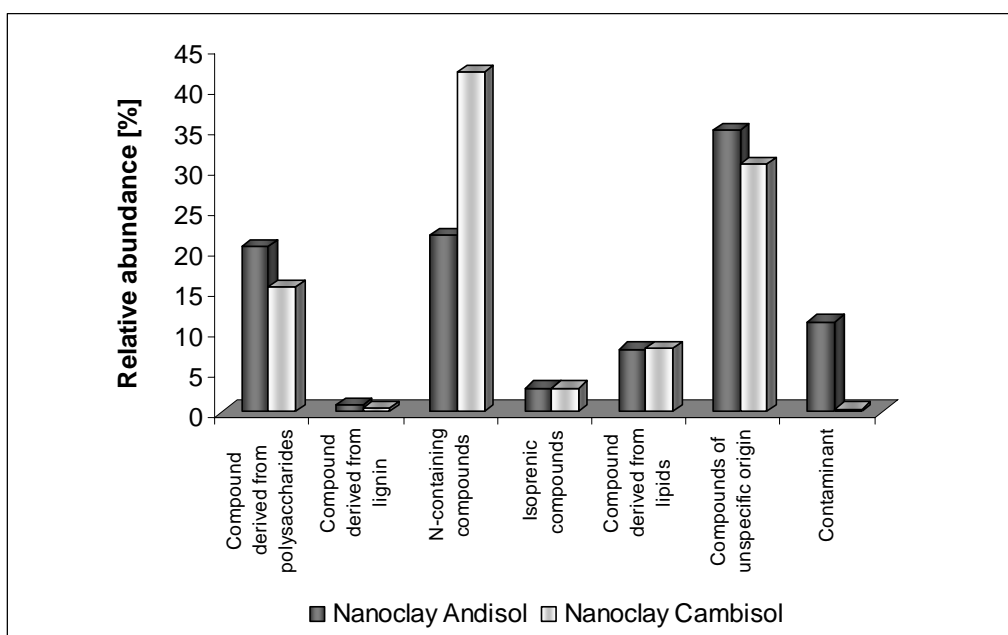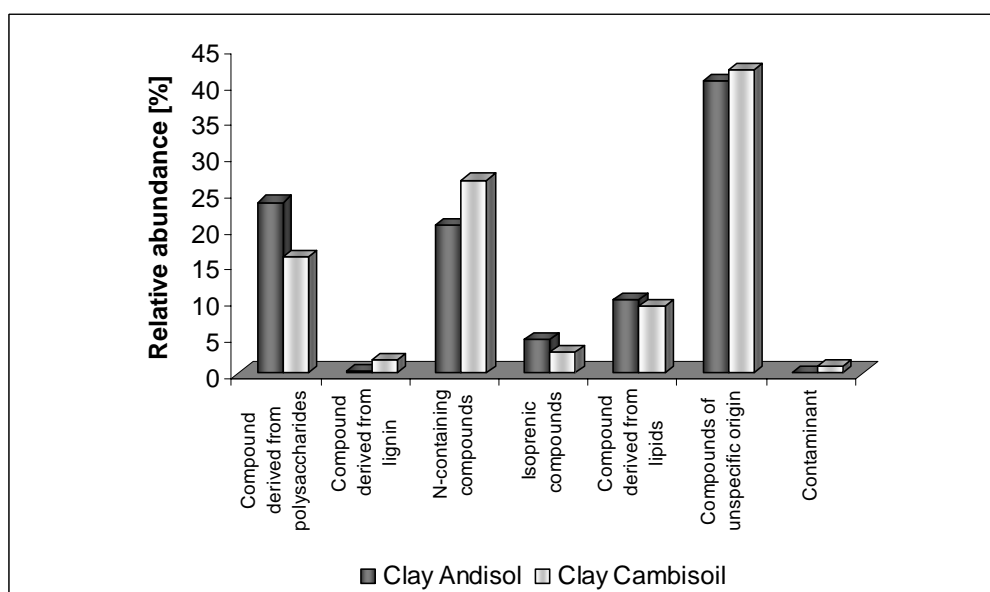- This French soil could have a great interest in nanotechnological and biotechnological applications.

