

Assessing the surface composition of soil particles from some Podzolic soils by X-ray photoelectron spectroscopy

G. Yuan ^{a,*}, M. Soma ^b, H. Seyama ^c, B.K.G. Theng ^a,
L.M. Lavkulich ^d, T. Takamatsu ^c

^a Landcare Research, PB 11052, Palmerston North, New Zealand

^b University of Shizuoka, 52-1 Yada, Shizuoka 422, Japan

^c National Institute for Environmental Studies, Tsukuba, Japan

^d University of British Columbia, Vancouver, Canada

Received 8 September 1997; accepted 22 April 1998

Abstract

We have applied X-ray photoelectron spectroscopy (XPS) to assess the surface composition of soil particles in the AB, Bf, and Bhf horizons of some Podzolic soils from British Columbia, Canada. Since the analysis is restricted to a 'depth' of < 10 nm from the particle surface, this technique is uniquely suited to this purpose. For the soils used here, the elements detected in decreasing order of abundance are oxygen (46–54%), carbon (13–38%), silicon (3.2–20%), aluminium (4.8–14%), iron (1.0–4.4%), and nitrogen (0.4–2.9%). Small amounts of sodium and magnesium are also measured. In comparison with the corresponding values for the bulk soils, the surface of soil particles is enriched in C, N, and Al. As C and N may be assigned to organic matter (OM), this finding is strongly indicative of the presence of Al–organic complexes as a coating over soil particle surfaces. Unlike Al, Fe is relatively depleted at the surface of soil particles probably because Fe tends to precipitate as an oxyhydroxide phase in the pH range (4.1–5.3) of the soils sampled. Silicon is also depleted at soil particle surfaces but the extent of depletion is smaller for the AB than for the underlying Bf horizons. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Podzol; soil particles; surface composition; XPS

* Corresponding author. Fax: +64-6-355-9230; E-mail: yuang@landcare.cri.nz

1. Introduction

It is generally accepted that the majority of chemical interactions in soil take place at the soil particle–soil solution interface (Bolt et al., 1991). As such, the nature and properties of soil particles would have a controlling influence on important soil processes. The expression of these properties would, in turn, depend on the composition of soil particle surfaces. For many soils, this composition is likely to differ from that of the bulk material since soil particles commonly have a covering of extraneous substances. In certain Podzol horizons, for example, humified organic matter (OM) complexed with Al (or Al and Fe) is known to form a coating around soil particles, or a lining over aggregate pores (De Coninck, 1980). The chemical composition of such coatings and other cementing agents has been extensively studied using various techniques, including selective dissolution, optical microscopy, scanning electron microscopy, and energy dispersive X-ray analysis (McKeague and Wang, 1980; McHardy and Robertson, 1983; McKeague et al., 1983; Lee et al., 1988; Courchesne et al., 1996).

Each of these ‘conventional’ analytical techniques, however, has its own limitation by being either invasive, incapable of detecting certain constituent elements, or not being surface-specific. On the other hand, X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA), as the technique is sometimes called, has none of these limitations. Besides being non-destructive, XPS has the added advantage of being able to detect all elements in soil (except for H and He). However, the principal advantage of XPS is its surface specificity in that the ‘depth’ of analysis only extends to several nanometres from the particle surface (Briggs and Seah, 1990). A possible drawback of XPS is the requirement for a high vacuum environment, giving rise to problems for some samples if surface dehydration is of concern.

As the name suggests, XPS involves irradiating the (solid) sample with X-ray photons, detecting the core and valence shell electrons ejected under an ultra-high vacuum, and measuring their kinetic energy. The difference between the incoming photon energy and the kinetic energy gives the binding energy of the escaping photoelectron. Since the ‘escape depth’ is limited to less than 10 nm, only electrons from elements at and near the surface of the solid can be detected and analysed (Paterson and Swaffield, 1994).

XPS has provided much valuable information on the composition of, and bonding state of elements in, surface and near-surface layers of many minerals (Koppelman, 1980; Hochella, 1988; Seyama and Soma, 1988; Soma et al., 1992; Cocke et al., 1994; Soma et al., 1996; Childs et al., 1997). To our knowledge, however, the technique has not been applied to probe the surface composition of soil particles. Here, we have used XPS to assess the chemical composition of soil particle surfaces in Podzolic soils (Spodosols) from British Columbia, Canada. These soils were chosen because podzolization involves the formation,

translocation, and deposition of amorphous materials within the soil profile, all of which are surface-controlled processes (De Coninck, 1980; Flach et al., 1980; McKeague et al., 1983). The information gained from this investigation would also have implications for, and help advance understanding of, the movement and retention of plant nutrients and introduced contaminants in soil.

