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Pyrolysis–gas chromatography applied to the study of organic matter evolution in sewage sludge-amended soils using nitrogen–phosphorus, flame ionization and mass spectrometric detection

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Abstract

Pyrolysis in combination with gas chromatographic separation and simultaneous nitrogen–phosphorus and flame ionization detection is proposed for the determination of nitrogen compounds in soils. Peak identification was performed by mass spectrometry. The technique is considered as a complementary tool for use with other techniques for soil organic matter studies. The pyrolysis probe was placed directly in the horizontal injection port of a Perkin-Elmer Model 8700 chromatograph coupled with a nitrogen-selective detector and a flame ionization detector and into the vertical injection port of an HP-5890A chromatograph coupled with an HP-5989 mass spectrometer. This technique was applied to study the evolution of the organic matter in soils amended with sewage sludge samples.

1. Introduction

The high volumes of sewage sludge generated during the processing of sewage is a matter of concern [1]. At present, the alternatives for their final destiny are elimination, by incineration or disposal (in the sea or controlled deposits), and recycling. Elimination is not a satisfactory solution, because it contributes to environmental contamination (chemical products, microorganisms and odours). The possibility of recycling sewage sludge of great interest and could lead to important economical and ecological benefits.

The high fertilization power of these matrices and their advantageous effects on the physical and chemical properties of soil have been demonstrated. For this reason, the possibility of reusing sewage sludge has been studied. This recycling would permit the restoration of impoverished soils, such as quarry stone and taluses.

Pyrolysis–Gas chromatographic (Py–GC) analysis appears to be a suitable technique for studying the characterization of soil organic matter [2–5], especially because of its polymeric nature, which makes analysis by other conventional techniques difficult. Moreover, Py–GC using MS detection [6] has emerged as an interesting technique for the identification of the main pyrolysis fragments.

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The simultaneous use of a universal detection method [flame ionization detection (FID)] and a selective one method [nitrogen–phosphorus detection (NPD)] permits the study of organic matter in general (FID) and particularly of nitrogenated organic matter (NPD), especially the non-proteic fraction (unidentified). The study of fragmentation is useful for elucidating the nature of the matrix. The correlation between pyrolysates and different kinds of original matrices (lignins, carbohydrates, proteins, fatty acids, humic substances) has been discussed [7–9].

In this work, the evolution of organic matter in soils amended with sewage sludge, in both laboratory and field experiments, was studied. The first aim was to study the evolution of organic matter by monitoring the different pyrolysates using a GC technique. Finally, it was checked whether the results obtained in the field experiments are comparable to those obtained in the laboratory experiments.

2. Experimental

For the laboratory experiments (lysimeter), a brownish limey soil (calcixerollic xerochrept) with a low content of organic matter was used. The samples were obtained from the Universitat Autònoma de Bellaterra (Bellaterra, Barcelona, Spain) [1]. Sewage sludge was obtained from the water-treatment plant DARGISA (Girona, Spain) after anaerobic treatment.

Two different amounts of sewage sludge were added to the soil. The first case, with a 7.5% content of sewage sludge in soil, refers to the maximum proportion allowed by the EEC, according to the amount of heavy metals present in sewage sludge [10]. The second case, with a 15% content of sewage sludge in soil, attempts to evaluate the possible effects of too high a proportion of sewage sludge in soil [1].

In the laboratory experiments, mixtures were made in 12-kg containers (lysimeters) provided with a drainage device that permits the lixivates coming from periodic irrigation to be collected. In the field experiments, sewage sludge was added to quarry stone (Rubau, Girona, Spain). The proportions of sewage sludge in the soils were the same as before, but the addition was made in two different ways; type A, direct application of sewage sludge to the soil and further mixing; and type B, prior mixing of the soil and the sludge and further application. A device to collect the lixivates originating from the percolation of rain water through the soil was incorporated. In both experiments sampling was carried out following statistical criteria that permit a good representativeness of samples [11]. Air-dried samples (<2 mm) were frozen to avoid evolution. Before being pyrolysed the samples were defrozen, dried at 105°C and sieved (<90 μm) to obtain a homogeneous sample.

