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Characteristics and potential pedogenetic processes of a Technosol developing on iron industry deposits

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Abstract

Purpose: Technosols include soils dominated or strongly influenced by human-made materials. Similarly to natural soils, technogenic parent materials submitted to environmental factors undergo weathering and transformation processes. But the pedogenesis of the Technosols remains little known. With this aim in view, a Technosol developing on purely technogenic materials resulting from iron industry was thoroughly characterized in order to discuss pedogenetic evolution of this Technosol using knowledge about pedogenesis of natural soils.

Materials and methods: The studied site was a former settling pond, where mainly sludge generated by wet cleaning of blast-furnace fumes was dumped until probably in the mid-20th century. Thereafter the pond has been colonized by vegetation and is covered by a diversified forest. The soil was composed of contrasted layers. A 20 cm organic layer has developed at the surface. Samples were collected in the first two meters which are under root influence. Elemental composition, agronomic parameters, mineralogy as well as physical and hydraulic properties of the soil materials were characterized.

Results and discussion: Some characteristics of the Technosol, *e.g.* elemental composition, mineralogy or profile stratification, resulted mainly from industrial processes. However, some properties of the Technosol can be compared to natural soils. Particularly, the presence of low periodic order minerals and physical and hydraulic properties were analogous to properties of Andosols. However, alkaline pH and carbonate contents made the Technosol closer to carbonated soils. Moreover, the presence of Mn oxides, high porosity and water retention were also encountered in Mn bearing soils. Early pedogenic processes *e.g.* development of organic surface layer and signs of mineral weathering were observed. But transfers seemed to be rather limited and/or slow in the profile. However, physical and chemical properties, *e.g.* high water retention and high pH, were rather favourable to element retention.

Conclusions: The evolution of the Technosol seemed to be still limited in the profile, which could be explained by high retention capacity of the soil. The presence of highly reactive mineral phases, such as low periodic order Mn oxides or allophane-like minerals, with high contents of carbonates was rarely encountered in the natural environment and may suggest an important potential for pedogenic evolution, which could be directed by the balance between the weathering processes of these phases.

Keywords Andosols • Iron industry deposits • Low periodic order minerals • Pedogenetic processes • Technosol

1 Introduction

Soils developed on human-made substrates increase dramatically in surface area. As a result, a new reference soil group, Technosols, was added to the latest version of the World reference base for soil resources (WRB 2006). Technosols include soils dominated or strongly influenced by technogenic materials, *e.g.* soils derived from wastes (landfills, sludge, cinders, mine spoils and ashes). They are defined as soils containing 20 % or more of technogenic materials in the upper 100 cm or by the presence of indurated layer (IUSS Working Group WRB 2006). They are generated by human activities and are mostly found in urban and industrial areas. They are also more likely contaminated than others soils (Rossiter 2007) and are often the support of vegetation, in parks, urban forests, civil engineering works, etc.

Natural parent materials undergo transformation under the influence of soil-forming factors, *i.e.* climate, organisms, topography and time, which contribute to the soil profile development (Jenny 1941). Pedogenic processes which affect natural parent material have been thoroughly studied for more than a century and they are now well established and described (*e.g.* Duchaufour 1991). Defined processes (*e.g.* carbonatation, podzolisation, andosolization) correspond to given sets of environmental conditions (*e.g.* parent rock, climate, vegetation). Similarly, technogenic materials evolve under the influence of environmental factors but little is known about the processes, which take place in Technosols.

This aspect is often linked to the difficulty for establishing a full cristallo-chemical description of the mineralogical complex present in Technosols. Hence, information is required as processes in Technosols may cause significant impacts to the environmental targets, as a result of the potential release of harmful compounds. Examples of metal-bearing technogenic materials in Technosols are numerous (*e.g.* Zevenbergen et al. 1999; El Khalil et al. 2008; Howard and Olszewska 2010). A large variety and mixing

of technogenic materials are encountered in Technosols, each offering specific physical and chemical properties, *e.g.* they are often alkalizing (Morel et al. 2005). The nature and characteristics of parent material (grain size, mineralogy) considerably influence the weathering kinetics and control pedogenesis by accelerating or slowing down chemical reactions (Duchaufour 1991). Some artefacts, *e.g.* bricks or steel, were rather stable in soil though their weathering is dependent on fragment size and porosity (Howard and Olszewska 2010). On the opposite, pedogenic evolution is a fast phenomenon with technogenic parent material exhibiting a high chemical reactivity and/or composed of finely divided materials offering a high specific surface (Séré et al. 2010). Therefore, pedogenesis of Technosols is strongly influenced by the characteristics of the technogenic parent material.

However some soils formed on technogenic materials can develop properties analogous to these ones of natural soils. For example, soils derived from lignite ash display some properties similar to andic properties whereas some characteristics such as high pH, high organic carbon content or presence of carbonates and sulphates due to the technogenic parent material (coal fly ash) are rarely encountered in Andosols but rather in calcaric soils (Zikeli et al. 2005). Thus, Technosols could be the place of the coexistence of properties, which are developed in different natural soils. But whether technogenic materials and their mixture could create the conditions necessary to specific pedogenetic processes or combination of processes stays unknown. It is generally assumed that the presence of low amounts of technogenic materials do not modify soil evolution and analogies between weathered human-made and natural soil materials are observed, *e.g.* weathering of coal fly ash was similar to that of natural volcanic ashes (Zevenbergen et al. 1999).

Although Technosols are generally young soils, early soil-forming processes and profile development were observed. One of the most obvious processes is the accumulation of pedogenic organic matter with time in the upper layers (Schafer et al. 1980; Zikeli et al. 2002; Howard and Olszewska 2010; Uzarowicz and Skiba 2011). Mineral transformations, such as formation of iron oxides, sulphates or clay minerals from weathering of primary phases (sulfides, carbonates, inherited clay minerals) were described in Technosols and could be an indicator of pedogenesis (Scholtus et al. 2009; Uzarowicz and Skiba 2011). Similarly, aggregation involving mineral and organic artefacts (Monserié et al. 2009; Séré et al. 2010) and evolution of soil structure and of physical properties (Hartmann et al. 2010) were reported. At the profile scale, some transfers were highlighted such as decarbonatation in upper layers or downward migration of gypsum (Zikeli et al. 2002; Séré et al. 2010). If some of these changes observed in Technosols were similar to those occurring in natural soils, they were often significantly more rapid and more intense than in natural soils (Zevenbergen et al. 1999; Rossiter 2007). This could be partly attributed to the recent age of these soils and the disequilibria existing between parent materials and environmental conditions (Chadwick and Chorover 2001; Séré et al. 2010). Moreover, the composition of technogenic parent materials and the soil conditions, *e.g.* pH, soil solution saturation or soil water movement, influence the weathering rates (Crow 2008). For example, high pH could promote dissolution of silicates (Zevenbergen et al. 1999; Zikeli et al. 2005; Sauer and Burghardt 2006) while the presence of salts or sulphates

resulting from human activities could accelerate the weathering of artefacts by corrosion (Howard and Olszewska 2010).

With the aim of better understanding pedogenesis of Technosols, it was undertaken to study a Technosol developing on deposit of iron industry by-products. Actually, iron industry generates numerous by-products and wastes during its process, which are found in brownfields resulting from cessation of this industry. Among these products, there is blast furnace sludge resulting from wet cleaning of blast furnace fumes during the production of pig iron. Due to their composition, they were not recycled and were dumped into settling ponds (Mansfeldt and Dohrmann 2004). After their cessation, some ponds have been colonized by vegetation and are nowadays support of forests analogous to natural forests (Schwartz et al. 2001) despite the potentially polluting compounds such as heavy metals or cyanides they contain (Mansfeldt and Dohrmann 2001). Thus, these purely technogenic materials undergo soil-forming factors (climate, organisms, time) and can be considered as parental material of Technosols. The objectives of this paper were:

- (i) to characterize the Technosol by determining physico-chemical and cristallographic characteristics as well as physical and hydraulic properties and pedological parameters and to compare them to properties of natural soils ;
- (ii) to discuss data in terms of pedogenic evolution mechanisms of this complex by-products deposit using the knowledge about pedogenesis of natural soils.

2 Materials and methods

2.1 Studied site

The studied site was a former settling pond of the iron industry of Pompey-Frouard-Custines (Lorraine, North-East France), which was in service from 1875 to 1986. This pond was located on an island at the confluence of the Moselle and the Meurthe rivers and occupied 2.6 ha (Fig. 1.a.). The geological substratum was constituted of marly formations of Lias and was covered by a superficial layer of alluvia of both the rivers (6-7 m thick). The alluvia were partially or totally extracted before the setting up of a slag pit composed of fill originally from iron industry wastes and by-products. The studied settling pond received mainly blast furnace sludge until *ca* the mid-20th century, which formed about 10 m thick deposits. Following the cessation, spontaneous vegetation has colonized the site and nowadays it was covered by a diversified deciduous forest. The climate of the region is semi-continental. The precipitation is spread regularly over the year (average precipitation: 737 mm per year) and the temperature range is high between January and July (average temperatures: 0.9°C in January and 17.3°C in July).

