

SOIL MINERALOGY EVOLUTION IN THE INRA 42 PLOTS EXPERIMENT (VERSAILLES, FRANCE)

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Abstract—Natural soils change by long-term pedogenetic mechanisms, but tillage effects can also strongly affect the evolution of soils, mainly their physicochemical properties. The present paper describes the impact of fertilizers and amendments on soil mineralogy in experimental plots, without plant interaction.

The soils of the 42 plots experiment at the INRA experimental station in Versailles (France) have been managed with fertilizers without plant growth since 1929. Strong changes in pH were observed and cation exchange capacities doubled between low and high pH (from 3.6 to 8.2). Strong acidification caused more evolution in the clay particle distribution without selective action on the clay composition.

While the clay content varied only slightly, the organic matter content changed considerably, decreasing with non-organic treatment and increasing in the plot with manure treatment. The major clay minerals in the experimental plots are two disordered illite-smectite mixed-layer minerals, with minor amounts of illite/mica and kaolinite. Most treatments effected only minor changes in clay mineralogy. However the illite (non-expandable mineral) content increased in plots with K addition either as KCl treatment or in manure amendments by increasing the illite content and the illite (non-expandable layer) content of the I-S minerals. Manure changed the I-S mineral to a greater extent.

Key Words—Fertilizers, Illite-smectite Mixed-layer Mineral, Long-term Experiment, Potassium.

INTRODUCTION

Experimental plots have been created to determine the effect of certain agricultural practices on soil and soil fertility. Most often such experiments are designed to determine the effect of cropping, with rotation or non-rotation of plantings, of soil tillage or of fertilizer treatments on the overall soil fertility. Recent studies (Velde and Peck, 2002) demonstrated the importance of plant species as they affect the soil clay mineralogy.

Most texts on soil chemistry tend to concentrate on the heritage and climatic effects on soil substrates as they produce and define the soil clay mineralogy. The chemistry of the soil solution is often considered the most important factor concerning the stability of the silicate mineralogy. However, it is well established that plant growth interacts with soil minerals by K fixation and release in controlled conditions (Badraoui *et al.*, 1992). This mechanism depends strongly on the clay mineralogy (Pal *et al.*, 2001). The illite and mica contents increase with the K fixation in clays under the influence of plants (Tice *et al.*, 1996) and with manure application (Ross *et al.*, 1985). The contribution of K to the transformation of smectite minerals into illite-smectite (I-S) mixed-layered minerals is also well known. But this transformation has been studied mainly in experimental systems at elevated temperatures or by chemical reactions (Inoue *et al.*, 1988; Eberl *et al.*,

1993). In the University of Illinois Morrow plot experiment, Velde and Peck (2002) found that I-S minerals play the role of K buffer for plant growth. The illite content decreased due to K release to plants. By contrast, Poonia (1996) demonstrated the contribution of organic matter in K fixation and in the conversion of smectite to illite.

Because, in long-term experiments, soils are always cropped, the effect of fertilizers on clay mineral properties cannot be demonstrated independently of the role of plants. It is particularly important to separate two main effects: the role of plants in K dynamics and the specific relationship between fertilizers and soil constituents. The '42 plots' experiment established by INRA (Institut National de la Recherche Agronomique) at Versailles (France) was designed to explore the mineralogical and physical evolution, after long-term application of fertilizing treatments, of soil which was kept free of plants. This paper deals with the clay mineralogy and structural changes in clay minerals in a large range of pH and of chemical environments, as well as those due to a loss or gain of organic matter. In particular, this study emphasizes exchangeable K and I-S minerals.