2.1. Pyrolysis–gas chromatography with simultaneous NPD–FID

The pyrolysis [12] unit employed was a CDS Pyroprobe 1000 (Chemical Data Systems, Oxford, PA, USA) with a platinum coil probe. All samples were pyrolysed at 700°C for 10 s at a heating rate of ca. 10°C/ms.

Milled and dried samples were placed into a quartz tube (Kromxpek, Barcelona, Spain). The tube was then placed in the platinum coil. The gas chromatograph was a Perkin-Elmer (Norwalk, CT, USA) Model 8700. Separation of the pyrolysis products was achieved using a Supelcowax 10M (Supelco, Bellefonte PA, USA) polythylene glycol bonded-phase fused-silica capillary column (30 m × 0.32 mm I.D.) with a 0.32-μm film thickness. Pyrolysis products were injected in the splitless mode with cold trapping at room temperature for 2 min. The column oven temperature was held at 50°C for 2 min, then programmed at 6°C/min to 240°C. Helium was employed as the carrier gas (0.1 MPa) and carbon dioxide–acetone was used as a coolant for the cold trap.

An splitter was available at the end of column,

allowing pyrolysates to be detected by NPD and FID.

2.2. Pyrolysis–gas chromatography–mass spectrometry

The gas chromatograph (HP-5890; Hewlett-Packard, Palo Alto, CA, USA) was programmed using the same temperature programme as used in Py–GC-NPD and the separations were performed on a Supelcowax 10 M column. The pyrolysis probe was directly connected to the capillary GC standard injection port without using any kind of interface [13], in order to avoid dead volumes, cold spots and expensive equipment. Helium was used as the carrier gas (0.1 MPa). The mass spectrometer was an HP-5989 (electron impact ionization, 70 eV). Identification was achieved by mass fragmentography, library searches and comparison with literature data.

2.3. Elemental analysis

Elemental analysis was performed with an EA 1108 elemental analyser (Carlo Erba, Milan, Italy).

3. Results

The chromatograms of the pyrolysis products obtained with FID and NPD are showed in Fig. 1. Compound identification (Tables 1 and 2) was achieved with standards [13] or from the MS analysis.

The identified NPD and FID peaks were grouped into families to assist the evolution study of different samples (Table 3). To calculate these families, the relative areas of each peak were added. This relative area was calculated as the ratio between the absolute area and the total of all selected peak areas.

The results obtained for the families in both laboratory and field experiments are shown in Figs. 2–5.

The results obtained for the elemental analysis of the samples in the laboratory experiments are given in Table 4.

4. Discussion

The satisfactory resolution achieved by using a Supelcowax 10 M column can be clearly appreciated from the chromatograms in Fig. 1. This good resolution is possible thanks to the polar nature of the pyrolysates. The use of NPD, which is more selective and sensitive, permits a more exhaustive study of the organic nitrogenated fraction to be performed.

The application of the pyrolytic method to the different samples leads to the following conclusions:

(1) In the results obtained in the laboratory experiments (lysimeter), no clear evolution is observed. However, Table 4 shows the evolution of organic matter, corroborating previous studies [1]. This evolution cannot be observed by using pyrolysis techniques. This is due to the high initial content of sewage sludge in the sample. Even though evolution takes place, the remaining organic fraction comes from the sludge. For this reason, the pyrograms of such samples are similar to those of sewage sludge.

(2) In the results obtained in the laboratory experiments, an important decrease in the indole family is observed. The precursors of this family are certain amino acids (e.g., tryptophan), belonging to the most easily degradable proteic fraction. Hence the amendment of sludge to the soil leads to a decrease in the content of fresh organic matter.