2.2 Sampling

Description and sampling were performed in a 2 m deep pit located in the northwest part of the pond and opened in June 2009 (see Fig. 1.a.). The profile displayed the superimposition of more or less thick horizontal layers with an alternation of blackish pasty and lighter (grey to rusty) layers constituted of numerous thin parallel *laminae* (see Fig. 1.b.). This stratification resulted from the settling of successive

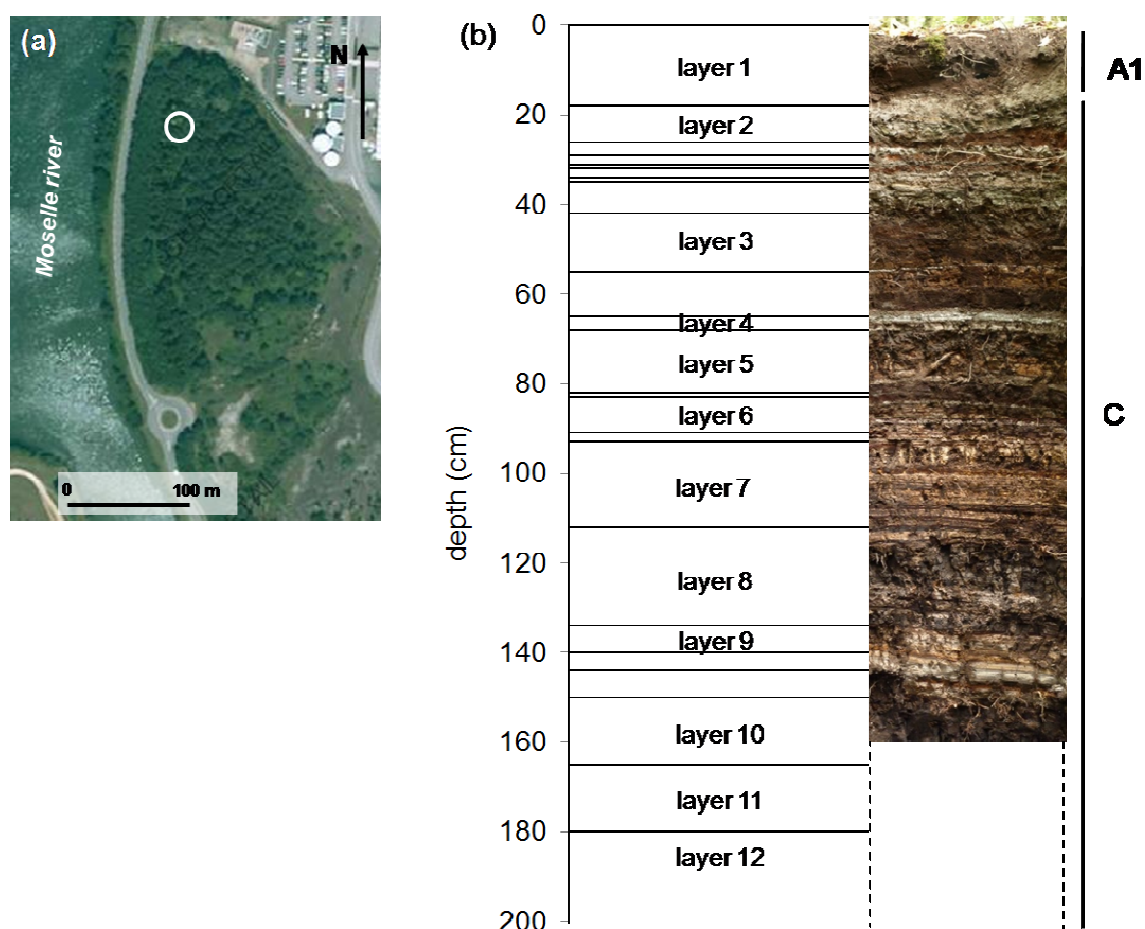
sludge supplies and a 20 cm thick organic layer has developed at the surface (Schwartz et al. 2001), which could be identified as clear A horizon enriched by organic matter deposits; hence, the profile was of the A1/C type. Roots were present in the first two meters but their distribution was heterogeneous depending on the layers.

In order to characterize this Technosol formed from stratified materials, twelve layers were sampled in May 2010 along the profile after the pit wall was refreshed. The layers were chosen owing to their contrasted morphological features and composition, which are presented Fig. 1.b. For each layer, 1 to 1.5 kg of field-wet bulk soil was collected for chemical and mineralogical analyses. After homogenisation and root removal, half of samples was freeze-dried and ground according to analyse requirements. So as to measure physical and hydraulic properties, cylinders of 251 cm³ (8 cm in diameter and 5 cm high) of undisturbed field-wet soil were sampled in triplicate in ten layers. They were covered with two parafilm sheets and stored at 4°C prior to analyses.

Fig. 1 Localization and sampling profile of the Technosol developing on a stratified deposit of iron industry by-products (Lorraine, North-East France).

a. Aerial view of the studied settling pond and localization of the pit

b. Technosol profile of the A1/C type and the twelve studied layers



2.3 Chemical and mineralogical analyses

Total contents of major and trace elements were analysed respectively using ICP-OES and ICP-MS after lithium metaborate attack and acid digestion of the resulting glass (Carignan et al. 2001) by the Service d'Analyse des Roches et des Minéraux (CNRS, Vandoeuvre-lès-Nancy). Total C (NF ISO 10694), N (NF ISO 10694) and S were determined by dry combustion and quantification of the emitted volume of CO₂, N₂ and SO₂.

Agronomic parameters were determined by the Laboratoire d'Analyse des Sols (INRA, Arras). Total carbonate (NF ISO 10693) was determined by measurement of the emitted volume of CO₂ during sample acidification with HCl. Active carbonate (NF X 31-106), which gives information about the reactivity of carbonates, was measured by the Drouineau-Galet method (determination of the amount of Ca²⁺ reacting with ammonium oxalate).

Organic carbon was calculated from total carbon and total carbonate. Available P was determined by the Olsen method (NF ISO 11263). Soil pH was measured in water suspension at the ratio 1/5 (v/v) (NF ISO 10390). Cation exchange capacity (CEC) was determined by using cobalt hexamine trichloride solution (2.5 g of soil with 50 mL of 50 mM solution) (NF ISO 31-130). Exchangeable cations (Ca, Mg, Na, K, Fe, Mn and Al) were analyzed by ICP-OES. Forms of Al, Fe, Mn and Si were studied by extractions according to Tamm method (extraction in the dark by solution of oxalic acid and ammonium oxalate buffered at pH 3) (Tamm 1922) and Mehra-Jackson method (extraction under heat with Na citrate, hydrogenocarbonate and dithionite) (Mehra and Jackson 1960). All the results were expressed with respect to 105°C-dried soil.

The main mineral phases were characterized on bulk dry samples with combined techniques: X-Ray Diffraction (Bruker D8 Advance), Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTS IFS 55 Bruker), Scanning Electron Microscopy (SEM Hitachi S-4800 and Jeol J7600F) and Transmission Electron Microscopy (TEM Philips CM20, 200 kV) coupled with Energy Dispersion Spectrometry (EDS). Six samples (layers 1, 2, 4, 5, 7 and 11) were chosen for their contrasted composition and characterized by electron probe methods. Observations and analyses were done on polished sections with SEM/EDS and on samples dispersed in ethanol and deposited on carbon films supported by Cu grids with TEM/EDS.