SOIL MATERIAL AND METHODS

The '42 plots' experiment of INRA in Versailles (France) received the same fertilizer or amendment applications each year since 1929. The plots were dug twice a year and left fallow, without plants. Samples were collected in 1999 and compared to a reference

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sample that has been kept air dried since 1929. The studied plots were as follows: plot number (11): reference plot without treatment; (12) organic matter (horse manure); (14): acid treatment ($(\text{NH}_4)_2\text{HPO}_4$); (17) sodic treatment (NaNO_3); (26) basic treatment (CaO); (35) basic treatment (basic slag); (37) potassic treatment (KCl)

Soil physicochemical characteristics (pH in water, clay fraction, organic carbon) of the <2 mm fraction were measured according to the French norms of AFNOR (1996). Fine clay-fraction particle-size distributions were measured by laser diffractometry. Cation exchange capacity (CEC) and exchangeable cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) were determined at soil pH by cobaltihexamine extraction (Ciesielski and Sterckeman, 1997) and exchangeable aluminum by the KCl method (McLean, 1986).

For XRD analysis, <2 μm and $2\text{--}5$ μm fractions were extracted by centrifugation from the initial sample without chemical treatment (natural clay) or after organic matter oxidation. If necessary, carbonates were removed using the method of Robert and Tessier (1974) (H_2O_2 -treated clay). X-ray diffraction patterns were obtained from Ca-saturated clay. All oriented air-dried or ethylene glycol-solvated specimens were analyzed using the same amount of clay. They were run on a Siemens D5000 diffraction system using $\text{CoK}\alpha$ radiation. The XRD patterns were recorded numerically using the Diffrac AT software (SOCABIM, France).

The spectra of the illite and I-S region between 2 and $12^\circ 2\theta$ ($\text{CoK}\alpha$) were decomposed into elementary component curves with the program DECOMPXR (Lanson, 1997). Comparisons between natural and treated clays were made using smoothed and background-stripped XRD patterns. The program used Gaussian-shaped peaks for $\text{K}\alpha_1 + \text{K}\alpha_2$ doublets. Best fits were made with three or four elementary peaks. The position, FWHM (full width at half maximum intensity) and intensity of every peak were adjusted until the fit parameters were optimized.

The NEWMOD program (Reynolds, 1985) was used for modeling changes in the I-S proportion. The model used for I-S is based upon a two-component, disordered ($R = 0$), mixed-layered mineral assemblage, the propor-

tions of illite and smectite components and coherent diffracting domain being the variables.

EXPERIMENTAL RESULTS

Soil constitution and physicochemical properties

Soil plot characteristics are presented in Table 1. The clay content was similar except for the most acidic and the sodic plots, according to the variation from the reference plot values (content in % ± 1.1). The proportion of fine clay (<0.4 μm) determined by laser diffractometry was $\sim 17\%$ of the clay fraction in the 1999 plots which were identical to the reference 1929 plot. For the acid and the sodic plots, fine clays were only $\sim 13\%$ of the clay fraction.

If particle-size distribution varied little, by contrast, the organic matter content changed considerably. In 1929 the total carbon content was 1.6%. In the 1999 plots, the whole-soil organic carbon ranged from 0.5 to 0.7% except in the case of manure treatment where it doubled to 3.2%. In the clay fraction, the organic carbon decreased from 4.1% in 1929 to $\sim 1.8\%$ in 1999, except for the organic plots (5.5%). After H_2O_2 treatment, carbon oxidation was not complete.

Chemical characteristics (Table 2) changed dramatically over 70 years. From a pH of 6.3 in 1929, the pH values in the plots either increased, did not change or decreased. In 1999, pH ranged from 3.6 to 8.2. More precisely, in the untreated reference plot, the pH decrease was ~ 0.7 units and the lowest decrease was in the acid plot receiving ammonium treatments with $(\text{NH}_4)_2\text{HPO}_4$ (pH = 3.6). On plots amended with CaO and basic slag, the pH was 8 or above. The manure also increased the pH. Neutral salts (KCl or NaNO_3) did not change the pH value.