2. Materials and methods

2.1. Soil samples

Podzolic soils are the dominant soils in many upland, well-drained areas of south-western British Columbia, Canada. These soils characteristically lack an Ae (or E) horizon, possibly as a result of physical disturbance, intensive chemical leaching, or both. The samples used were taken from two separate areas under forest. In both instances, the soils have developed over glacial till, and are classified as Orthic Humo-Ferric Podzols in the Canadian soil classification system (Agriculture Canada Expert Committee on Soil Survey, 1987), or Typic Haplorthods in Soil Taxonomy. The first set of samples, prefixed 'V' in Table 1, came from the Pacific Spirit Park (49°16'N, 123°14'W) in Vancouver, forming part of the Bose and Summer series (Luttmerding, 1981). The second set of soils, denoted by prefix 'C' in Table 1, were sampled at the Cowichan Lake Research Station (48°50'N, 128°8'W) on Vancouver Island, and belonged to the Rumsley and Shawnigan soil series (Jungen et al., 1989).

For this study, we took 18 soil samples representing 12 pedons in terms of genetic horizons. For each pedon, we used at least one sample from the B horizon, where intensive mineral–organic interactions are likely to occur. Where possible samples from the AB horizons were used for comparison. The samples were air dried, gently crushed with a wood rolling pin, and sieved to pass a 2-mm sieve. The < 2 mm fraction was used without any further treatment. A description and some properties of the soils are given in Table 1.

2.2. XPS measurements

XP spectra were obtained from samples mounted on 10-mm diameter stainless steel holders by a double-sided adhesive tape. A sufficient amount of each sample was placed on the tape by repeated sprinklings. The spectra were recorded on a Vacuum Generators ESCALAB 5 instrument using Mg K_{α} (for Si, Al, C, O, N, and Na) and Al K_{α} (for Si, Fe, and Mg) X-ray sources at 12 kV and 10 mA. Two wide-scan spectra, covering a binding energy (BE) range from 0 to 1250 eV, were obtained for each soil. As an example, Fig. 1 shows the wide-scan spectrum for sample C928-3. For each visible peak, a narrow-scan

Table 1
Description and properties of the soil samples

| Soil sample ^a | Depth (cm) | Horizon | pH (H ₂ O) | Bulk composition (g/kg) ^b | | | | | | | Sand (g/kg) | Silt | Clay ^c |
|--------------------------|------------|---------|-----------------------|--------------------------------------|----|-----|------|------|----|-----|-------------|------|-------------------|
| | | | | Al | Fe | Si | C | N | Ca | K | | | |
| V911-3 | 2–10 | Bf | 5.34 | 67 | 42 | 191 | 21.4 | 0.69 | 21 | 7.7 | 743 | 158 | 99 |
| V912-3 | 10–30 | Bf | 4.75 | 66 | 32 | 200 | 13.3 | 0.48 | 20 | 7.0 | 728 | 195 | 77 |
| V913-4 | 2–10 | Bhf | 4.79 | 65 | 33 | 174 | 46.8 | 1.54 | 19 | 7.6 | 742 | 177 | 81 |
| V914-2 | 0–10 | AB | 4.23 | 48 | 24 | 200 | 34.2 | 1.32 | 20 | 7.7 | 619 | 319 | 62 |
| V914-3 | 10–30 | Bf | 5.18 | 59 | 32 | 196 | 33.0 | 0.97 | 19 | 7.8 | 646 | 280 | 74 |
| C921-3 | 0–10 | Bf | 4.08 | 63 | 50 | 202 | 38.9 | 0.96 | 21 | 7.9 | 430 | 439 | 131 |
| C921-4 | 10–35 | Bf | 4.37 | 77 | 56 | 203 | 29.6 | 1.00 | 21 | 8.1 | 438 | 432 | 130 |
| C922-3 | 20–40 | Bf | 5.06 | 77 | 58 | 207 | 10.6 | 0.30 | 22 | 8.4 | 493 | 388 | 119 |
| C923-2 | 0–15 | Bf | 4.80 | 75 | 54 | 198 | 15.2 | 0.50 | 22 | 8.4 | 493 | 406 | 101 |
| C924-2 | 0–2 | AB | 4.28 | 50 | 35 | 232 | 14.7 | 0.40 | 23 | 5.8 | 341 | 584 | 75 |
| C924-3 | 2–15 | Bf | 4.89 | 78 | 56 | 199 | 16.1 | 0.53 | 23 | 7.4 | 500 | 387 | 113 |
| C925-2 | 0–15 | AB | 4.53 | 53 | 40 | 218 | 29.8 | 0.50 | 25 | 6.9 | 330 | 568 | 102 |
| C925-3 | 15–40 | Bf | 5.16 | 77 | 61 | 205 | 11.5 | 0.63 | 22 | 9.8 | 670 | 232 | 98 |
| C926-2 | 0–25 | AB | 4.81 | 60 | 52 | 211 | 23.9 | 0.93 | 24 | 7.5 | 349 | 538 | 113 |
| C926-3 | 25–55 | Bf | 5.04 | 70 | 56 | 202 | 8.8 | 0.53 | 24 | 8.6 | 538 | 376 | 86 |
| C927-2 | 0–20 | Bf | 4.89 | 65 | 50 | 205 | 29.0 | 1.10 | 24 | 7.7 | 441 | 450 | 109 |
| C927-3 | 20–40 | Bf | 5.07 | 59 | 51 | 221 | 13.6 | 0.63 | 25 | 7.8 | 355 | 539 | 106 |
| C928-3 | 20–50 | Bf | 5.04 | 70 | 57 | 206 | 13.4 | 0.76 | 24 | 8.7 | 515 | 395 | 90 |

^aSamples with the same prefix (e.g., V914-2 and V914-3) are from the same pedon.