2.4 Physical methods

Textural analyses were carried out on dry samples to determine distribution of five grain size fractions (< 2 µm ; 2-20 µm ; 20-50 µm ; 50-200 µm and 200-2000 µm) without prior decarbonation (NF X 31-107). After organic matter removal and dispersion, coarse fractions were collected by sieving and fine fractions with Robinson pipette. Specific surface area was measured on freeze-dried samples by applying the BET method to the N₂ adsorption-desorption isotherms (Sorptomatic 1990 Thermo Scientific) at 77 K. The out gassing conditions were 16 h at 100°C at 0.1°C min⁻¹. Saturated hydraulic conductivity, porosity and water retention curve were determined on cylinders of 251 cm³ with three replicates per

layer. Field-wet cylinders of soil were saturated by capillary rise to determine capillary porosity. The samples were placed with membranes on a grid in a closed PVC box filled with demineralized water until 1mm above the contact between cylinders and grid. Capillary rise occurred for at least 48 h. Saturated hydraulic conductivity was determined according to constant head method on saturated samples (Klute and Dirksen 1986). For each sample, measurements were done at three hydraulic heads in order to control the stability of saturated hydraulic conductivity. Samples were subsequently introduced into an extractor plate apparatus (Labotest) and water content was determined for successive decreasing water potentials. For each water potential, samples stayed during a week (168 h) (except for pF 2 for layers 10 and 11 only 48 h) in the apparatus and water content was determined by weight difference after drying at 105°C. For a given layer, the available water content (mm per cm of soil) was calculated by difference between water contents at the field capacity and at the wilting point, measured respectively at pF 2 and 4.2. Microporosity (pores with diameter lower than 0.2 μm) was estimated from water contents at pF 4.2 (Duchaufour 1991). Bulk density was determined from volume and weight of 105°C-dried soil cylinders. For some samples, shrinkage during drying was observed and can reach 25 % of initial volume. The volume loss was estimated to correct data. An aliquot of 105°C-dried soil samples (3-4 g) were ground and sieved at 100 μm to measure the solid density by He pycnometry (Micromeritics AccuPyc 1330). The total porosity (ε) was calculated from bulk (ρ_b) and solid density (ρ_s) according to following relation: $\varepsilon = 1 - \frac{\rho_b}{\rho_s}$.

2.5 Statistical analyses

In order to establish analogies between the characteristics of the studied materials and volcanic soils, results were compared with the physico-chemical data base of a collection of European volcanic soils (n=39) built within the framework of the scientific program of EU-COST action 622 “Soil Resources of European Volcanic Systems” (Buurman et al. 2007). Statistical analyses were performed with XLSTAT 2010. A non-parametric test of comparison of mean of Mann-Withney was used considering a significance level of $p < 0.05$.

3 Results

3.1 Elemental composition

Average elemental composition was dominated by Mn, Ca, Si, Fe, C and Al (see Table 1). Mn content reached 341 g kg^{-1} of dry soil. Some usual soil trace elements such as Pb, Zn, Ba and Sn behaved like major elements (average contents more than 1 g kg^{-1}). Pb and Zn contents respectively reached 109 and 81 g kg^{-1} of dry soil. On the contrary, conventional soil major elements such as Na or Ti had the status of trace elements. Also, some trace metals and metalloids such as As, Cu, Sb, Ni and Cd were present at high concentration. Similarly, Sr, V and B reached significant contents. Elemental concentrations were variable along the Technosol profile for major (Fig. 2) and trace elements (Table 2). Contents were highly contrasted even between consecutive layers, *e.g.* Mn content reached 21 g kg^{-1} in layer 4 and 341 g kg^{-1} in layer 5. Each layer had a specific composition, a difference which was also recorded from morphological

observations. The distribution of contents along the profile was rather distinct depending on the element. However, some element profiles showed similarities, *e.g.* Cu, Sb, Sn and Pb contents were very high in layer 7 and Ti, V and Ni displayed greater concentrations in layers 1, 4, 7 and 11. On the contrary, some elements were anti-correlated such as Mn and Fe. No particular trend with depth was observed though S seemed to be present at higher concentration in deeper layers while the surface layer was enriched in Fe, C, P and N.

Table 1 Variability of chemical composition for major and main trace elements in the Technosol developing on a stratified deposit of iron industry by-products (Lorraine, North-East France).

Mean, median, minimal and maximal values are calculated from analyses on twelve layers sampled along the profile. Elements are classified in decreasing order relative to their average content.

| | Major elements (average content above 1 g kg ⁻¹) | | | | | | | | | | | | | | | |
|---------|--|-------|-------|-------|-------|------|-------|------|------|------|------|------|------|-----|-----|-----|
| | Mn | Ca | Si | Fe | C | Al | Pb | Zn | Mg | K | Ba | S | Sn | P | N | F |
| | g kg ⁻¹ | | | | | | | | | | | | | | | |
| mean | 135.7 | 113.0 | 82.6 | 63.6 | 54.8 | 45.8 | 24.8 | 21.1 | 12.1 | 6.7 | 6.1 | 5.0 | 3.9 | 2.3 | 1.5 | 1.2 |
| median | 124.4 | 115.3 | 82.0 | 55.3 | 40.8 | 45.0 | 16.6 | 14.2 | 12.2 | 7.1 | 4.0 | 3.0 | 1.4 | 2.0 | 0.9 | 1.1 |
| minimum | 10.7 | 55.0 | 54.0 | 6.0 | 12.2 | 34.3 | 2.9 | 3.9 | 7.6 | 2.0 | 1.2 | 0.6 | 0.4 | 0.7 | 0.2 | 0.6 |
| maximum | 340.8 | 188.7 | 123.2 | 214.5 | 131.8 | 58.1 | 108.9 | 81.5 | 15.7 | 12.6 | 15.2 | 21.3 | 17.4 | 5.2 | 6.5 | 2.9 |

| | Trace elements (average content between 100 and 1000 mg kg ⁻¹) | | | | | | | | | |
|---------|--|--------|--------------------|--------|--------|-------|-------|-------|-------|-------|
| | Sr | Ti | Na | V | As | Cu | Sb | Ni | Cd | B |
| | mg kg ⁻¹ | | | | | | | | | |
| mean | 785.3 | 731.7 | 582.2 | 421.8 | 238.5 | 205.3 | 121.6 | 107.7 | 106.0 | 104.3 |
| median | 790.1 | 779.0 | 367.1 | 348.9 | 110.7 | 174.6 | 74.2 | 90.2 | 67.5 | 65.3 |
| minimum | 287.6 | 137.5 | < 220 ^a | 30.2 | 52.8 | 78.5 | 36.6 | < 4.5 | 10.1 | 24.3 |
| maximum | 1169.9 | 1974.0 | 1316.0 | 1191.3 | 1131.5 | 656.6 | 434.0 | 271.7 | 352.5 | 257.6 |

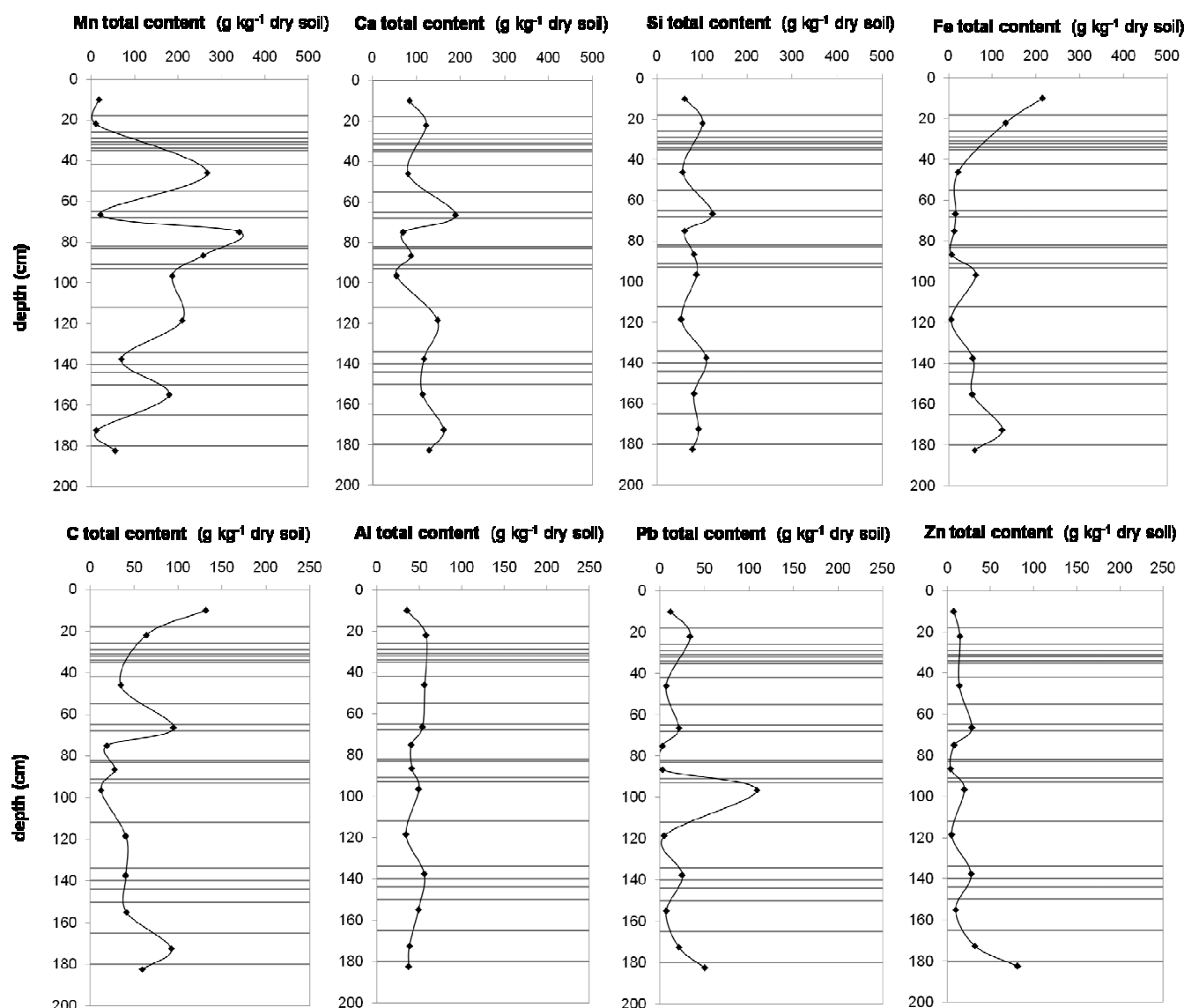
^a Content value preceded by < was below the analytical detection limit for that element