The soil cation exchange capacity (CEC_{soil}) doubled from acid plots to basic plots. In the reference plot, the CEC_{soil} decreased from 15.3 to 8.7 $\text{cmol}^+ \text{kg}^{-1}$ while the ammonium-treated plot had the lowest CEC (6.2 $\text{cmol}^+ \text{kg}^{-1}$) and the organic plot the highest value (18.7 $\text{cmol}^+ \text{kg}^{-1}$). Neutral treatments had no specific effect compared to that of the reference plot. In the basic plots, the CEC_{soil} had decreased a little since 1929 ($\sim 13.8 \text{ cmol}^+ \text{kg}^{-1}$).

Table 1. Organic matter and particle-size distribution.

Plot (number) Year	Clay fraction <2 μm (g kg^{-1} of <2 mm)	Fine clay fraction <0.4 μm (g kg^{-1} of <2 μm)	Organic carbon (g kg^{-1})		
			In soil	In clay	In H_2O_2 -treated clay
Reference (11) 1929	194	170	16	41	3.0
Reference (11) 1999	184	181	7.1	18	2.3
Basic (26) 1999	169	168	5.8		
Basic (35) 1999	173	167	7.1		
Sodic (17) 1999	152	135	6.1		
Acid (14) 1999	146	126	9.2		
Potassic (37) 1999	189	174	5.1	17	2.1
Manure (12) 1999	201	161	32	55	5.5

Table 2. Physicochemical characteristics of some plots in the '42 plots' experiment in 1929 (for reference) and in 1999.

Plot (number)	Year	pH (in water)	At soil pH (measured by cobaltihexamine method)	CEC	Ca^{2+}	Mg^{2+}	K^+	Na^+	(in $\text{cmol}^\circ \text{kg}^{-1}$)	Al^{3+}
Reference (11)	1929	6.3	15.3	13.3	1.3	0.2	0.2	0.1	0	0
Reference (11)	1999	5.6	8.7	5.1	0.7	0.2	0.2	0.04	0.04	2.2
Basic (26)	1999	8.2	13.6	13.1	0.3	0.2	0.2	0.03	0	0
Basic (35)	1999	8.0	14.0	13.0	0.4	0.1	0.1	0.04	0	0
Sodic (17)	1999	6.4	8.5	4.7	0.5	0.3	0.3	1.0	1.0	1.1
Acid (14)	1999	3.6	6.2	0.2	0.2	0.2	0.1	0.01	0.01	6.4
Potassic (37)	1999	6.3	10.2	6.5	0.7	2.0	2.0	0.04	0.04	0.4
Manure (12)	1999	7.8	18.7	12.4	2.4	3.4	3.4	0.1	0.1	0

Exchangeable cations depend on pH and CEC_{soil} values. For the lowest pH values, the dominant exchange cation was Al and other cations represented <10% of the CEC_{soil} . On the other hand, in basic plots, the alkaline and alkaline-earth cations saturated the CEC_{soil} . Exchangeable Al was only present below $\sim\text{pH } 6.5$. Exchangeable K and Na were $<0.3 \text{ cmol}^\circ \text{ kg}^{-1}$ and $0.05 \text{ cmol}^\circ \text{ kg}^{-1}$, respectively, except in specific K^+ or Na^+ treatments. In the KCl treatment plot, exchangeable K was 18.7% and was ~ 10 times greater ($2.0 \text{ cmol}^\circ \text{ kg}^{-1}$) than in the acid-treated soil. Notice that the organic plot is distinguished by having the highest exchangeable K content ($3.4 \text{ cmol}^\circ \text{ kg}^{-1}$), greater than that with KCl treatment.