(3) The results obtained in the field experiments (quarry stone) led to similar conclusions. Using FID and NPD, no evolution is observed. Moreover, an important decrease in the indole family is also observed, with a resulting decrease in the content of fresh organic matter. However, a difference between the two types of experiments is observed. In the first case (quarry stone), a considerable decrease in the aromatic nitrile compounds is observed, possibly because

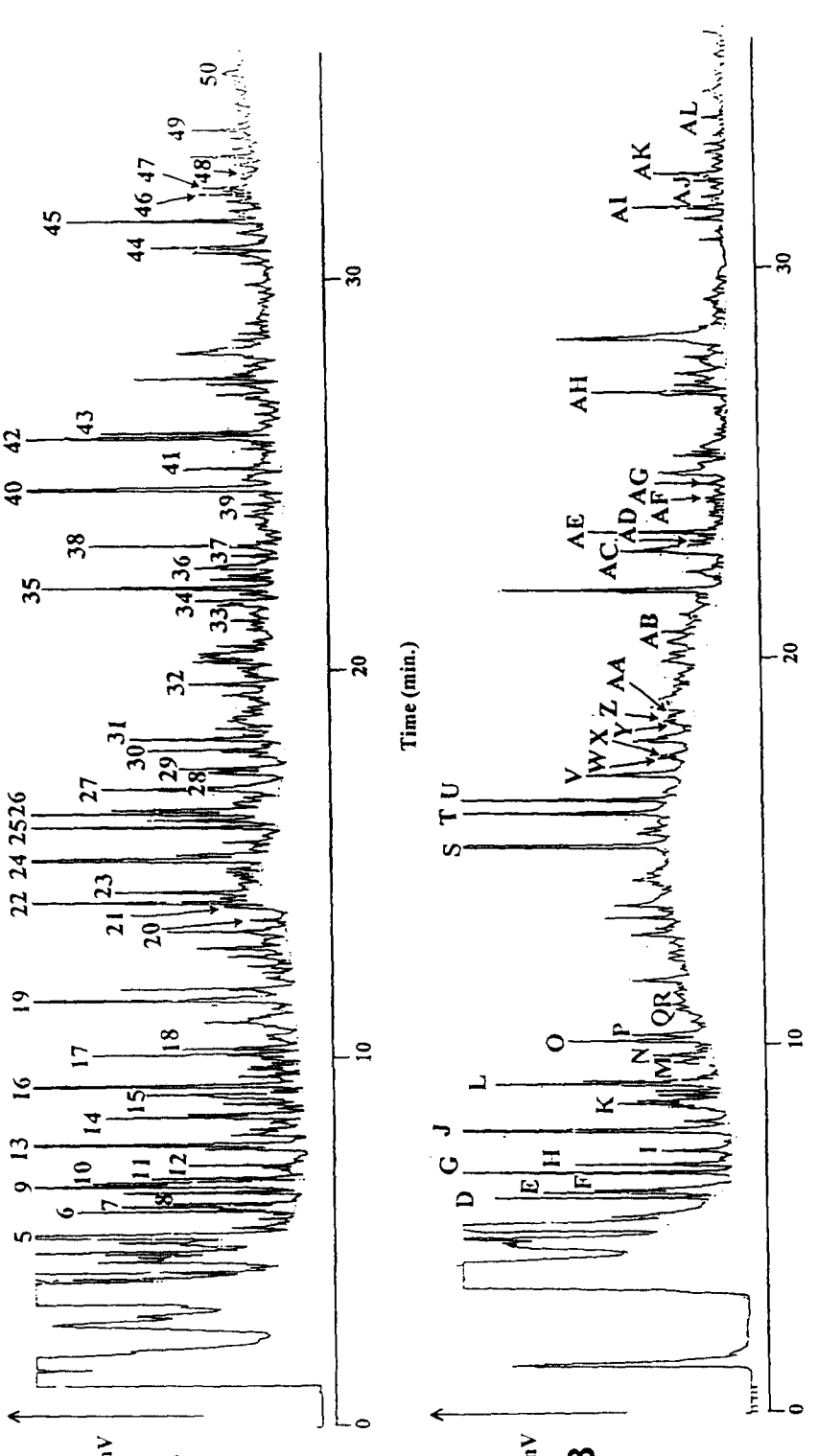

Fig. 1. (A) FID chromatogram. The numbers indicate the compounds identified in Table 1. (B) NPD chromatogram. The letters indicate the compounds identified in Table 2.