Table 2 Distribution of elemental composition for some major and main trace elements in twelve layers along the profile of the Technosol developing on a stratified deposit of iron industry by-products (Lorraine, North-East France).

| layer | layer depth cm | Mg | K | Ba | S | Sn | P | N | F | Sr | Ti | Na | V | As | Cu | Sb | Ni | Cd | B |
|-------|-------------------|--------------------|------|------|------|------|-----|-----|-----|---------------------|------|-------|------|------|-----|-----|------------------|-----|-----|
| | | g kg ⁻¹ | | | | | | | | mg kg ⁻¹ | | | | | | | | | |
| 1 | 0 - 18 | 8.8 | 3.7 | 1.2 | 1.5 | 0.8 | 5.2 | 6.5 | 1.1 | 288 | 1133 | 323 | 355 | 135 | 136 | 65 | 90 | 27 | 57 |
| 2 | 18 - 26 | 14.7 | 9.5 | 1.4 | 1.5 | 1.4 | 2.9 | 1.3 | 1.3 | 418 | 1070 | 1316 | 343 | 98 | 209 | 165 | 42 | 45 | 73 |
| 3 | 42 - 55 | 10.8 | 4.2 | 3.8 | 1.2 | 1.1 | 1.9 | 0.2 | 1.1 | 729 | 336 | < 220 | 73 | 736 | 165 | 188 | 23 | 90 | 30 |
| 4 | 65 - 68 | 13.2 | 12.6 | 4.0 | 4.0 | 7.0 | 0.7 | 1.8 | 0.7 | 1116 | 779 | 585 | 957 | 81 | 246 | 82 | 215 | 352 | 55 |
| 5 | 68 - 82 | 13.0 | 7.2 | 2.6 | 0.6 | 0.6 | 2.2 | 0.5 | 0.6 | 811 | 137 | < 220 | 52 | 1131 | 147 | 150 | 21 | 134 | 36 |
| 6 | 82 - 91 | 15.7 | 8.1 | 15.2 | 2.7 | 0.4 | 1.6 | 0.5 | 0.7 | 1170 | 178 | < 220 | 35 | 123 | 128 | 52 | 8 | 10 | 24 |
| 7 | 93 - 112 | 10.3 | 7.4 | 5.8 | 2.1 | 17.4 | 2.1 | 0.4 | 0.7 | 678 | 794 | < 220 | 719 | 157 | 657 | 434 | 212 | 29 | 76 |
| 8 | 112 - 134 | 10.8 | 8.6 | 13.3 | 3.3 | 1.0 | 1.3 | 0.3 | 0.6 | 934 | 204 | 367 | 30 | 53 | 86 | 54 | < 4 ^a | 12 | 46 |
| 9 | 135 - 150 | 13.7 | 7.0 | 7.7 | 6.9 | 5.4 | 1.6 | 3.1 | 1.2 | 889 | 568 | < 220 | 241 | 78 | 212 | 110 | 14 | 313 | 165 |
| 10 | 150 - 165 | 7.6 | 5.8 | 10.7 | 6.0 | 1.3 | 3.4 | 0.4 | 1.5 | 1041 | 827 | < 220 | 423 | 130 | 78 | 55 | 93 | 17 | 255 |
| 11 | 165 - 180 | 15.2 | 4.4 | 4.0 | 8.9 | 4.6 | 2.9 | 1.4 | 2.9 | 769 | 1974 | 320 | 1191 | 78 | 215 | 37 | 272 | 133 | 174 |
| 12 | > 180 | 11.3 | 2.0 | 3.5 | 21.3 | 5.5 | 1.9 | 1.6 | 1.6 | 580 | 779 | < 220 | 642 | 60 | 184 | 67 | 194 | 109 | 258 |

^a Content value preceded by < was below the analytical detection limit for that element

Fig. 2 Distribution of major elements (Mn, Ca, Si, Fe, C, Al, Pb and Zn) along the profile of the Technosol developing on a stratified deposit of iron industry by-products (Lorraine, North-East France).



3.2 Parameters for soil fertility

Organic matter quantity and nature varied significantly depending on layers (Table 3). Organic carbon content ranged from 5 g kg⁻¹ in layers 5 to 8 (68-134 cm depth) to 114 g kg⁻¹ at the surface. The C/N ratio was 18 in the surface layer and varied between 5 and 81 in deeper layers. The high values reflected the lack of organic N in some layers. Phosphorus extracted by Olsen method (P_{Olsen}) ranged from 0.01 to 0.15 g kg⁻¹ (see Table 3) and represented 0.7 to 7% of the total soil phosphorus. The highest values of P_{Olsen} were found in the surface layer and in layers 3, 5 and 10 as well.

The water pH was slightly alkaline and relatively constant along the soil profile (7.8 - 8.4) (Table 3). Total carbonate was quite substantial varying from 57 to 320 g kg⁻¹ (Table 3). Active carbonate contents varied between 48 and 135 g kg⁻¹ and represented 27 to 89% of total carbonate. Distribution along the soil profile seemed to show enrichment in active carbonate in deeper layers (layers 8-12).

Table 3 Parameters for soil fertility in the twelve studied layers along the profile of the Technosol developing on a stratified deposit of iron industry by-products (Lorraine, North-East France).

| layer | layer depth cm | organic matter | | | | carbonate | | cation exchange capacity and exchangeable cations | | | | | | | |
|-------|-------------------|--------------------|-----|--------------------|---------------------|--------------------|--------------------|---|--------------------|--------------------|-------------------|--------------------|---------------------|--------------------|--------------------|
| | | C _{org} | C/N | P _{Olsen} | pH _{water} | total | active | CEC | Ca _{exch} | Mg _{exch} | K _{exch} | Na _{exch} | Al _{exch} | Mn _{exch} | Fe _{exch} |
| | | g kg ⁻¹ | - | g kg ⁻¹ | - | g kg ⁻¹ | g kg ⁻¹ | | | | | | | | |
| | | | | | | | | | | | | | | | |
| | 0-18 | 113.6 | 17 | 0.15 | 7.9 | 151.9 | 47.7 | 51.4 | 51.9 | 3.6 | 2.0 | 0.1 | 0.09 | 0.03 | 0.03 |
| | 18 - 26 | 36.4 | 28 | 0.02 | 8.4 | 227.0 | 81.8 | 24.2 | 22.0 | 2.6 | 1.8 | 0.1 | 0.06 | 0.01 | 0.01 |
| | 42 - 55 | 15.3 | 81 | 0.10 | 8.1 | 160.4 | 86.5 | 61.8 | 52.1 | 9.5 | 4.2 | 0.3 | 0.05 | 0.05 | < 0.005 |
| | 65 - 68 | 56.5 | 31 | 0.01 | 8.3 | 320.4 | 85.5 | 29.7 | 20.2 | 8.6 | 4.2 | 0.4 | < 0.02 ^a | 0.06 | < 0.005 |
| | 68 - 82 | 4.8 | 9 | 0.14 | 8.2 | 118.0 | 79.1 | 63.3 | 44.1 | 15.2 | 5.9 | 0.4 | 0.10 | 0.17 | < 0.005 |
| | 82 - 91 | 5.1 | 11 | 0.08 | 8.3 | 188.2 | 88.8 | 78.4 | 53.8 | 21.8 | 11.7 | 0.7 | 0.09 | 0.08 | < 0.005 |
| | 93 - 112 | 5.3 | 15 | 0.06 | 8.3 | 57.5 | 51.2 | 70.4 | 39.8 | 20.5 | 12.3 | 0.8 | 0.16 | 0.07 | 0.05 |
| | 112 - 134 | 5.3 | 21 | 0.09 | 8.2 | 292.0 | 114.0 | 67.6 | 50.9 | 11.5 | 10.5 | 1.5 | 0.06 | 0.06 | < 0.005 |
| | 135 - 150 | 14.8 | 5 | 0.04 | 8.1 | 213.8 | 134.9 | 69.5 | 63.1 | 13.3 | 9.6 | 1.3 | 0.08 | 0.03 | 0.01 |
| | 150 - 165 | 18.5 | 47 | 0.12 | 8.0 | 188.6 | 111.4 | 83.0 | 91.6 | 8.5 | 9.1 | 1.1 | 0.36 | 0.17 | 0.03 |
| | 165 - 180 | 62.7 | 46 | 0.06 | 8.0 | 247.4 | 108.8 | 50.1 | 68.6 | 8.4 | 4.0 | 0.6 | 0.10 | 0.05 | 0.02 |
| | > 180 | 35.7 | 23 | 0.04 | 7.8 | 196.3 | 120.2 | 62.3 | 150.0 | 15.0 | 3.4 | 0.3 | 0.04 | 0.03 | 0.01 |
| | mean | 31.2 | 28 | 0.08 | 8.1 | 196.8 | 92.5 | 59.3 | 59.0 | 11.5 | 6.6 | 0.6 | 0.11 | 0.07 | 0.02 |
| | median | 16.9 | 22 | 0.07 | 8.1 | 192.5 | 87.7 | 62.8 | 52.0 | 10.5 | 5.1 | 0.5 | 0.1 | 0.1 | 0.02 |
| | minimum | 4.8 | 5 | 0.01 | 7.8 | 57.5 | 47.7 | 24.2 | 20.2 | 2.6 | 1.8 | 0.1 | < 0.02 | 0.01 | < 0.005 |
| | maximum | 113.6 | 81 | 0.15 | 8.4 | 320.4 | 134.9 | 83.0 | 150.0 | 21.8 | 12.3 | 1.5 | 0.36 | 0.17 | 0.05 |