Clay mineralogy

Clay minerals present. The XRD analysis on the $<2 \mu\text{m}$ soil fraction shows a large peak in the $15\text{--}17 \text{ \AA}$ region, which is displaced to 17 \AA upon glycol solvation indicating the presence of a disordered mixed-layer I-S. Other peaks, near 10 and 7.14 \AA , indicate the presence of illite-like layers (referred to as illite-mica peaks) and kaolinite. The illite-mica peak was decomposed into a wider illite band near 10.3 \AA and a sharp mica band at 10.0 \AA . The XRD patterns of the $2\text{--}5 \mu\text{m}$ fraction present the same mineral assemblage with the addition of a chlorite peak at 14.4 \AA .

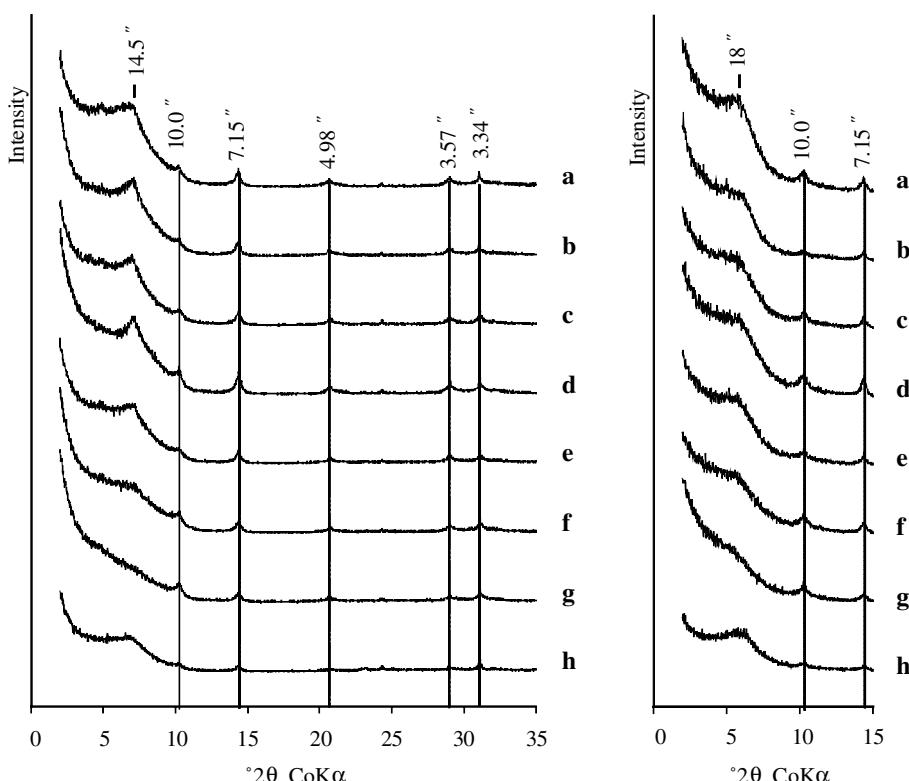


Figure 1. XRD patterns for the $<2 \mu\text{m}$ fraction of some plots of the 42 experimental plots. H_2O_2 -treated, Ca-saturated, air-dried (left) or ethylene glycol-solvated (right). $\text{CoK}\alpha$ radiation. Comparison between: (a) reference in 1929, (b) reference in 1999, and different treatments in 1999: (c,d) basic, (e) sodic, (f) potassic, (g) manure, (h) acid.