- The organic matter governs the physico-chemical properties of the clay and nanoclay of Andisol.

- In this research we found that nanoclays from an Andisol of the southern Chile have a probable stabilize effect in the carbon sequestration. However, more studies are needed to evaluate the real importance of the allophanic nanoclays, in the global carbon sequestration and stabilization in the Andisols of the Southern Chile.

Future collaboration with host institution

We expect continuum our collaboration between BIOEMCO and Universidad de La Frontera Chile. For the moment as part of my postdoctorade I will visit BIOEMCO to increase the knowledge in the organic matter interaction and composition on the soil fractions.

Projected publications/articles resulting or to result from your grant

We had 2 possible publications as results of this grant
- Nanoclays from allophanic and non-allophanic soils: their implications on carbon sequestration potential
- Methodology for naoclay extraction.

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Appendix

Table 1. Pyrolysis product in clay and nanoclays from Chilean Andisol Series Piedras Negras depth 0-20 cm

Nanoclay Andisol		Clay Andisol	
Name	Nº	Name	Nº
Compound derived from polysaccharides			
2-methylfuran	Ps1	2-methylfuran	Ps1
2,5-dimethylfuran	Ps2	2,5-dimethylfuran	Ps2
2-ethylfuran	Ps4	2,3,5-trimethylfuran	Ps3
2-furancarboxaldehyde	Ps5	2-furancarboxaldehyde	Ps5
5-methylfurfural	Ps7	5-methylfurfural	Ps7
2-cyclopentenone	Ps8	2-cyclopentenone	Ps8
2-methyl-2-cyclopentenone	Ps9	2-methyl-2-cyclopentenone	Ps9
3-methyl-2-cyclopentenone	Ps10	3-methyl-2-cyclopentenone	Ps10
3-ethyl-2-cyclopentenone	Ps11	3-ethyl-2-cyclopentenone	Ps11
2,3-dimethyl-2-cyclopentenone	Ps12	2,3-dimethyl-2-cyclopentenone	Ps12
2-hydroxy-3-ethyl-2-cyclopentenone	Ps14	2,5-dimethyl-2-cyclopentenone	Ps13
2-hydroxy-3-methyl-2-cyclopentenone	Ps15	2-methylbenzofuran	Ps16
2-methylbenzofuran	Ps16	2-vinyl-5-methylfuran	Ps18
2-vinylfuran	Ps17	(E/Z)-3-methyl-2-(2-methyl-2-butenyl)-furan	Ps21
2-vinyl-5-methylfuran	Ps18		
1-methylene-2-vinylcyclopentane	Ps19		
2-isopropylfuran	Ps20		
Compound derived from lignin			
2-methoxyphenol/guaiacol	Ln1	isopropylphenylacetilene	Ln3
2-methoxyphenolacetylene	Ln2		
N-containing compounds			
1-methylpyrrole	N1	1-methylpyrrole	N1
2-methylpyrrole	N2	2-methylpyrrole	N2
2,5-dimethyl-1H-pyrrole	N5	3-ethyl-1H-pyrrole	N3
2-ethyl-4-methyl-1H-pyrrole	N6	2,4-dimethyl-1H-pyrrole	N4
2-formylpyrrole	N9	2,5-dimethyl-1H-pyrrole	N5
2-methylpyridine	N14	2-ethyl-4-methyl-1H-pyrrole	N6
3-methylpyridine	N15	2,3,5-trimethyl-1H-pyrrole	N7