^bAl, Si, Fe, Ca, and K were determined by X-ray fluorescence. Pressed pellets made from pulverized samples with silicon dioxide and/or cellulose were analysed using calibration curves. Carbon by dry combustion in a Leco analyzer and N by the Dumas method in a Carlo Elba 1106 analyzer.

^cSand (2–0.05 mm), silt (0.05–0.002 mm), and clay (< 0.002 mm) contents were determined by the pipette method after oxidizing OM with H₂O₂ and removing sesquioxides with citrate–bi-carbonate–dithionite reagent.

Table 2
Relative sensitivity factors used in calculating surface atomic ratios by XPS (Si(2s) = 1.00)

| Element | Line | Sensitivity factor (X-ray source) |
|---------|-----------|-----------------------------------|
| Si | 2p | 1.24 (Mg) |
| | 2p | 0.969 (Al) |
| C | 1s | 0.955 (Mg) |
| O | 1s | 2.02 (Mg) |
| Al | 2p | 0.741 (Mg) |
| | 2p | 0.520 (Al) |
| N | 1s | 1.53 (Mg) |
| Na | KLL Auger | 6.69 (Mg) |
| Fe | 2p | 10.2 (Al) |
| Mg | KLL Auger | 8.00 (Al) |

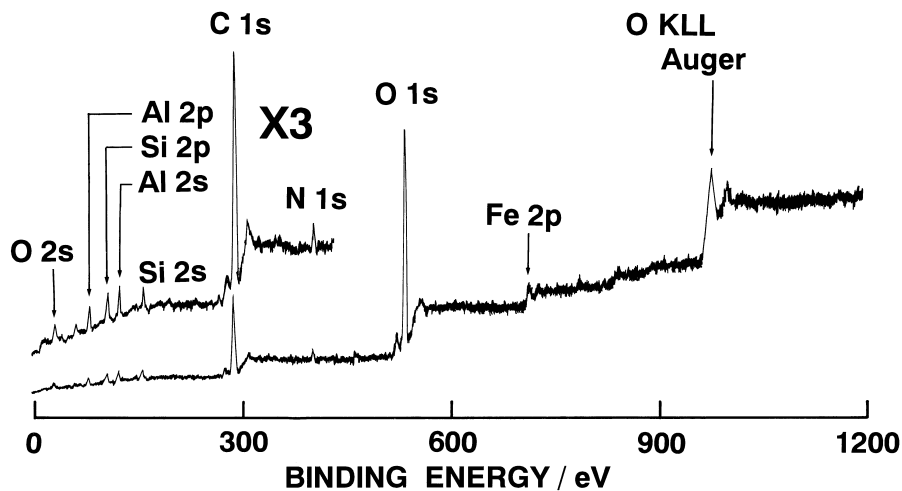


Fig. 1. Wide-scan X-ray photoelectron spectrum of soil C928-3 excited by Al K_{α} radiation (upper band is the enlargement of the left part of the spectrum).

spectrum (50 eV for the Fe(2p) photoelectron, and 25 eV for all others) was also determined, the signals of which were accumulated. The resultant enhancement in the signal/noise ratio allowed the position of each narrow-scan peak to be determined accurately. The binding energies of ejected photoelectrons were obtained from the corresponding peak positions, and calibrated against the 4f7/2 line at 84.0 eV of gold deposited on the soil sample under vacuum. The uncertainty in BE values is typically ± 0.2 eV.

Atomic ratios of Al, Fe, C, O, N, Na, and Mg, relative to Si, were calculated from the areas of the Al(2p), Fe(2p), C(1s), O(1s), N(1s), Na(KLL Auger), Mg(KLL Auger), and Si(2s) peaks, respectively, using the experimentally determined atomic sensitivity factors listed in Table 2. Silicon was chosen as the common denominator because of its ubiquitous occurrence in soil, and its well-defined XPS signal. Table 3 gives the atomic ratios of the elements and their contents. The elemental compositions were calculated from individual atomic ratios and atomic weights, assuming that the contribution of H was negligible.