^a Content value preceded by < was below the analytical detection limit for that element

Cation exchange capacity was quite high and ranged from 24 to 83 cmol⁺ kg⁻¹. It was mainly saturated by Ca²⁺. Cations were retained according to the following order: Ca > Mg > K > Na > Al > Mn > Fe. In comparison with total content, exchangeable fraction represented 11-12% for Ca and Mg, 30-40% for Na and K and 0.01-0.03% for Al, Mn and Fe on average. The distribution of cation exchange capacity and exchangeable basic cations (Mg, K and Na) was heterogeneous along the profile and exhibited the highest values in the layers 6-10 between 80 and 165 cm of depth. Extractions by Tamm (oxalate) and Mehra-Jackson (citrate, hydrogeno-carbonate, dithionite) methods gave information about mineral forms of elements like Si, Al, Fe or Mn in soil. Oxalate extractable contents of Si (Si_o) and Al (Al_o) are used to quantify amorphous aluminosilicates. Tamm method extracted amorphous or poorly crystalline Fe oxy-hydroxides (Fe_o) whereas Mehra-Jackson method also extracted Fe in crystalline oxides forms. It allowed to determine 'free Fe' (Fe_d), which represent total Fe except Fe included in silicate lattices. Data for Si, Al, Fe and Mn are shown in Table 4. Si_o contents were quite significant and varied from 4 to 32 g kg⁻¹ depending on layers while contents of Si_d concentrations were lower and rather constant along the soil profile between 3 and 4 g kg⁻¹. Similarly to Si, Al_o contents varied from 12 to 28 g kg⁻¹ while Al_d contents were lower or similar than Al_o contents and contained between 6 and 21 g kg⁻¹. The higher Si_o and Al_o values in comparison with Si_d and Al_d indicated preferential dissolution in oxalate of aluminosilicates because of their sensibility to acidity (Jeanroy 1983). These aluminosilicates were characterized by a molar ratio Al_o/Si_o ranging from 0.8 to 3. Fe_o contents varied between 1 and 63 g kg⁻¹, corresponding to

12-31% of Fe total content, whereas Fe_d contents ranged from 4 to 123 g kg⁻¹ according to layers, corresponding to 40-72% of Fe total content (see Table 4). The ratio Fe_o/Fe_d was lower or equal to 0.5 in most layers, which indicated rather a predominance of crystalline Fe oxides. However some limitations must be considered, since oxalate can dissolve some crystalline oxides such as magnetite (Walker 1983) and a single oxalate extraction would be insufficient to dissolve the totality of Fe oxides (Meijer et al. 2007). Oxalate extractable Mn contents (Mn_o) varied between 2 and 25 g kg⁻¹, corresponding to 7-62% of Mn total content while Mehra-Jackson method extracted higher concentrations of Mn ranged from 6 to 225 g kg⁻¹, corresponding to 51-77% of Mn total content according to layers. The distribution of Fe_o , Fe_d , Mn_o and Mn_d along the profile followed respectively the distribution of total Fe and Mn, which seemed to be specific for each layer.

Table 4 Forms of Al, Si, Fe and Mn along the profile of the Technosol developing on a stratified deposit of iron industry by-products (Lorraine, North-East France).

Results presented are Al, Si, Fe and Mn contents obtained with extractions by Tamm (oxalate (o)) and Mehra-Jackson (citrate, hydrogeno-carbonate, dithionite (d)) methods and characteristic ratios. The ($Al_o + \frac{1}{2} Fe_o$) value of 2 % (w/w) or more is a diagnostic criterion of andic properties (WRB).

| layer | layer depth cm | Tamm | | | | Mehra-Jackson | | | | molar ratio Al_o/Si_o | Fe_o/Fe_d | $Al_o + \frac{1}{2} Fe_o$ % (w/w) |
|---------|-------------------|--------------------|--------|--------|--------|--------------------|--------|--------|--------|----------------------------|-------------|--------------------------------------|
| | | Si_o | Al_o | Fe_o | Mn_o | Si_d | Al_d | Fe_d | Mn_d | | | |
| | | g kg ⁻¹ | | | | g kg ⁻¹ | | | | - | - | |
| 1 | 0 - 18 | 19.9 | 18.5 | 63.2 | 11.0 | 3.7 | 9.6 | 123.4 | 13.0 | 1,0 | 0.5 | 5.0 |
| 2 | 18 - 26 | 32.1 | 27.3 | 32.1 | 5.8 | 3.2 | 10.0 | 82.7 | 7.8 | 0,9 | 0.4 | 4.3 |
| 3 | 42 - 55 | 7.1 | 18.9 | 2.9 | 23.0 | 3.6 | 20.8 | 8.8 | 175.7 | 2,8 | 0.3 | 2.0 |
| 4 | 65 - 68 | 27.9 | 28.4 | 3.7 | 8.2 | 2.6 | 6.9 | 7.4 | 14.9 | 1,1 | 0.5 | 3.0 |
| 5 | 68 - 82 | 6.1 | 14.3 | 3.2 | 24.8 | 3.5 | 13.1 | 7.6 | 225.2 | 2,4 | 0.4 | 1.6 |
| 6 | 82 - 91 | 4.9 | 14.3 | 1.7 | 23.6 | 3.2 | 13.3 | 4.4 | 192.6 | 3,0 | 0.4 | 1.5 |
| 7 | 93 - 112 | 11.1 | 21.8 | 16.9 | 22.8 | 3.8 | 17.3 | 30.9 | 142.1 | 2,0 | 0.5 | 3.0 |
| 8 | 112 - 134 | 4.4 | 12.0 | 1.5 | 23.7 | 3.2 | 11.6 | 4.3 | 160.6 | 2,8 | 0.4 | 1.3 |
| 9 | 135 - 150 | 18.9 | 26.0 | 10.5 | 18.6 | 3.4 | 13.6 | 31.8 | 45.5 | 1,4 | 0.3 | 3.1 |
| 10 | 150 - 165 | 7.1 | 17.6 | 6.6 | 22.8 | 3.5 | 15.3 | 29.6 | 132.8 | 2,6 | 0.2 | 2.1 |
| 11 | 165 - 180 | 15.9 | 16.2 | 37.5 | 2.3 | 2.9 | 6.0 | 57.1 | 6.3 | 1,1 | 0.7 | 3.5 |
| 12 | > 180 | 23.6 | 18.3 | 12.4 | 12.1 | 3.3 | 9.3 | 24.0 | 32.2 | 0,8 | 0.5 | 2.4 |
| mean | | 14.9 | 19.5 | 16.0 | 16.6 | 3.3 | 12.2 | 34.3 | 95.7 | 1,8 | 0.4 | 2.7 |
| median | | 13.5 | 18.4 | 8.5 | 20.7 | 3.3 | 12.4 | 26.8 | 89.2 | 1,7 | 0.4 | 2.7 |
| minimum | | 4.4 | 12.0 | 1.5 | 2.3 | 2.6 | 6.0 | 4.3 | 6.3 | 0,8 | 0.2 | 1.3 |
| maximum | | 32.1 | 28.4 | 63.2 | 24.8 | 3.8 | 20.8 | 123.4 | 225.2 | 3,0 | 0.7 | 5.0 |