4-methylpyridine	N16	2-acetylpyrrole	N8
2-ethylpyridine	N17	1-methyl-1H-pyrrole-2-ethanamine	N9
4-ethylpyridine	N19	2-formylpyrrole	N10
2,3-dimethylpyridine	N20	3-methylpyridazine	N12
2,4-dimethylpyridine	N21	3-methylpyridine	N15
2-pyridinecarbonitrile	N25	4-methylpyridine	N16
2-pyridinamine	N26	2-ethylpyridine	N17
4-methylbenzonitrile	N28	3-ethylpyridine	N18
benzeneacetonitrile	N29	2,4-dimethylpyridine	N21
benzenepropanenitrile	N30	3,4-dimethylpyridine	N23
2,4-pentadienenitrile	N34	4-methylbenzonitrile	N28
Isoquinoline	N35	benzeneacetonitrile	N29
2-methylbenzoxazole	N37	3,4-dimethylbenzonitrile	N32
indole	N39	1,2-benzenediamine	N33
3-methyl-3-butenitrile	N40	2,4-pentadienenitrile	N34
3-methylaminopropionitrile	N41	Isoquinoline	N35
4,6-dimethylthiopicolinamide	N42	2,5-dimethylbenzoxazole	N38
		dodecanenitrile	N43

Isoprenic compounds

2--methylbutanal	I1	3--methylbutanal	I1
3--methylbutanal	I2	(Z)-1,3-Pentadiene	I3
1,3- Cyclopentadiene	I4	1,3- Cyclopentadiene	I4
2,5-dimethyl-2,4-hexadiene	I8	1-methyl-1,4-cyclohexadiene	I5
trimethyl-1,3-cyclopentadiene	I9	1,2-dimethyl-1,4-cyclohexadiene	I7
Isoprene	I10	2,5-dimethyl-2,4-hexadiene	I8
		tricyclo(3,2,1,0^2,7)oct-3-ene	I11
		7-methyl-bicyclo[4.2.0]octa-1,3,5-triene	I12

Compound derived from lipids

1-decene	Lp1	1-decene	Lp1
4-decene	Lp2	4-decene	Lp2
undecane	Lp6	(Z)-3-decen-1-ol	Lp5
1-undecene	Lp7	undecane	Lp6
1-tetradecene	Lp12	1-undecene	Lp7
pentadecane	Lp16	5-undecene	Lp8
1-pentadecene	Lp17	(E)-2-tetradecene	Lp13
dodecane	Lp20	hexadecane	Lp14
1-dodecene	Lp21	1-hexadecene	Lp15
tridecane	Lp23	pentadecane	Lp16
1-tridecene	Lp24	1-pentadecene	Lp17
1-octadecene	Lp27	dodecane	Lp20
1-nonene	Lp28	1-dodecene	Lp21
(E)-2-pentenal	Lp34	tridecane	Lp23
10-methyl-1-undecene	Lp35	1-tridecene	Lp24
		1-octadecene	Lp27
		heptadecane	Lp32
		1-ethyl-2methylcyclododecane	Lp33
		1-octadecene	Lp27

Compounds of unspecific origin

phenol	U1	phenol	U1
1,1'-biphenyl	U2	1,1'-biphenyl	U2
4-ethylphenol	U5	2-ethylphenol	U3
2-methylphenol	U6	3-ethylphenol	U4
4-methylphenol	U8	2-methylphenol	U6
naphthalene	U11	3-methylphenol	U7
1-methylnaphthalene	U12	4-methylphenol	U8
indene	U16	2,5-dimethylphenol	U10
1-methyl-1H-indene	U17	naphthalene	U11
2,3-dihydro-1H-indenone	U20	1-methylnaphthalene	U12
3-methylindanone	U21	1,3-dimethylnaphthalene	U14
styrene/ethylbenzene	U23	1,4-dimethylnaphthalene	U15
Toluene/ methylbenzene	U24	indene	U16
1-ethyl-2-methylbenzene	U25	1-methyl-1H-indene	U17
1,2,4-trimethylbenzene	U28	1,1-dimethyl-1H-indene	U18
p-xylene	U30	1,3-dimethyl-1H-indene	U19
1,2-xylene	U31	2,3-dihydro-1H-indenone	U20
1,3-xylene	U32	benzene	U22
2,6-xylenol	U33	styrene/ethylbenzene	U23
(Z)-3-methyl-1,3,5-hexatriene	U41	Toluene/ methylbenzene	U24
1,3-dimethyl-1-cyclohexene	U42	1-ethyl-2-methylbenzene	U25
5,6-dimethyliene-exo-2-norborneol (C9H12O)	U43	1-ethyl-3-methylbenzene	U27
9H-fluorene	U44	1,2,4-trimethylbenzene	U28
		1,2,3-trimethylbenzene	U29
		p-xylene	U30
		1,2-xylene	U31
		1,3-xylene	U32
		2,6-xylenol	U33
		vinyltoluene/methylstyrene	U34
		2,4-hexadienal/ sorbaldehyde	U37
		2-propenylbenzene	U40
		cyclopropylbenzene	U45
		2-butenylbenzene	U46
		1-methyl-3-(1-methylethyl)-benzene	U47
		fluorene	U48
		3-methylacetophenone	U49
		1-methyl-2-phenylcyclopropane	U50
		1-phenylethanone/acetophenone	U51
		(Z)-3-methyl-1,3,5-hexatriene	U52