2.3. Quantitative analysis

The absolute intensities of photoelectron peaks are influenced by such factors as the density, chemical composition, and surface roughness of the sample. However, the intensity of a given peak relative to that of another may be assumed to be proportional to the atomic ratio of the corresponding elements. XPS quantitative analysis with accuracy as good as 10% is possible (Paterson and Swaffield, 1994; Vempati et al., 1996) for spectra recorded under identical

Table 3
Atomic ratios and elemental compositions by XPS

| Soil sample/horizon | Atomic ratios to Si | | | | | | | Elemental composition (g/kg) | | | | | | | |
|---------------------|---------------------|------|-------|-------|-------|-------|-------|------------------------------|-----|-----|------|------|-----|-----|------|
| | O | C | Al | N | Fe | Na | Mg | O | C | Al | N | Fe | Si | Na | Mg |
| V911-3/Bf | 8.90 | 6.31 | 1.13 | 0.317 | 0.169 | 0.054 | 0.057 | 486 | 258 | 104 | 15.1 | 32.2 | 96 | 4.2 | 4.7 |
| V912-3/Bf | 10.3 | 6.31 | 1.33 | 0.421 | 0.180 | 0.050 | 0.040 | 511 | 235 | 111 | 18.3 | 31.1 | 87 | 3.6 | 3.0 |
| V913-4/Bhf | 24.9 | 27.4 | 2.65 | 1.79 | 0.300 | 0.067 | 0.163 | 455 | 377 | 82 | 28.7 | 19.2 | 32 | 1.8 | 4.5 |
| V914-2/AB | 4.70 | 2.94 | 0.270 | 0.143 | 0.026 | 0.059 | 0.032 | 496 | 233 | 48 | 13.2 | 9.6 | 185 | 9.0 | 5.1 |
| V914-3/Bf | 10.0 | 7.61 | 1.22 | 0.515 | 0.147 | 0.076 | 0.048 | 485 | 276 | 99 | 21.8 | 24.8 | 85 | 5.3 | 3.5 |
| C921-3/Bf | 7.19 | 3.21 | 0.850 | 0.140 | 0.119 | 0.060 | 0.087 | 531 | 178 | 105 | 9.1 | 30.7 | 130 | 6.4 | 9.8 |
| C921-4/Bf | 14.4 | 11.0 | 1.65 | 0.428 | 0.185 | 0.075 | 0.104 | 505 | 290 | 98 | 13.2 | 22.7 | 62 | 3.8 | 5.6 |
| C922-3/Bf | 12.6 | 5.64 | 1.99 | 0.272 | 0.299 | 0.075 | 0.109 | 536 | 180 | 143 | 10.1 | 44.4 | 75 | 4.6 | 7.1 |
| C923-2/Bf | 10.3 | 4.46 | 1.59 | 0.210 | 0.179 | 0.074 | 0.090 | 537 | 175 | 140 | 9.6 | 32.7 | 92 | 5.6 | 7.2 |
| C924-2/AB | 4.83 | 1.84 | 0.460 | 0.040 | 0.071 | 0.061 | 0.060 | 525 | 150 | 84 | 3.8 | 26.9 | 191 | 9.5 | 9.9 |
| C924-3/Bf | 8.67 | 3.69 | 1.27 | 0.165 | 0.161 | 0.055 | 0.067 | 534 | 171 | 132 | 8.9 | 34.6 | 108 | 4.9 | 6.3 |
| C925-2/AB | 4.84 | 1.49 | 0.440 | 0.068 | 0.082 | 0.049 | 0.063 | 541 | 125 | 82 | 6.6 | 31.9 | 196 | 7.8 | 10.7 |
| C925-3/Bf | 11.6 | 6.05 | 1.50 | 0.448 | 0.239 | nd | 0.097 | 533 | 208 | 116 | 18.0 | 38.2 | 80 | nd | 6.7 |
| C926-2/AB | 6.70 | 3.95 | 0.640 | 0.200 | 0.110 | 0.087 | 0.104 | 502 | 222 | 81 | 13.1 | 28.8 | 132 | 9.4 | 11.8 |
| C926-3/Bf | 13.8 | 6.93 | 2.16 | 0.467 | 0.253 | 0.070 | 0.098 | 532 | 201 | 140 | 15.8 | 34.1 | 68 | 3.9 | 5.7 |
| C927-2/Bf | 9.00 | 5.48 | 1.01 | 0.357 | 0.134 | 0.067 | 0.106 | 511 | 234 | 97 | 17.7 | 26.6 | 100 | 5.5 | 9.1 |
| C927-3/Bf | 6.14 | 2.11 | 0.650 | 0.140 | 0.120 | 0.075 | 0.095 | 540 | 139 | 96 | 10.8 | 36.9 | 154 | 9.5 | 12.7 |
| C928-3/Bf | 12.7 | 9.48 | 1.51 | 0.600 | 0.265 | 0.068 | 0.137 | 490 | 275 | 99 | 20.3 | 35.8 | 68 | 3.8 | 8.1 |

nd = not detectable.