3.3 Mineralogical characterization

Characterization carried out on six layers by combined techniques (X-ray diffraction, IR spectroscopy, SEM/EDS and TEM/EDS) showed that soil mineralogy was dominated by X-ray poorly crystalline phases and by aluminosilicates, Mn and Fe oxides and hydroxides and carbonates (Table 5). Sulphates were present in the deeper layers. Most aluminosilicates were poorly crystalline, displayed acicular morphology and varying elemental bulk compositions (variable Si/Al ratio and Fe, Mn, Ca, K or Mg

contents). They were also present as glassy spheres rich in Ca in some layers (1, 2 and 11). Such poorly crystalline hydrated aluminosilicates can be assigned to “allophane-like” minerals. Some crystalline clay minerals (probably of the kaolinite and chlorite groups) were also detected. Mn oxides were mainly present as amorphous phases with acicular morphology and containing Al, Si and Ca. Crystalline phases (of MnO₂ formula) were observed in some layers. Fe was present as different oxides and hydroxides and also as metallic form in varying quantity according to layers. Crystalline oxides and hydroxides (mainly magnetite, hematite and goethite) were detected in Fe-rich layers, namely layers 1, 2 and 11. As for carbonate, calcite (CaCO₃) was detected in most layers in varying quantity. Barium sulphate (BaSO₄) was observed in layers 7 and 11 and gypsum (CaSO₄.2H₂O) in layer 11.

Table 5 Main mineral phases in six layers along the profile of the Technosol developing on a stratified deposit of iron industry by-products (Lorraine, North-East France).

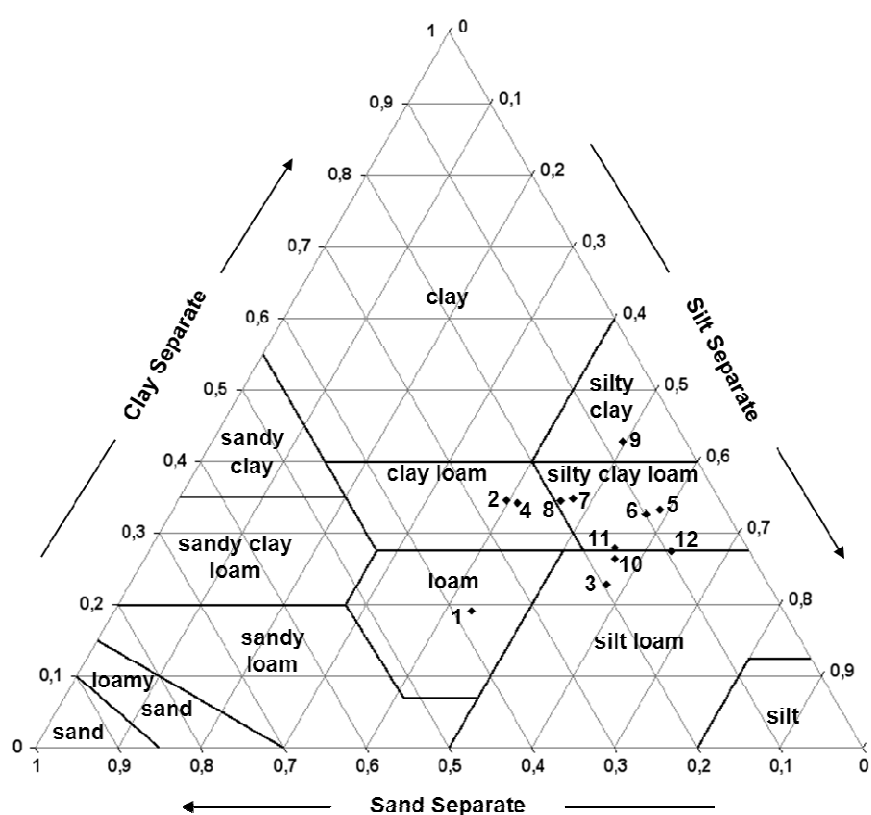
Mineralogy was determined from observations and analyses obtained by combined techniques (XRD, DRIFTS, TEM/EDS and SEM/EDS).

| layer | layer depth cm | main mineral phases |
|-------|-------------------|--|
| 1 | 0-18 | amorphous (Fe, Mn, Ca, Mg and K) and crystalline (Fe and Mg) aluminosilicates Fe oxides and hydroxides amorphous Mn oxides Ca carbonates |
| 2 | 18 - 26 | amorphous (Ca, Fe and Mg) and crystalline (Fe and Mg) aluminosilicates Fe oxides and hydroxides Ca carbonates |
| 4 | 65 - 68 | amorphous (Fe, Mn, Ca and Mg) aluminosilicates Mn crystalline oxides Ca carbonates |
| 5 | 68 - 82 | amorphous (Mn, Ca, Mg and K) aluminosilicates amorphous and crystalline Mn oxides Ca carbonates |
| 7 | 93 - 112 | amorphous (Fe, Mn, Ca and Mg) aluminosilicates amorphous and crystalline Mn oxides Ba sulphates |
| 11 | 165 - 180 | amorphous (Ca, Fe, Mg and Mn) and crystalline (Fe, Mg and K) aluminosilicates Fe oxides and hydroxides Ca carbonates Ca sulphates and Ba sulphates amorphous Mn oxides |

3.4 Physical and hydraulic properties

These materials were dominated by clay ($< 2 \mu\text{m}$) and silt ($2\text{-}50 \mu\text{m}$) fractions, which represent respectively 19 to 43% (w/w) and 40 to 63% (w/w) of dry soil. However sand contents reached 38% (w/w) of dry soil in surface layer. According to the United States Department of Agriculture (USDA) soil texture triangle, most layers were found in the silty clay loam textural class while the surface layer (A horizon) was in the loam class (Fig. 3).

Fig. 3 Soil texture triangle with the major textural classes defined by USDA showing the position of twelve layers along the profile of the Technosol developing on a stratified deposit of iron industry by-products (Lorraine, North-East France).



These materials were characterized by a low bulk density, ranging from 0.2 to 0.7 g cm^{-3} , in comparison to natural soil (Duchaufour 1991) (Table 6). Bulk density seemed to be rather constant along the profile between 0.2 and 0.3 g cm^{-3} except in the surface layer and layer 11 that were denser. Solid density varied from 2.5 to 2.9 g cm^{-3} according to the layers and their constituents.

All layers, except the A horizon, displayed a water content at wilting point higher than 100% (w/w). Water contents at field capacity and at wilting point ranged respectively from 52 to 85% (v/v) and from 42 to 78% (v/v). Hence, available water content varied between 0.5 and 1 mm per cm of soil. The total porosity of these materials represented 75 to 92% of soil volume (Table 6). Capillary porosity, *i.e.* porosity filled by capillarity rise, ranged from 71 to 90% (v/v) (85 to 100% of the total porosity). These materials exhibited a high porosity dominated by micropores ($< 0.2 \mu\text{m}$), according to our measurement

conditions (extractor plate apparatus). Actually, micropores occupied 42 to 79% of soil volume (56 to 87% of the total porosity). They developed also high specific surface area, which varied from 54 to 321 $\text{m}^2 \text{g}^{-1}$ and could be contrasted in consecutive layers, *e.g.* layers 4 and 5 (see Table 6). The surface horizon displayed higher bulk density, lower porosity and specific surface than the other layers.

Saturated hydraulic conductivity (K_s) varied from $2 \cdot 10^{-6}$ to $1 \cdot 10^{-3} \text{m s}^{-1}$ with significant variability between samples for a layer (CV ranged from 30 to 150%). Most of the layers had a K_s ranging between $5 \cdot 10^{-5}$ and $5 \cdot 10^{-4} \text{m s}^{-1}$. Layer 11 was less permeable while layers 5 and 8 had higher conductivity. All layers were considered as semi-permeable materials (Musy and Soutter 1991).

Table 6 Physical and hydraulic parameters (specific surface area (SSA), bulk and solid density, porosity, characteristic water contents and permeability) for ten layers along the profile of the Technosol developing on a stratified deposit of iron industry by-products (Lorraine, North-East France).