biomass (Pognani et al., 2011)

hexamethyl-cyclotrisiloxane	S1
octamethyl-cyclotetrasiloxane	S2
decamethylcyclopentasiloxane	S3
tetradecamethylcycloheptasiloxane	S4
dodecamethylcyclohexasiloxane	S5
hexadecamethylcyclooctahexasiloxane	S6

Table 2. Pyrolysis product in clay and nanoclays from French Cambisol (P07)

Nanoclay Cambisol		Clay Cambisol	
Name	**Nº**	**Name**	**Nº**

Compound derived from polysaccharides

Nanoclay Cambisol		Clay Cambisol	
2-methylfuran	Ps1	2-methylfuran	Ps1
2-furancarboxaldehyde	Ps5	2-furancarboxaldehyde	Ps5
3-furancarboxaldehyde	Ps6	5-methylfurfural	Ps7
5-methylfurfural	Ps7	2-cyclopentenone	Ps8
2-cyclopentenone	Ps8	2-methyl-2-cyclopentenone	Ps9
2-methyl-2-cyclopentenone	Ps9	3-methyl-2-cyclopentenone	Ps10
2-methylbenzofuran	Ps16	2,3-dimethyl-2-cyclopentenone	Ps12

Compound derived from lignin

Nanoclay Cambisol		Clay Cambisol	
3-methoxypirydine?	Ln4	2-methoxyphenol/guaiacol	Ln1
		isopropylphenylacetilene	Ln3

N-containing compounds

Nanoclay Cambisol		Clay Cambisol	
1-methylpyrrole	N1	1-methylpyrrole	N1
2-methylpyrrole	N2	2-methylpyrrole	N2
1-methyl-1H-pyrrole-2-ethanamine	N9	pyridine	N13
2-formylpyrrole	N10	3-methylpyridine	N15
pyrazine	N11	4-methylpyridine	N16
3-methylpyridazine	N12	2-ethylpyridine	N17
2-methylpyridine	N14	4-ethylpyridine	N19
4-methylpyridine	N16	2,4-dimethylpyridine	N21
2-ethylpyridine	N17	2,6-dimethylpyridine	N22
3-ethylpyridine	N18	8-methyl-2H-pyrano(2,3-c)pyridine	N24
2,3-dimethylpyridine	N20	2-pyridinecarbonitrile	N25
2,4-dimethylpyridine	N21	2-pyridinamine	N26
2,6-dimethylpyridine	N22	3-methylbenzonitrile	N27
4-methylbenzonitrile	N28	4-methylbenzonitrile	N28
benzeneacetonitrile	N29	benzeneacetonitrile	N29
4-hydroxybenzonitrile	N31	2-methylbenzoxazole	N37
2,4-pentadienenitrile	N34	2-methylenebutyronitrile	N51
Isoquinoline	N35	hexadecanenitrile	N52
1,2-benzisoxazole	N36	dodecanenitrile	N53
2-methylbenzoxazole	N37	heptadecanenitrile	N54
4-methylphenylisocyanide	N44		
3-methylphenylisocyanate	N45		
benzothiazole	N46		
aniline	N47		
1H-indol-5-ol	N48		
undecanenitrile	N49		
tricyclo[3.1.0.02,6]hex-3-ene-3-caarbonitrile	N50		