Table 4
Comparison of XPS and ideal compositions of zeolites

| Mineral | Ideal Al/Si atomic ratio ^a | X-ray | XPS atomic ratio | |
|----------------------------|---------------------------------------|-----------------|------------------|---------------|
| | | | Al/Si | Si(2p)/Si(2s) |
| Analcime (Yamagata, Japan) | 0.50 | Mg K_{α} | 0.50 | 0.99 |
| | | Al K_{α} | 0.52 | 1.02 |
| Natrolite (NJ, USA) | 0.67 | Mg K_{α} | 0.71 | 0.95 |
| | | Al K_{α} | 0.71 | 1.01 |
| Scolecite (Poona, India) | 0.67 | Mg K_{α} | 0.69 | 0.98 |
| | | Al K_{α} | 0.72 | 1.01 |
| Stilbite (Poona, India) | 0.38 | Mg K_{α} | 0.33 | 0.99 |
| | | Al K_{α} | 0.34 | 0.99 |

^aData from Anthony et al. (1995).

experimental conditions, and using peaks with binding energies within a few hundred electron volts of each other. In analysing the principal elements of clay minerals, Adams et al. (1977) were able to obtain an accuracy, on average, of 5% by comparison with established wet-chemical methods.

Here, we used finely ground crystalline zeolites (analcime, natrolite, scolecite, and stilbite) to evaluate the accuracy of the XPS measurements. A maximum difference of 13% was observed between the Al/Si atomic ratio, measured by XPS, and the value derived from the ideal composition of the different zeolites (Table 4). Although this result was acceptable for our purposes, we also derived the Si(2p)/Si(2s) ratio as a further check for accuracy. Since the photoelectrons were of the same element (Si), but ejected from different core levels, this ratio should ideally be unity. For the zeolites, the experimentally derived Si(2p)/Si(2s) ratio was close to 1.00 (Table 4). In the case of the soil samples, this ratio ranged from 0.93 to 1.03 (0.98 ± 0.03) which was within acceptable limits.

3. Results and discussion

3.1. Carbon, nitrogen, and organic matter coatings

Fig. 2 shows an example of a narrow-scan C(1s) peak with its typical asymmetric shape, tailing towards the high binding energy end (c). The signal may be decomposed into two components (a and b). Band 'a' is the C(1s) reference peak of tetraethylammonium chloride, representing carbon in C–H and C–C bonds. The BE values (283.8–285.4 eV) of band 'a' of the soils are in good agreement with the C(1s) binding energy of about 285 eV for carbon in such bonds (Stipp and Hochella, 1991). Band 'b' is the residue of band 'c' minus band 'a', indicating carbon in bonds other than C–H and C–C. By

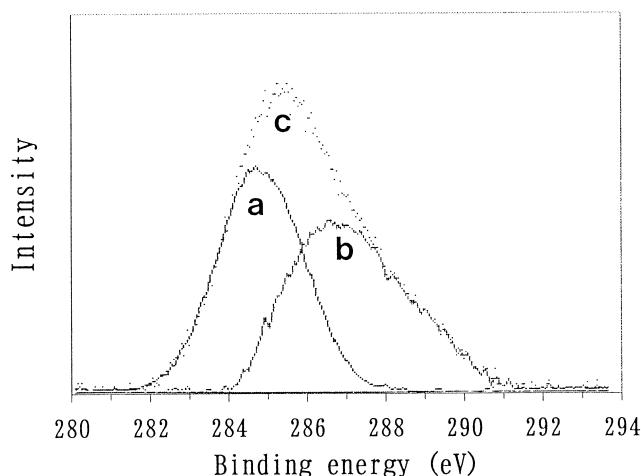


Fig. 2. Observed C(1s) spectrum 'c' of soil C928-3 with computer fit components 'a' and 'b'. Bands 'a' and 'b' indicate C(1s) spectra due to hydrocarbon and non-hydrocarbon (e.g., carbonyl group), respectively.

comparison, the BE values for component 'b' are significantly larger, varying from 285.7 to 287.3 eV in the 18 soil samples. Since O bound to C is known to increase C(1s) binding energies by 1.5 eV per C–O bond (Briggs, 1990), band 'b' may be assigned to carbon in C–O, C=O, and COO groups.

The N(1s) binding energies of 399.4 to 400.1 eV of the 18 soil samples are much lower than those for N in inorganic compounds, such as ammonium (401.7 eV) and nitrate (407.3 eV), as reported by Wagner (1990). However, the BE values are consistent with nitrogen in NR_3 groups (where R represents hydrogen and/or alkyl) as in amides and amines.

The XPS data suggest that most of the carbon in the samples is due to soil OM associated with particle surfaces. Although some contamination by hydrocarbons from external sources (e.g., pump oil) during analysis cannot be ruled out, its effect on the C(1s) peak in the XPS spectra is unlikely to be significant. In the case of nitrogen, the possibility of sample contamination by adventitious nitrogenous compounds does not arise. The N(1s) band can thus be ascribed entirely to N in OM. The postulate that both C and N have their origin in OM on surfaces of soil particles is further supported by the close correlation ($r = 0.87^{**}$) between the C and N contents (g/kg) measured by XPS. In addition, the correlation coefficient by XPS agrees well with the corresponding value obtained for the C and N contents ($r = 0.84^{**}$) of the bulk samples (Table 1).