Table 1
Pyrolysates detected by FID

No.	Pyrolysis product	t_R (min)	No.	Pyrolysis product	t_R (min)
1	Benzene	4.2	26	2-Methylpyrrole	16.4
2	Acrylonitrile	4.7	27	Benzonitrile	17.0
3	Acetonitrile	4.8	28	2,5-Dimethylpyrrole	17.5
4	Propionitrile	5.0	29	2,4-Dimethylpyrrole	17.6
5	Toluene	5.1	30	Hexadecane	18.1
6	Isocyanoethane	5.8	31	Hexadecene	18.4
7	Butyronitrile	5.9	32	Naphthalene	19.8
8	3-Butenenitrile	6.0	33	2-Methylnaphthalene	21.5
9	*m*, *p*-Xylene	6.5	34	1-Methylnaphthalene + guaiacol	22.1
10	*o*-Xylene	6.6	35	Octadecene	22.4
11	N-Methylpyrrole	6.7	36	3-Nitrilepyridine	23.0
12	2-Butenenitrile	7.1	37	2-Aminopyridine	23.3
13	Pyridine	7.6	38	Benzyle cyanide	23.5
14	2-Methylpyridine	8.3	39	2,3-Dihydro-1*H*-inden-1-ona	24.6
15	Dodecene	8.9	40	Phenol + *o*-cresol	25.0
16	Styrene	9.1	41	Benzenepropanitrile	25.6
17	3-Methylpyridine	10.0	42	*m*-Cresol	26.3
18	4-Methylpyridine	10.1	43	*p*-Cresol	26.5
19	Cyclopentenone + 2-methylcyclopentenone	11.4	44	Coumaran (2,3-dihydrobenzofuran)	31.4
20	Tetradecene	13.6	45	Indole	32.1
21	Indene	13.9	46	3-Methylindole (skatole)	32.8
22	Furfural	14.0	47	2-Methylindole (skatole)	33.0
23	Acetic acid	14.3	48	Dodecanoic acid	33.4
24	Pyrrole	15.2	49	Hepta- + octadecanenitrile	34.5
25	3-Methylpyrrole	16.0	50	Tetradecanoic acid	36.0

Table 2
Pyrolysates detected by NPD

Identification	Pyrolysis product	t_R (min)	Identification	Pyrolysis product	t_R (min)
A	Acrylonitrile	4.7	T	3-Methylpyrrole	16.0
B	Acetonitrile	4.8	U	2-Methylpyrrole	16.4
C	Propionitrile	5.0	V	Benzonitrile	17.0
D	Isocyanoethane	5.8	W	2,5-Dimethylpyrrole	17.5
E	Butyronitrile	5.9	X	2,4-Dimethylpyrrole	17.6
F	3-Butenenitrile	6.0	Y	2,3,5-Trimethylpyrrole	18.3
G	Valeronitrile	6.5	Z	4-Ethyl-2-methylpyrrole	18.4
H	N-Methylpyrrole	6.7	AA	2-Methylbenzonitrile	18.5
I	2-Butenenitrile	7.1	AB	Acetamide	20.8
J	Pyridine	7.6	AC	3-Nitrilepyridine	23.0
K	2-Methylpyridine	8.3	AD	2-Aminopyridine	23.3
L	4,5-Dihydro-4,5-dimethyl-1H-pyrazol	8.8	AE	Benzyl cyanide	23.5
M	2,6-Dimethylpyridine	9.3	AF	Acetylpyrrole	24.6
N	2,4 + 2,5-Dimethylpyridine	9.6	AG	2-Aminobenzonitrile	24.8
O	3-Methylpyridine	10.0	AH	Benzenepropanitrile	25.6
P	4-Methylpyridine	10.1	AI	Indole	32.1
Q	2,3 + 3,4-Dimethylpyridine	10.8	AJ	3-Methylindole (skatole)	32.8
R	3,5-Dimethylpyridine	11.0	AK	2-Methylindole (skatole)	33.0
S	Pyrrole	15.2	AL	Hepta- + octadecanitrile	34.5