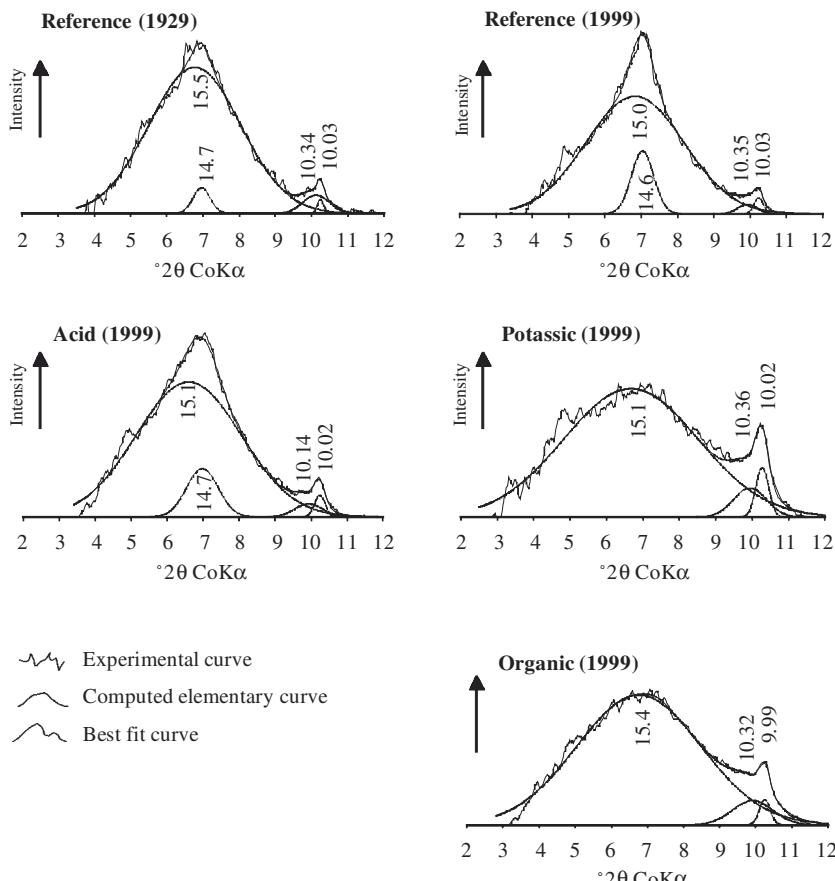


Figure 2. Decomposed XRD diagrams of H_2O_2 -treated clay fraction; Ca-saturated, air-dried. $\text{CoK}\alpha$ radiation, d spacing in \AA .

Mixed layer I-S minerals. Figure 1 shows the XRD pattern of the $<2 \mu\text{m}$ samples run in the air-dried and glycol-saturated states. The clay mineral assemblage is dominated by a mixed-layered I-S indicated by a wide peak in the $15\text{--}17 \text{\AA}$ region and the high background to higher d values and low diffraction angles. The background-subtracted patterns of treated clay and the decomposition peaks derived from them (Figure 2, Table 3) show that this mixed-layer I-S is composed of two peaks, one small and sharp peak at 14.7\AA and a large peak near 15.2\AA . Both are displaced to 17\AA upon glycol saturation and disappear on heating at 200°C .

In order to follow more closely the evolution of the I-S minerals with treatment, the NEWMOD program (Reynolds, 1985) was used to model the XRD pattern of I-S for air-dried samples (Figure 3). The assumption has been made that this is a two-component system in which smectite has two water layers around the Ca exchange cation. The best simulation was obtained using a rather small coherent diffraction domain (1–4 layers) which gives a wide 15.4\AA peak. The XRD spectrum for the 1929 sample has been modeled using a 50% mica–50% smectite component interstratified structure ('a' in Figure 3). Such a model is valid for all except the KCl

and manure treatment plots. The best fit for clay minerals from the manure-treated plot was made using a proportion of 70% mica–30% smectite ('c' in Figure 3). An intermediate composition simulated the clays from the K-treated plot clays (40% smectite, 'b' in Figure 3). The smaller, sharper diffraction peak (revealed on spectrum decomposition) can be modeled using a larger domain size of layer stacking. The 3–6 layer model displaced this peak to near 14.5\AA .

Given the above, we identify the following minerals in the various plots: minor kaolinite, minor illite and mica, and a minor large domain size I-S of near 50% smectite and a much more abundant I-S with smaller diffracting domain but the same smectite content.