The high carbon (12.5–37.7%) and nitrogen (0.4–2.9%) contents of the samples, measured by XPS (Table 3), are in sharp contrast with the low values determined for the corresponding bulk soils (Table 1). This observation strongly indicates that the OM in the samples occurs as a coating over particle surfaces, rather than being dispersed throughout the whole soil. The coating may not

necessarily be continuous at the molecular scale, nor needs its thickness be the same from place to place because XPS cannot distinguish between a mineral surface that is completely and homogeneously covered by OM and one containing ‘islands’ of OM. The existence of an OM coating is further supported by comparing the Si content by XPS with that of the bulk (by XRF) on the assumption that the Si measured by XPS is entirely due to the surface which is not covered by OM. Surface coverages by OM estimated from the ratio $(Si_{\text{bulk}} - Si_{\text{XPS}})/Si_{\text{bulk}}$ average 56% for the samples from B horizons, and 24% for samples from AB horizons.

3.2. Surface composition

Table 3 shows that the surface of soil particles in the AB, Bhf, and Bf horizons is abundant in oxygen, aluminium, and silicon (as well as carbon). Fe and N were detected in lesser quantities by XPS together with minor amounts of sodium and magnesium. Since Na and Mg were not determined in the bulk samples, direct comparisons between surface and bulk compositions could not be made. Interestingly, Ca and K were not detected by XPS although they occurred in significant concentrations in the bulk soils (Table 1). The surface depletion of Ca and K suggests that these elements have been leached out from soil-particle surfaces because they are only weakly bound to OM (McBride, 1994).

The concentration of Al at the surface, measured by XPS (Table 3), is appreciably larger than that in the bulk soil (Table 1). Thus, for all samples, except V914-2, the ratio of $Al_{\text{XPS}}/Al_{\text{bulk}}$ is greater than unity with an average of 1.57. Because of the ‘diluting’ effect of OM, the surface accumulation of Al is an absolute, rather than a relative, enrichment. Although Al is known to be closely associated with OM in Podzols (McKeague and Wang, 1980; McHardy and Robertson, 1983; Lee et al., 1988; Courchesne et al., 1996), this is the first direct evidence for the surface accumulation of Al–organic complexes in such soils.

The Si detected by XPS probably originates from clays and other silicate minerals. In contrast to Al, the ratio of $Si_{\text{XPS}}/Si_{\text{bulk}}$ is less than unity, averaging 0.52 for all samples. Further, this ratio is greater for samples from the AB horizons than from the corresponding Bf horizons. Since the Bf horizons are more enriched in carbon than the AB horizons, the depletion of Si at particle surfaces is due, at least partly, to dilution by OM.

Like Si, but again unlike Al, Fe is relatively depleted at the surface of soil particles, giving an average value of 0.65 for the $Fe_{\text{XPS}}/Fe_{\text{bulk}}$ ratio. The contrast in surface abundance between Fe and Al is also apparent when the Al/Fe ratio, measured by XPS, is compared with the same ratio for the bulk soil (Fig. 3). For the soils used, the average value of $(Al/Fe)_{\text{XPS}}/(Al/Fe)_{\text{bulk}}$ is about 2.5. This finding is, at first sight, somewhat surprising since in Podzols Al

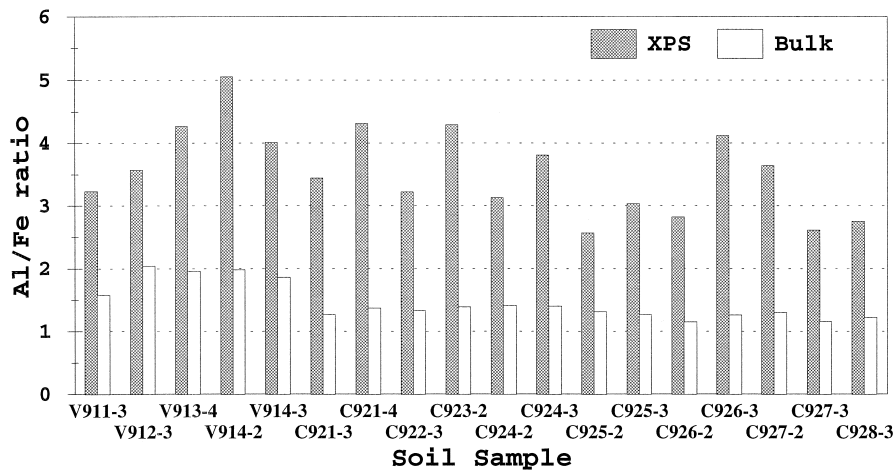


Fig. 3. The XPS and bulk ratios of Al/Fe show the differential behaviours of Al and Fe in soils.

and Fe often tend to form complexes with OM (Flach et al., 1980; McKeague et al., 1983). Using pyrophosphate-extractable sesquioxides as chemical criteria of Podzolic horizons also implies the formation of Al and Fe complexes with OM. However, the pK_1 for Fe^{3+} hydrolysis (2.19) is much smaller than that for Al^{3+} hydrolysis (5.02) (Lindsay, 1979). In the pH range of the soils used here (4.1–5.3), ferric ions, liberated from primary minerals, would quickly form short-range oxyhydroxides. This and the protonation of carboxylate (ligand) groups of OM would disfavour formation of Fe–organic complexes. On the other hand, at pH 4.1–5.3, Al would exist as Al^{3+} , $Al(OH)^{2+}$, and $Al(OH)_2^+$ species, all of which are capable of forming complexes with OM (McBride, 1994).