Table 3
Grouping of pyrolysates in different families by FID and NPD

Detection method	No.	Family	Pyrolysis products[a]
FID	1	Nitrogenated compounds	6, 7, 8, 11, 12, 13, 14, 17, 18, 24, 25, 26, 27, 28, 29, 36, 37 38, 41, 45, 46, 47, 49
	2	Aromatic hydrocarbons	5, 9, 10, 16, 21, 32, 33, 34, 44
	3	Phenolic compounds	40, 42, 43
	4	Carbonyl compounds	19, 22, 23, 39
	5	Aliphatic hydrocarbons	15, 20, 30, 31, 35
	6	Fatty acids	48, 50
NPD	A	Pyrroles	H, S, T, U, W, X, Y, Z, AF
	B	Pyridines	J, K, M, N, O, P, Q, R, AD
	C	Aliphatic nitriles	E, F, G, I, AL
	D	Aromatic nitriles	V, AA, AC, AE, AG, AH
	E	Others	D, L, AB
	F	Indoles	AI, AJ, AK

[a] See Tables 1 and 2 for identification.

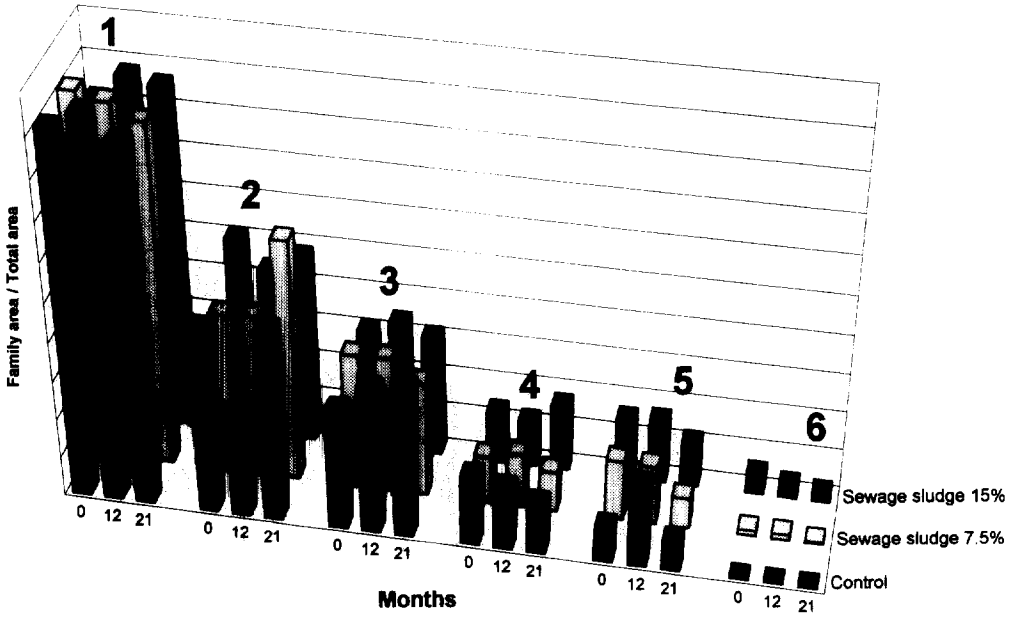

Fig. 2. Lysimeter family analysis with FID. (1) Nitrogen-containing compounds; (2) aromatic hydrocarbons; (3) phenolic compounds; (4) carbonyl compounds; (5) aliphatic hydrocarbons; (6) fatty acids.