Effect of organic matter oxidation. Subtracted-background patterns for samples in the air-dried state, before and after oxidation of the organic matter (which removes easily oxidized matter), are presented in Figure 4. After H_2O_2 treatment, XRD patterns from the 1929 reference sample, from the manure-treated plot and from the KCl-treated plot showed an overall shift to higher d value of the mixed-layered minerals. However, there is no oxidation effect of the organic matter in the 1999 untreated sample.

Table 3. Characteristics of decomposed XRD patterns.

Plot (Number)	Year	Natural clay		Treated clay	
		Peak position	FWHM	Peak position	FWHM
a	Reference (11) 1929	14.74	3.23	15.54	3.44
		14.46	0.53	14.70	1.03
		10.25	1.21	10.34	0.92
		10.01	0.31	10.03	0.35
b	Reference (11) 1999	15.14	3.61	15.03	3.18
		14.56	0.76	14.58	0.73
		10.31	1.14	10.35	0.62
		10.04	0.46	10.03	0.29
c	Acid (14) 1999			15.14	2.99
				14.74	0.55
				10.14	0.84
				10.02	0.20
d	Potassic (37) 1999	14.90	4.50	15.17	4.04
		—	—	—	—
		10.38	1.02	10.36	1.32
e	Manure (12) 1999	10.01	0.33	10.02	0.35
		15.20	4.15	15.38	4.35
		—	—	—	—
		10.28	1.00	10.32	1.06
		10.01	0.32	9.99	0.42

Changes in mineralogy in different plots

The XRD patterns and their decomposed peaks indicate that only minor changes in clay mineralogy occurred from one treatment to another (Figures 1 and 2).

The major change observed is in the background intensity at low angles. This effect is especially clear in the glycol-saturated samples. The highest low-angle background and the most poorly defined 17 Å peak is seen in the pattern of the sample from the manure-treated plot. The next most affected pattern is that of the sample from the K-treated plot. These observations suggest that one change in clay mineralogy is an increase in the illite (non-expandable layer) content of the clays with both KCl and manure treatments (see Moore and

Reynolds, 1997). This effect is stronger in the sample from the manure-treated plot. On the other hand, samples from the acid-treated plot and, to a lesser extent, from the sodic plot could be distinguished by their low background intensity and hence a lower smectite content.

The decomposition of the background-subtracted patterns (Figure 2) shows that the sharper 14.7 Å peak seen in the 1929 reference sample is lost in the samples from the manure- and K-treated plots. There is also a widening of the remaining I-S peak and a strengthening of the illite/mica peaks in these samples. Indeed, visual inspection of the decomposed patterns given in Figure 2 shows that the illite/mica content of the KCl plot is increased. This is true to a lesser extent for the sample from the manure-treated plot.

From these observations it is clear that the peaks themselves show a small but distinct change with treatment for the 70 y period. The clearest change is an increase of both mica layer contents in the mixed-layered mineral and illite/mica content represented by the peak at 10 Å for the sample from the KCl- and manure-treated plots.

DISCUSSION

Our data show that the particle-size distributions differ as a function of the plot treatment (Table 1). Samples from the sodic and acid plots show a decrease of clay content mainly for fine particles. With other treatments the clay contents are retained in both coarse and fine clay sizes. The clay mineralogy changes only slightly in most of the plots. Our interpretation is that

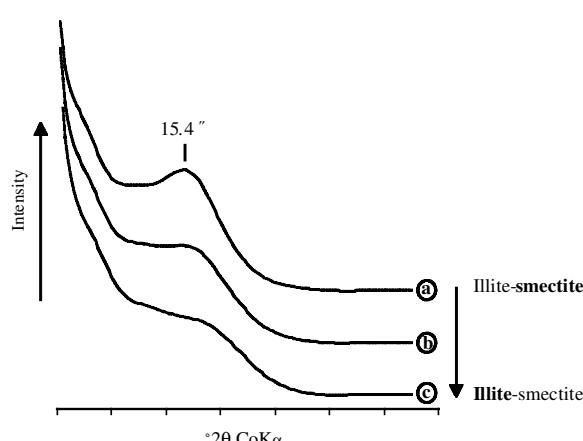


Figure 3. XRD simulation with NEWMOD program (Reynolds, 1985). Disordered I-S interlayered mineral (1–4 layers), Co radiation. (a) 50% illite, (b) 60% illite, (c) 70% illite.