4. Conclusions

XPS is uniquely capable of probing the surface composition of soil particles because it can ‘see’ both inorganic and organic constituents only up to a depth of 10 nm. By this means, we have been able to show that the surfaces of soil particles in some Podzolic soils from British Columbia, Canada, are enriched in Al, C, and N. As the latter two elements may largely be assigned to OM, the XPS data strongly indicate the presence over soil particle surfaces of Al–organic complexes probably in the form of a coating. Similar conclusions have previously been drawn from a combination of analytical techniques, notably electron microscopy and energy dispersive analysis (EDA). By itself, however, EDA cannot detect the major elements (C, N, and O) of soil OM, the presence of which is usually inferred from that of other elements, such as P and S. Since the

depth of analysis is also much greater than that attainable with XPS, EDA cannot be regarded as a surface-specific technique.

XPS further shows that, in contrast to Al, Si and Fe are relatively depleted from soil particle surfaces. The surface depletion of Fe is somewhat unexpected in that Fe, like Al, has a propensity for complexing OM in many Podzols. We suggest that in the pH range of the soils (4.1–5.3) Fe is quickly precipitated as an oxyhydroxide phase. On the other hand, Al and positively charged Al-hydroxide species remain soluble, and can form complexes with OM.

The results of this investigation are clearly important to understanding podzolization. The accumulation of OM at particle surfaces also has implications for other soil processes. Besides acting as a stabilizing agent of soil aggregates, this organic material would play an active role in the retention of introduced non-ionic organic compounds (e.g., pesticides, polycyclic aromatics) because such compounds are essentially sorbed by partition into soil OM (Chiou, 1989). On this basis, the extent to which introduced organic compounds are sorbed on particle surfaces of these soils might be expected to exceed the level predicted from the carbon content of the bulk soils.

Acknowledgements

G. Yuan thanks the Japan Science and Technology Agency for a fellowship during which tenure this work was carried out. We acknowledge the helpful suggestions and comments by Dr. H.J. Percival, Dr. R. Gilkes and an anonymous reviewer.

References

- Adams, J.M., Evans, S., Reid, P.I., Thomas, J.M., Walters, M.J., 1977. Quantitative analysis of aluminosilicate and other solids by X-ray photoelectron spectroscopy. *Anal. Chem.* 49, 2001–2008.
- Agriculture Canada Expert Committee on Soil Survey, 1987. *The Canadian System of Soil Classification*, 2nd edn. Agric. Can. Publ. 1646, 164 pp.
- Anthony, J.W., Bideaux, R.A., Bladh, K.W., Nichols, M.C., 1995. *Silica, Silicates*. Handbook of Mineralogy, Vol. 2. Mineral Data Publishing, Tucson, AZ.
- Bolt, G.H., De Boodt, M.F., Hayes, M.H.B., McBride, M.B., 1991. *Interactions at the Soil Colloid–Soil Solution Interface*. NATO ASI Series Vol. 190. Kluwer Academic Publishers, Dordrecht, 603 pp.
- Briggs, D., 1990. Application of XPS in polymer technology. In: Briggs, D., Seah, M.P. (Eds.), *Auger and X-ray Photoelectron Spectroscopy*. Practical Surface Analysis, 2nd edn., Vol. 1. Wiley, Chichester, UK, pp. 437–483.
- Briggs, D., Seah, M.P., 1990. *Auger and X-ray Photoelectron Spectroscopy*. Practical Surface Analysis, 2nd edn., Vol. 1. Wiley, Chichester, UK.