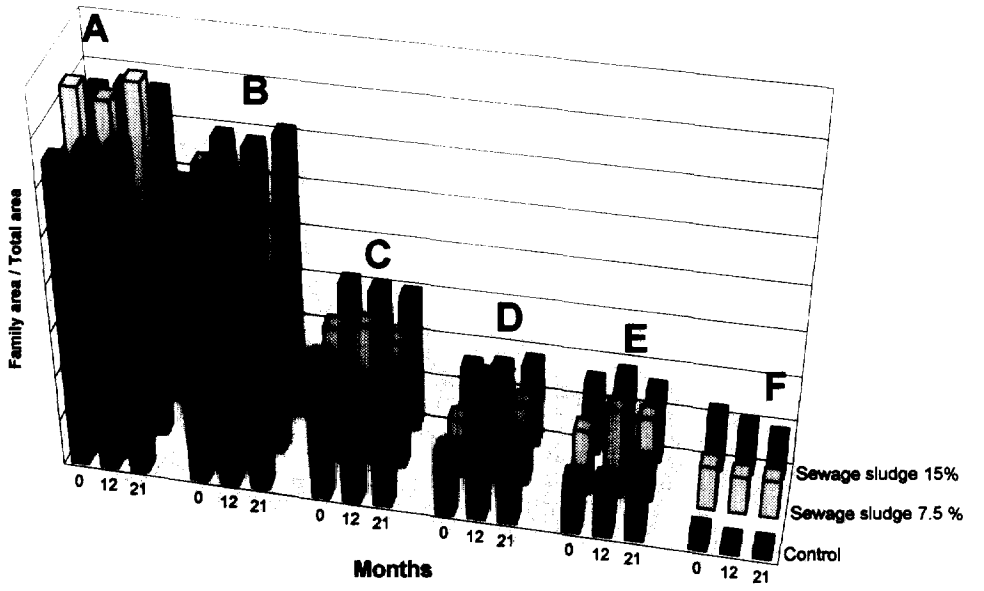

Fig. 3. Lysimeter family analyses with NPD detection. (A) Pyrroles; (B) pyridines; (C) aliphatic nitriles; (D) aromatic nitriles; (E) others; (F) indoles.