some of the clay has been translocated from the top to the bottom of the soil profiles. However, there appears to be no mineral species selectivity (loss) due to such a loss of clay particles. This suggests that the mineralogy of the finest fraction has the same mineralogy as the coarse clay fraction. The strong acidification caused more changes in the particle size than in the clay mineralogy. It is important to note that this acidification phenomenon was not selective according to the nature of the clay minerals. Indeed the clay corrosion, shown by the presence of exchangeable Al, and the clay translocation have not significantly modified the clay mineralogy.

After 70 years of lying fallow, the soils in the experiment changed from their original state (soil pH, CEC and exchangeable cations content) to very acid or to basic according to the type of treatment they received. These changes are consistent with the literature, *i.e.* low CEC and high Al content in acid soils, high CEC and Ca saturation in basic plots (Pernes-Debuyser and Tessier, 2002a).

Manure and potassic treatment increased the exchangeable K content. However, although manure added much less K to the soil than the K treatment (~25 times less), the amount of exchangeable K is greater in manure than in the KCl plot. Also, the clay minerals changed more in the manure-treated plot. Thus K was more available with organically treated than with chemically treated soils. This suggests that the way K is applied to the soil strongly influences the ability of the soil to retain K. Getman and Ladd (1925) observed that K is present in large quantities in most soils but is made available by the action of decaying organic matter.

With H_2O_2 treatment, the carbon oxidation was incomplete which means that some organic material was trapped and not oxidized. The XRD patterns taken

before and after H_2O_2 treatment show an increase in the relative intensity of the mixed-layered minerals, suggesting that interactions of clay and organic material inhibit good orientation of the clay particles. This is probably due to the freeing of individual clay platelets from clay-organic associations, which prevents proper orientation upon sample slide preparation. Without fertilizer treatment, the reference soil shows no change with the oxidation procedure indicating that there is very little active organic material present. Most of the organic matter responsible for the poor orientation was degraded after 70 years.

From another point of view, the K application caused mineralogical evolution. The KCl treatment and manure tend to produce a mixed-layered clay mineral with a higher proportion of non-expanding layers, *i.e.* more illitic behavior, and also an increase of the illite/mica content. In terms of cation availability, the K content is higher in these plots than in others. Some of the K can be fixed, creating new illitic layers. However, the pure chemical treatments (KCl) increased K in the mixed-layered clay mineral to a lesser extent than in the manure treatment and to a greater extent for the illite/mica mineral. This suggests that the change depends on the K availability in the soil. As seen before, the way in which the K is applied is critical. A parallel can be drawn with the observations of Blake *et al.* (1999) who concluded that organic fertilizers were the preferred source of K for plant nutrition. Notice that in the K-treated plots, new illite material appears as the sharper peak of I-S disappears (Figure 2). Comparison between XRD patterns of untreated and H_2O_2 -treated samples suggests that the relationship between K and organic constituents created more disordered I-S mixed-layered minerals even when organic matter content is low (Figure 4).