- Childs, C.W., Inoue, K., Seyama, H., Soma, M., Theng, B.K.G., Yuan, G., 1997. X-ray photoelectron spectroscopic characterization of silica springs allophane. *Clay Miner.* 32, 565–572.
- Chiou, C.T., 1989. Theoretical considerations of the partition uptake of non-ionic organic compounds by soil organic matter. In: Sawhney, B.L., Brown, K. (Eds.), *Reactions and Movement of Organic Chemicals in Soils*. SSSA Special Publication Number 22. Soil Science Society of America, Madison, WI, pp. 1–29.
- Cocke, D.L., Vempati, R.K., Loeppert, R.H., 1994. Analysis of soil surfaces by X-ray photoelectron spectroscopy. In: Amonette, J.E., Zelazny, L.W. (Eds.), *Quantitative Methods in Soil Mineralogy*. SSSA Miscellaneous Publication, SSSA, Madison, WI, pp. 205–235.
- Courchesne, F., Turmel, M.C., Beauchemin, P., 1996. Magnesium and potassium release by weathering in Spodosols: grain surface coating effects. *Soil Sci. Soc. Am. J.* 60, 1188–1196.
- De Coninck, F., 1980. Major mechanisms in formation of spodic horizons. *Geoderma* 24, 101–128.
- Flach, K.W., Holzhey, C.S., De Coninck, F., Bartlett, R.J., 1980. Genesis and classification of Andepts and Spodosols. In: Theng, B.K.G. (Ed.), *Soils with Variable Charge*. New Zealand Society of Soil Science, Soil Bureau, DSIR, Lower Hutt, New Zealand.
- Hochella, M.F., Jr., 1988. Auger electron and X-ray photoelectron spectroscopies. In: Hawthorne, F.C. (Ed.), *Spectroscopic Methods in Mineralogy and Geology*. *Rev. Mineral.*, Vol. 18. Mineral. Soc. Am., Washington, DC, pp. 573–637.
- Jungen, J.R., Christie, P.J., Philp, J.P., 1989. *Soils of Southeast Vancouver Island Parksville, Qualicum Beach, Courtenary, and Port Alberni Areas*. B.C. Soil Survey Report No. 57, Ministry of Environment and Ministry of Agriculture and Fisheries, Victoria, British Columbia, Canada.
- Koppelman, M.H., 1980. Application of X-ray photoelectron spectroscopy to the study of mineral surface chemistry. In: Stucki, J.W., Banwart, W.L. (Eds.), *Advanced Chemical Methods for Soil and Clay Minerals Research*, D. Reidel Publishing, Dordrecht, pp. 205–243.
- Lee, F.Y., Yuan, T.L., Carlisle, V.W., 1988. Nature of cementing materials in Ortstein horizons of selected Florida Spodosols: I. Constituents of cementing materials. *Soil Sci. Soc. Am. J.* 52, 1411–1418.
- Lindsay, W.L., 1979. *Chemical Equilibria in Soils*. Wiley, New York, 449 pp.
- Luttmerding, H.H., 1981. *Soils of the Langley–Vancouver Map Area*. Soil Survey Report No. 15. Ministry of Environment, Kelowna, British Columbia, Canada.
- McBride, M.B., 1994. *Environmental Chemistry of Soils*. Oxford Univ. Press, Oxford.
- McHardy, W.J., Robertson, L., 1983. An optical, scanning electron microscopic and microanalytical study of cementation in some podzols. *Geoderma* 30, 161–170.
- McKeague, J.A., Wang, C., 1980. Micromorphology and energy dispersive analysis of ortstein horizons of podzolic soils from New Brunswick and Nova Scotia, Canada. *Can. J. Soil Sci.* 60, 9–21.
- McKeague, J.A., DeConinck, F., Franzmeier, D.P., 1983. Spodosols. In: Wilding, L.P., Smeck, N.E., Hall, G.F. (Eds.), *Pedogenesis and Soil Taxonomy*. II. Elsevier, Amsterdam, pp. 217–252.
- Paterson, E., Swaffield, R., 1994. X-ray photoelectron spectroscopy. In: Wilson, M.J. (Ed.), *Clay Mineralogy: Spectroscopic and Chemical Determinative Methods*. Chapman & Hall, London, pp. 226–259.
- Seyama, H., Soma, M., 1988. *Application of X-ray Photoelectron Spectroscopy to the Study of Silicate Minerals*. Research Report 111. National Institute for Environmental Studies, Japan, 121 pp.
- Soma, M., Churchman, G.J., Theng, B.K.G., 1992. X-ray photoelectron spectroscopic analysis of halloysites with different composition and particle morphology. *Clay Miner.* 27, 413–421.

- Soma, M., Seyama, H., Yoshinaga, N., Theng, B.K.G., Childs, C.W., 1996. Bonding state of silicon in natural ferrihydrites by X-ray photoelectron spectroscopy. *Clay Sci.* 9, 385–391.
- Stipp, S.L., Hochella, M.F. Jr., 1991. Structure and bonding environments at the calcite surface as observed with X-ray photoelectron spectroscopy (XPS) and low energy electron (LEED) diffraction. *Geochim. Cosmochim. Acta* 55, 1723–1736.
- Vempati, R.K., Hess, T.R., Cocke, D.L., 1996. X-ray photoelectron spectroscopy. In: Sparks, D.L. (Ed.), *Methods of Soil Analysis, Part 3—Chemical Methods*. Soil Science Society of America, Madison, WI, pp. 357–375.
- Wagner, C.D., 1990. Photoelectron and auger energies and the auger parameter: a data set. In: Briggs, D., Seah, M.P. (Eds.), *Auger and X-ray Photoelectron Spectroscopy. Practical Surface Analysis*, 2nd edn., Vol. 1. Wiley, Chichester, UK, pp. 595–634.