The available water content (AWC) was calculated from the difference of water contents at field capacity (pF 2) and wilting point (pF 4.2). Parameters of porosity, water retention and conductivity are presented with mean value \pm standard deviation ($n=3$).

| layer | layer depth cm | SSA $\text{m}^2 \text{g}^{-1}$ | density and porosity | | | | water retention | | | saturated hydraulic conductivity m s^{-1} |
|-------|-------------------|-----------------------------------|------------------------------------|-------------------------------------|---------------------------|-------------------------------|---------------------------|--------------------------|----------------------------|---|
| | | | bulk density g cm^{-3} | solid density g cm^{-3} | total porosity % (v/v) | capillary porosity % (v/v) | field capacity % (v/v) | wilting point % (v/v) | AWC mm cm^{-1} | |
| | | | | | | | | | | |
| 1 | 0 - 8 | 54 | 0.68 ± 0.08 | 2.71 ± 0.25 | 75.0 ± 1.5 | 70.8 ± 2.2 | 51.8 ± 6.4 | 42.0 ± 5.6 | 1.0 | $7 \cdot 10^{-5} \pm 8 \cdot 10^{-5}$ |
| 3 | 42 - 55 | 215 | n.d.* | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | $1 \cdot 10^{-4} \pm 5 \cdot 10^{-5}$ |
| 4 | 65 - 68 | 75 | 0.33 ± 0.02 | 2.62 ± 0.05 | 87.0 ± 0.8 | 75.3 ± 1.3 | 69.8 ± 1.0 | 64.8 ± 1.4 | 0.5 | $9 \cdot 10^{-5} \pm 6 \cdot 10^{-5}$ |
| 5 | 68 - 82 | 219 | 0.26 ± 0.03 | 2.78 ± 0.06 | 91.0 ± 1.0 | 77.3 ± 1.6 | 69.3 ± 3.1 | 59.5 ± 3.0 | 1.0 | $1 \cdot 10^{-3} \pm 4 \cdot 10^{-4}$ |
| 6 | 82 - 91 | 288 | 0.24 ± 0.002 | 2.66 ± 0.04 | 91.0 ± 0.03 | 88.8 ± 0.8 | 81.7 ± 1.0 | 73.7 ± 0.8 | 0.8 | $5 \cdot 10^{-5} \pm 2 \cdot 10^{-5}$ |
| 7 | 93 - 112 | 321 | 0.22 ± 0.01 | 2.85 ± 0.01 | 92.1 ± 0.3 | 87.0 ± 3.1 | 75.7 ± 3.6 | 65.9 ± 6.3 | 1.0 | $4 \cdot 10^{-4} \pm 4 \cdot 10^{-4}$ |
| 8 | 112 - 134 | 211 | 0.29 ± 0.02 | 2.57 ± 0.03 | 88.8 ± 0.6 | 80.0 ± 2.2 | 72.6 ± 3.3 | 63.3 ± 2.5 | 0.9 | $1 \cdot 10^{-3} \pm 4 \cdot 10^{-4}$ |
| 9 | 135 - 150 | 304 | 0.25 ± 0.01 | 2.48 ± 0.02 | 89.9 ± 0.3 | 90.5 ± 0.6 | 84.9 ± 0.3 | 78.5 ± 0.4 | 0.6 | $1 \cdot 10^{-4} \pm 3 \cdot 10^{-4}$ |
| 10 | 150 - 165 | 261 | 0.28 ± 0.02 | 2.46 ± 0.02 | 89.0 ± 1.0 | 87.2 ± 1.9 | 80.9 ± 1.7 | 72.9 ± 2.9 | 0.8 | $2 \cdot 10^{-4} \pm 2 \cdot 10^{-4}$ |
| 11 | 165 - 180 | 161 | 0.53 ± 0.01 | 2.67 ± 0.04 | 80.4 ± 0.1 | 81.6 ± 1.2 | 76.5 ± 1.2 | 70.1 ± 3.4 | 0.6 | $2 \cdot 10^{-6} \pm 1 \cdot 10^{-6}$ |

*n.d.: non determined

4 Discussion

The understanding of the pedogenesis of Technosols needs to know the characteristics of the specific materials they contain. In comparison to similar materials, *i.e.* blast furnace sludge deposit (Mansfeldt and Dohrmann 2004), the composition and the mineralogy were quite different, *e.g.* presence of Mn oxides. The evolution of the Technosol, which led to towards a profile of A1/C type, seemed to be rather slower than this one observed on constructed Technosols (Séré et al. 2010). The coexistence of mineral phases, such as allophane-like minerals, Mn oxides and carbonates is rather rare in natural environment. Hypothesis on future prevailing pedogenetic processes in the Technosol could be made using knowledge about the pedogenesis of the natural soils containing these phases.

4.1 Characteristics of the Technosol developing on iron industry deposit

In comparison with average compositions of surface soils (Sposito 1989; Kabata-Pendias and Pendias 2001), these studied materials were enriched with numerous elements, particularly Mn, Pb, Zn, Ba, Sn, Sr, As, Cu, Sb, Ni, Cd and V and depleted in Si, Al, K and Na. This elemental composition was mostly explained by the composition of the raw materials introduced in the blast furnace and the industrial processes. Contents were comparable to elemental composition of other abandoned landfills of blast furnace sludge (Mansfeldt and Dohrmann 2004). The higher Mn contents may be due to production of ferromanganese, a ferroalloy made out of a mixture of Mn and Fe ore in the iron industry of Pompey-Frouard-Custines from 1922 (Truffaut 2004) and/or to additives for production of special steel. Most elements found in deposit originated from the raw materials used to the production of pig iron, *i.e.* coke as combustible, Fe or Mn ore and often limestone as flux to improve gangue and ashes melting. Enrichment in Pb and Zn as well as As, Cd, Sb, Sn, Cu and B of sludge is due to the fact that they are partially transformed into volatile forms at the bottom of the blast furnace and leave it in the top fumes, though one part condenses in the cooler upper zone and depose on the walls of the blast furnace. Thus they are found in high contents in the sludge resulting from wet cleaning of fumes (Mansfeldt and Dohrmann 2004). The depletion in K and Na, which are quite volatile, might be due to leaching in deposits and/or low amount of these elements in raw materials. On the contrary, the significant concentrations of rather refractory elements such as Ba, V or Ni may suggest that other industrial organic or inorganic by-products could have been dumped in the settling pond, *e.g.* sludge from cleaning of other installations (steel mill, rolling mill) of iron industry. Actually, V and Ni could be used for the production of special steels and/or contained in oil products as metalloporphyrins (Filby and Van Berkel 1987). The variability of the C/N ratio revealed the presence of organic matters of different nature. High values of C/N, which are often encountered in industrial soil materials, mark rather a technogenic origin, *e.g.* oily wastes (Morel et al. 2005). In the blast furnace sludge, the main organic carbon form is the coke (Mansfeldt and Dohrmann 2004), which could also be a potential source of trace elements, such as Ba, V or Ni (Wang et al. 2008). However, the surface layer exhibited an enrichment in C, N and P, which can be explained by natural biogeochemical cycles (Duchaufour 1991).

The detected mineral phases had different origins. Some phases derived from the anthropic processes, *e.g.* the spherical glassy aluminosilicates formed during the high temperature process (Vassilev and Vassileva 1996) or Ba sulphates, which may result from a process often used to remove sulphates or arsenical compounds from water or suspensions (Joussemet et al. 2001). Some Fe oxides could originate from raw materials (iron ore) whereas a set of mineral phases, such as clay minerals, iron hydroxides and calcite, were probably formed after dumping during the evolution of the material submitted to environmental factors, as they would be destroyed by the high temperature in the blast furnace. Hence, they may be considered as secondary minerals.

To characterize the properties of the Technosol, a comparison was made with “natural” soils, which exhibit analogous composition and mineralogy. Volcanic soils were chosen, as they develop on materials

resulting from thermic processes. The physical and hydraulic properties of the studied materials were characterized by a low bulk density, a high porosity and a high water retention capacity. These properties are also encountered in Andosols and a bulk density lower than 0.9 g cm^{-3} is one of the diagnostic criteria of andic properties defined by the WRB classification (IUSS Working Group WRB 2006). Andosols are also characterized by a high total porosity dominated by capillary porosity and microporosity, which can respectively reach 87 to 100% of total porosity (Bartoli et al. 2007) and 90% (v/v) (Baize and Girard 2009) and explain high water retention capacity of these soils. The water content at wilting point of hydric Andosols exceeds 100% (w/w) (IUSS Working Group WRB 2006). Thus, the studied Technosol could be described as hydric as well as thixotropic soil. Andic properties are mainly explained by the presence of low periodic order minerals such as aluminosilicates (allophane, imogolite) and Al and Fe oxyhydroxides resulting from a fast weathering of volcanic materials (Shoji and Fujiwara 1984). As these reactive compounds are extractable by oxalate, one of WRB diagnostic criterion of andic properties is a $(\text{Al}_o + \frac{1}{2} \text{Fe}_o)$ value of 2% or more (IUSS Working Group WRB 2006). In the Technosol, most of studied layers fulfilled this criterion and $(\text{Al}_o + \frac{1}{2} \text{Fe}_o)$ reached 2.7% on average on the profile. In comparison with a collection of European Andosols (Buurman et al. 2007), contents of Si_o are similar (Mann-Whitney test, $p=0.28 > 0.05$) whereas Al_o contents were lower ($p=0.04 < 0.05$). Consequently molar ratio Al_o/Si_o is lower here than in Andosols. Contents of amorphous or poorly crystalline Fe oxides (Fe_o) were comparable to those found in European Andosols ($p=0.33 > 0.05$). However, presence of magnetite in some layers can contribute to oxalate extractable Fe since this oxide was dissolved by oxalate in spite of its good periodic order (Walker 1983). Thus oxalate extractable contents of Si, Al and Fe revealed the presence of short-range order mineral phases as in Andosols but the composition of aluminosilicates seemed to be different (Al/Si ratio). However, one major feature of the studied materials was the high contents of Mn and Mn oxides. Some natural manganese bearing soils exist and are characterized by a dark or purple color, high Mn and Fe contents, low bulk density, high particle density and also high porosity, which can reach 88% and contributes to high water retention capacity of these soils (Bourgault and Rabenhorst 2011). Thus Mn oxides could also explain physical and hydraulic properties of the Technosol.