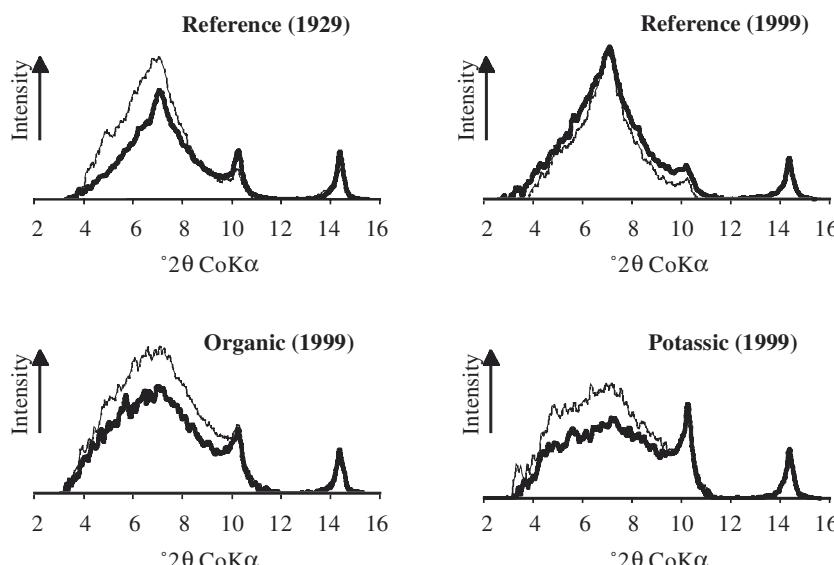


Figure 4. XRD smoothed and background-subtracted diagrams of clay fraction; Ca-saturated, air-dried, $CoK\alpha$ radiation.
— Natural clay; - - H_2O_2 treated clay.

There is a strong contrast between the samples of the Versailles study and samples from the Morrow plots at the University of Illinois experimental farm. In the Morrow plots, different types of cropping changed the clay minerals (largely the same disordered mixed-layered I-S) to a much larger extent (Velde and Peck, 2002). In the Morrow plots, continuous corn cropping increases the smectite content of the mixed-layered minerals and reduces the amount of illite/mica minerals considerably. The NPK fertilizer treatment (nitrogen, phosphate, potassium) restored the lost illite layer behavior content in the mixed-layered minerals in a 40-year treatment period. However, crop rotation in the Morrow plots (corn, oats, hay) left the clays essentially unchanged after 80 y of cropping. Thus, not all plants interact in the same way with the soil clay minerals. Our results from the Versailles experiment indicate that a similar effect would occur when no plants are present.

In considering these two sets of results, the Versailles experiment and the Illinois crop rotation and fertilizer system, it appears that the fertilization treatments of this study can change the clay minerals in the same way as can plant-clay interaction mechanisms. The use of manure or potassic fertilizer in the Versailles experiment increases the illite or non-expanding mineral content of the mixed-layer clay as in the Morrow plots. However, plants can change the clay mineralogy more than the fertiliser treatments of the present study.

CONCLUSIONS

The long-term experiment on uncultivated plots at Versailles changed the soil properties according to the chemical or organic fertilizer; physicochemical properties fluctuated with soil pH. Chemical variations influenced physical soil properties (Pernes-Debuyser and Tessier, 2002b). However, most treatments caused only minor changes in the clay mineralogy. Strong acidification with ammoniacal treatment caused more changes in the clay particle organization and distribution than in their mineralogy. Those results show that clay corrosion and translocation were not selective according to the nature of the clay minerals. Only plots with K application as in organic or potassic treatment changed the clay mineralogy. The disordered I-S mixed-layered mineral, a major clay mineral in the samples, and the illite/mica mineral became more illitic (non-expanding mineral). However the mixed-layered mineral content increased less in plots with K-chemical-treatment than with manure application. This change was influenced by the exchangeable K content that depends on the method of application of K and the ability of soil to retain it. Moreover, as shown by comparison of crop and non-crop practices, it appears that the crops can cause greater changes in clay mineralogy than inorganic chemical treatments. The organic matter effect, either as crop plants or as manure, can have a greater effect on soil

clay mineralogy than that of pure chemicals. This appears to be a determining factor of clay evolution in soils and should be taken into account in order to differentiate K from organic-matter recycling (manure) and that from chemical fertilizers.

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