Isoprenic compounds

Nanoclay Cambisol		Clay Cambisol	
2--methylbutanal	I1	2--methylbutanal	I1
3--methylbutanal	I2	3--methylbutanal	I2
2-methyl-cyclohexa-1,3-diene	I6	(Z)-1,3-Pentadiene	I3

| Isoprene | I10 | trimethyl-1,3-cyclopentadiene | I9 |
| bicyclo[4.2.0]octa-1,3,5-triene | I13 | | |

Compound derived from lipidsç

1-decene	Lp1	(Z)-2-decene	Lp3
4-decene	Lp2	undecane	Lp6
(Z)-2-decene	Lp3	1-undecene	Lp7
(Z)-3-decene	Lp4	5-undecene	Lp8
undecane	Lp6	tetradecane	Lp11
5-undecene	Lp8	1-tetradecene	Lp12
(E)-3-undecene	Lp9	hexadecane	Lp14
(E)-4-undecene	Lp10	nonadecane	Lp19
(E)-2-tetradecene	Lp13	dodecane	Lp20
1-hexadecene	Lp15	1-dodecene	Lp21
pentadecane	Lp16	tridecane	Lp23
octadecane	Lp18	1-tridecene	Lp24
dodecane	Lp20	1-octadecene	Lp27
(Z)-2-dodecene	Lp22	1-nonadecene	Lp27
(Z)-6-tridecene	Lp25	1-nonene	Lp28
1-tridecene	Lp24	1-docosene	Lp29
heptadecane	Lp32	heneicosane	Lp30
		2-methyl-Z-2-docosane	Lp31

Compounds of unspecific origin

phenol	U1	phenol	U1
1,1'-biphenyl	U2	1,1'-biphenyl	U2
2-methylphenol	U6	2-methylphenol	U6
3-methylphenol	U7	4-methylphenol	U8
4-methylphenol	U8	2,3-dimethylphenol	U9
naphthalene	U11	naphthalene	U11
indene	U16	2-methylnaphthalene	U13
benzene	U22	indene	U16
styrene/ethylbenzene	U23	1-methyl-1H-indene	U17
Toluene/ methylbenzene	U24	benzene	U22
1-ethyl-2-methylbenzene	U25	styrene/ethylbenzene	U23
1-ethyl-2,3-dimethylbenzene	U26	Toluene/ methylbenzene	U24
1,2,4-trimethylbenzene	U28	1-ethyl-2-methylbenzene	U25
1,2,3-trimethylbenzene	U29	1,2,4-trimethylbenzene	U29
p-xylene	U30	1,2,3-trimethylbenzene	U30
1,2-xylene	U31	p-xylene	U31
1,3-xylene	U32	1,2-xylene	U32
vinyltoluene/methylstyrene	U34	3-methylstyrene/3-vinyltoluene	U35
3-methylstyrene/3-vinyltoluene	U35	4-methylstyrene/4-vinyltoluene	U36
2,4-hexadienal/ sorbaldehyde	U37	2,4-hexadienal/ sorbaldehyde	U37
1-propylbenzene	U39	propylbenzene	U38
2-propenylbenzene	U40	1-butylbenzene	U62
1-methylpropylbenzene	U53	2-phenyl-1-methylenecyclopropane	U63
1-methyl-4-(2-methylpropyl)-benzene	U54	hexylbenzene	U64
hexylbenzene	U55	C17H26NO5P (PM 355,15)	U65
heptylbenzene	U56		
1-hetylheptyl-benzene	U57		

benzaldehyde	U58		
1-ethylundecyl-benzene	U59		
1-methyldodecyl-benzene	U60		
1-butylnonylbenzene	U61		

biomass (Pognani et al., 2011)

decamethylcyclopentasiloxane	S3	hexadecamethylcyclooctahexasiloxane	S1