Concerning the physico-chemical and fertility properties, the studied materials were characterized by slightly alkaline pH, high carbonate contents, high cation exchange capacity (CEC) saturated by Ca^{2+} . Moreover, they fulfilled one other diagnostic criterion of andic properties, namely a content of organic carbon lower than 25% (w/w). Whereas Andosols were also characterized by high CEC, some dissimilarities existed between properties of the Technosol materials and andic properties. Thus, the main difference was the alkaline pH, which could be due to carbonates and formation of CaO, MgO, K_2O and Na_2O during heating in the blast furnace, that alkaline the solution (Sauer and Burghardt 2006). Similarly, presence of carbonates and sulphates was rather rarely encountered in Andosols (Zikeli et al. 2005). However, characteristics as alkaline pH, high content of carbonates and complex saturated by

Ca²⁺, made the Technosol closer to other natural soils such as carbonated soils. According to the WRB, these materials were calcareous since they contained more than 2% of calcium carbonate.

Thus the Technosol developing on deposits of industrial by-products had properties comparable to these developed in some natural soils and could be classified according to the WRB as Spolic Technosol (Calcaric, Loxic, Hydric, Thixotropic, Andic, Toxic).

4.2 Potential pedogenetic processes in the Technosol

At the profile scale, a strong vertical heterogeneity of composition and chemical and physical parameters was recorded with large shifts even between consecutive layers. This reflects a morphological stratification of the Technosol, resulting from settling of successive dumping of sludge of varying nature. The variability of the sludge composition could be mainly explained by the evolution of the raw materials (ore, coke) that had been used and of the techniques of pig iron production as well as possible mixing with other industrial waste. These stratigraphic discontinuities are also found in some volcanic soils due to the gradual or repeated processes of soil burial and deposition of fresh materials (Taboada et al. 2007). They are commonly found in anthropic soils, *e.g.* minesols (Schafer et al. 1980) and make tough observation of weathering and profile development in soils. However, the surface layer exhibited particular characteristics, *e.g.* a coarser texture and enrichment in C, N and P as well as a rather low C/N ratio, which revealed an input of natural organic matter. This feature is one of the early pedogenic processes in most soils (Simonson 1959). In general, C accumulation in the soil profile is rapid particularly in the first 15 or 20 years of forest development on reclaimed soils (Sourkova et al. 2005).

Although it is difficult to assess the mineral weathering without knowing the phases present at the initial state of the materials, some mineral phases seemed to display weathering features. Actually, aluminosilicates with acicular morphology could result from the weathering of the phases present as glassy spheres while some Mn oxides could show signs of carbonatation. At the profile scale, some parameters seemed to show an upward trend with depth, such as S, B, active carbonate or specific surface area. Enrichment in S and presence of sulphates in deeper layers could be due to a downward movement and reprecipitation of sulphates, as it has been observed for gypsum in others Technosols (Zikeli et al. 2002; Séré et al. 2010). However, the heterogeneous distribution of properties along the profile may suggest that interactions and transfers between layers were still rather limited. Physical properties of these materials, such as high microporosity and high water retention, were rather consistent with low and/or very slow vertical transport. Furthermore, the presence of low periodic order phases, such as Mn oxides or allophane-like minerals and an alkaline pH, were rather favourable to the retention of elements, *e.g.* metals (McKenzie 1980; Sauvé et al. 2000).

From the characterization of the soil profile, it could be concluded that these materials, which were dumped over a period of almost one century and were submitted to environmental factors during more than half a century, showed a relatively slow evolution. Pedogenesis was obvious in the upper horizon as a large amount of organic matter accumulated. However, evolution seemed rather limited in this profile,

despite the dominance of finely divided material, a characteristic of most Technosols, where evolution is generally rapid (Séré et al. 2010). The presence of large amounts of low periodic order phases, dominated by Mn oxides and allophane-like minerals, along with a significant amount of calcite suggest a high reactivity and high potential for pedogenetic evolution. But this evolution seems to be blocked by the chemical and physical properties of the materials, *e.g.* the excess of immobile water.

As a forest has developed on this Technosol, changes could be expected from the action of roots which are present in the whole profile, no matter the presence of high concentration of toxic metals (*e.g.* Pb, Zn) as well as from the input of organic matter. In this case, pedogenetic processes would be mainly dependant on the presence of highly reactive minerals (*e.g.* low periodic order minerals) and the excess of carbonate, a feature quite unusual in natural environment. Actually, natural Mn bearing soils are very rare and their formation could be the result of dissolution of carbonated parent rocks, which are the source of oxidized Mn and Fe in the soils and accumulation of non-carbonate residuum (Bourgault and Rabenhorst 2011). Moreover, Andosols are rarely alkaline and carbonated. The particular composition of the Technosol could influence the weathering and the transformation of the components, *e.g.* high pH could favour the formation of amorphous aluminosilicates with Al/Si ratio lower than those resulting from the weathering of volcanic ashes (Zevenbergen et al. 1999) as well as the content of carbonates and salts (Na, Mg) could influence the nature of formed silicates (Sauer and Burghardt 2006). The balance between the transformation processes of these phases and their interactions with other components could direct the future evolution of the materials and the pedogenetic processes that will occur in the soil. Also, this Technosol is quite different than natural soils of the area, which are mainly Cambisols, Luvisols and calcareous soils developed on secondary (calcareous rocks) and quaternary deposits (loess). But with time, it could be assumed that decarbonation and oxidation would occur, followed probably by brunification.

5 Conclusions

Technosols are characterized by the technogenic origin of a part or total of their parent material and the pedogenesis of these soils is still little known. The investigation of a Technosol developing on a former settling pond of the iron industry and supporting a forested ecosystem showed that soil characteristics, *e.g.* elemental composition, mineralogy or stratification, can mainly be explained by the anthropogenic processes they underwent. However, the Technosol displayed properties comparable to those developed in natural soils, such as Andosols, carbonated or manganese bearing soils. If some signs of mineral weathering and of early soil-forming processes such as development of an organic surface layer were observed, the pedogenic evolution seemed to remain still limited and/or slow in the profile in comparison to rapid evolution observed in some Technosols composed of finely divided materials. However, soil physical properties, *e.g.* high water retention and chemical conditions, *e.g.* alkaline pH were rather favourable to low and/or slow transfers in the soil. The presence of highly reactive mineral phases, such as low periodic order Mn oxides or allophane-like minerals, may suggest an important potential for pedogenic evolution. However, the pedogenesis of the soils, which contained these phases (*e.g.* Andosols, Mn bearing and carbonated soils) depended on components and conditions (*e.g.* pH), which rarely coexist in natural environments. The balance between the different ways of weathering of these phases and their consequences on the material (neoformation, change of physico-chemical conditions) could determine the

pedogenesis of the Technosol. With time, some major processes could prevail and lead to the development of a soil profile, which could be similar to those observed in natural environment.

6 Recommendations and perspectives

Current physico-chemical conditions and structure of the Technosol were rather favourable to physical stabilization of potentially harmful compounds it contains. However the evolution of the Technosol under the influence of soil-forming factors could change this state. In particular, the influence of vegetation could be substantial through the input of organic matter and the rhizospheric effects. Indeed, roots could act both on soil structure and transport by generating preferential flows and on mobilisation of elements by changing physico-chemical conditions in the rhizosphere, *e.g.* pH and redox potential and by exuding some chelating components, *e.g.* organic acids. Thus, assessment of the influence of vegetal cover on soil evolution could be considered to find sustainable solutions of management for such brownfield sites.

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