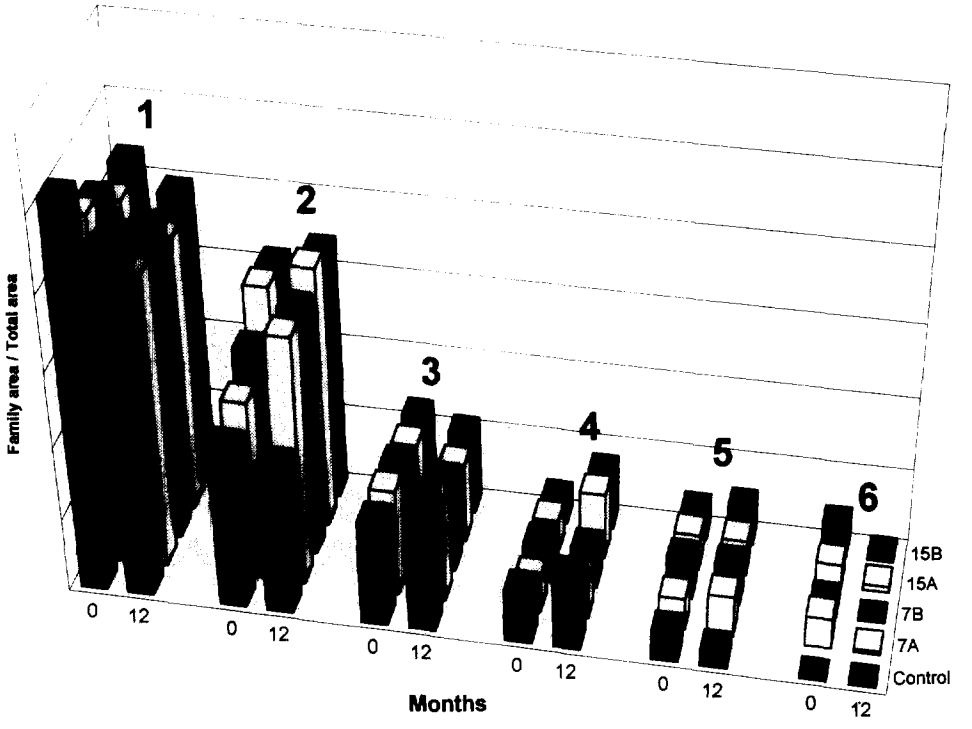

Fig. 4. Quarry stone family analyses with FID. (1) Nitrogen-containing compounds; (2) aromatic hydrocarbons; (3) phenolic compounds; (4) carbonyl compounds; (5) aliphatic hydrocarbons; (6) fatty acids.

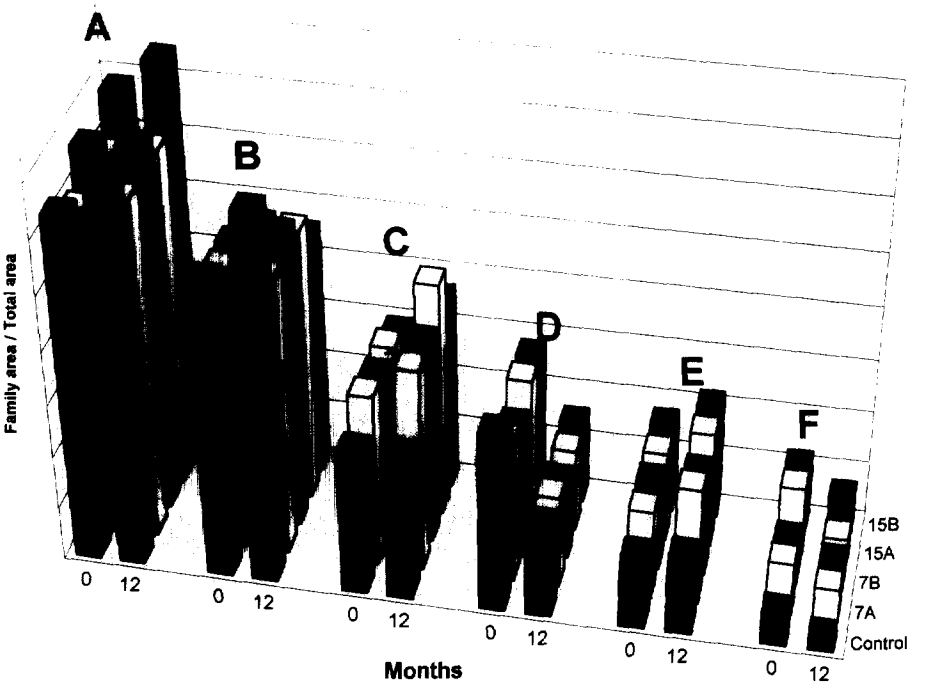

Fig. 5. Quarry stone family analyses with NPD. (A) Pyrroles; (B) pyridines; (C) aliphatic nitriles; (D) aromatic nitriles; (E) others; (F) indoles.

Table 4
Elemental analysis (laboratory experiments)

Element	Control			Sewage sludge 7.5%			Sewage sludge 15%			Sewage sludge
	0[a]	1[a]	1.7[a]	0[a]	1[a]	1.7[a]	0[a]	1[a]	1.7[a]	
Total N (%)	0.10	0.10	0.10	0.33	0.28	0.29	0.56	0.41	0.41	4.45
Total C (%)	3.81	3.81	3.69	5.25	4.91	4.89	6.59	5.70	5.56	29.71

[a] Evolution time (years)

of the presence of vegetation and other kinds of bacteria in the field experiments.

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