

The Effect of Organic Structures on the Water Stability of Macro-aggregates.

C.M. Monreal,* C.A. Campbell, D.W. Anderson¹ and M. Schnitzer. Agriculture Canada, Ottawa and Swift Current and the ¹University of Saskatchewan, Saskatoon.

ABSTRACT

A study was conducted to identify the chemical structures of soil organic matter and examine their effect on the water stability of macro-aggregates (>250 μ m) in a SiL Brown Chernozem under wheat-fallow (WF) and continuous wheat (CW).

The proportion of water stable macro-aggregates were determined by wet sieving. Chemical structures of soil organic matter were characterized by pyrolysis field ionization mass spectrometry (Py-FIMS), and grouped into seven classes: carbohydrates, phenolic and lignin monomers, lignin dimers, lipids + alkanes and alkenes, sterols, alkyl aromatic and N-compounds.

In comparison with CW, there was a reduction in the proportion of macro-aggregates and an increase of micro-aggregates in the WF crop rotation. Sixty-five percent of all the soil organic matter (SOM) was identified by Py-FIMS. The average concentration of each class of compound in whole soil and macro-aggregate samples ranged between 0.1 and 15% of the total identified SOM. Carbohydrates, phenolic and lignin monomers were the most abundant compounds (>10%). Linear regression models ($r^2 \geq 0.96$, $p=0.05$) showed that the stability of macro-aggregates was highly correlated with the concentration of the least abundant (<3.5%) structures of sterols, lipids and lignin dimers. These compounds are metabolic products of plants and soil organisms.

INTRODUCTION

Soil aggregation is essential for producing good structure and optimum tilth for crop growth. Aggregates are classified according to shape, pore size, toughness and size (Kemper and Chepil, 1965; Reeve, 1965). Water stable aggregates >250 μ m are called macro-aggregates, and they may consist of a clay-polyvalent metal-organic matter complex, where clay is bonded to humified organic matter through polyvalent metals (Edwards and Bremner, 1967). The architecture and formation of soil aggregates have been described based on size and organic binding agents. The organic binding agents that stabilize aggregates were classified as: (a) *transient* (mainly polysaccharides), (b) *temporary* (roots and hyphae) and (c) *persistent* (resistant aromatic compounds associated with polyvalent metal cations and strongly sorbed polymers). Macro-aggregates are stabilized by roots and fungal hyphae

and micro-aggregates by persistent binding agents (Tisdall and Oades, 1982).

The stability of aggregates may be related to total SOM (Strickling, 1950) or associated with part of the organic materials (Dormaar, 1983). The chemical composition and the origin of organic binders are essential to promote adequate soil structure and implement effective soil and crop management practices that will conserve SOM and enhance soil quality.

The objectives of this study were to: (a) examine the effects of continuous wheat (CW) and wheat fallow (WF) crop rotations on the stability of macro-aggregates, (b) define the classes of chemical structures of organic matter in macro-aggregates and whole soil samples, and (c) identify the chemical structures of SOM that control water-stable aggregation.

MATERIALS AND METHODS

Soil

The soil corresponds to a Brown Chernozem (Swinton, SiL). Soils from the long-term (25y) crop rotations at Swift Current were collected with a shovel in late May of 1991. Samples were taken from the 0-7.5cm depth of the wheat phase of the wheat-fallow (WF, rotation 11) and continuous wheat (CW, rotation 8) plots. Both crop rotations received N and P (Biederbeck et al. 1984). Soil samples were subsequently stored undisturbed in a cold room at 3 °C.

Wet Sieving

Subsamples consisting of 50g moist soil were placed in a 250 μm sieve and submersed in a pan containing water for 5 min prior to sieving. Samples were then sieved through water by moving gently 3cm vertically 50 times during a 2 min period. The soil left on the screen represented the macro-aggregate fraction. These aggregates were transferred to a plastic container, freeze dried and ground to pass a 100 mesh sieve. The various aggregate sizes were expressed as a proportion of total soil dry weight.

Pyrolysis Field Ionization Mass Spectrometry (Py-FIMS), Soil C and N

About 100-200 μg of soil from two field replicates for each crop rotation were analyzed by Py-FIMS as described by Schulden and Schnitzer (1990). Total C was measured by dry combustion and inorganic-C by acid digestion (Tiessen et al. 1981). Soil organic C was determined by difference between

total and inorganic-C. Organic N was determined by the Kjeldahl method (Bremner and Mulvaney, 1982).

RESULTS AND DISCUSSION

1. The stability and elemental composition of soil aggregates.

The type of crop rotation had a significant effect on the relative proportion of water stable aggregates and their C and N concentration. A significantly greater proportion of macro-aggregates was found under CW than under WF. In contrast, a higher proportion of aggregates $<250\mu\text{m}$ was found under WF (Table 1). Plant roots and the amount of plant residues increase the stability of aggregates (Tisdall and Oades, 1982), and the mean weight diameter of water stable aggregates (Angers and Mehuys, 1989). Therefore, greater aggregate stability under CW may be associated with a higher production of plant residue, maintenance of trash cover and the size or activity of the microbial biomass and fungal population reported earlier for both rotations (Monreal et al. 1992; Biederbeck et al. 1984).

The concentration of C and N in aggregate fractions decreased as follows: macro-aggregates $>$ whole soil $>$ micro-aggregates (50-250 μm) $>$ micro-aggregates ($<50\mu\text{m}$) (Table 1). Macro-aggregates serve as storage of nutrients and form micro-habitats for soil organisms. It is hypothesized that the difference in C and N content among size fractions may be associated with: 1) a higher proportion of plant and microbial tissues protected within macro-aggregates and/or 2) losses of organic matter by oxidation and erosion from whole soil and smaller size aggregates. The enrichment of SOM in macro-aggregates as compared to whole soil strongly supports the second hypothesis. Soil losses by erosion have been reported for the same rotations and were higher under WF than under CW (Monreal et al., 1992). The mean average C/N ratio of macro-aggregates (10.5) was higher than that of micro-aggregates (50-250 μm) (10.1), whole soil (9.8) and micro-aggregates ($<50\mu\text{m}$) (9.7). Higher C/N ratios in macro-aggregates suggests the presence of partially decomposed or fresh plant residues of wheat plants (wide C/N ratio), therefore, supporting our first hypothesis. Similar results have been reported for aggregate fractions in cultivated and native soils of Nebraska (Elliot, 1986). On average, the concentration of C and N for the various aggregate sizes was close to 17% higher under CW than under WF. The greater number of tillage operations under WF (4 to 5) causes greater disruption of macro-aggregates thereby exposing labile SOM to biochemical oxidation and soil erosion.

2. Chemical structures in whole soil and macro-aggregates.

Py-FIMS was used to investigate the chemical constituents of SOM that may contribute to the stability of soil aggregates. Our results showed that >90% of the SOM was volatilized during pyrolysis. In addition, between 48 and 66% of the detected SOM was identified and macromolecules were classified under seven different classes. There were no qualitative differences in chemical composition of SOM among soil samples. All seven classes of compounds were present in whole soil and macro-aggregate fractions (Table 2). The concentration of chemical classes of compounds in whole soils was similar under both CW and WF crop rotations. In general, the most abundant class of macromolecules was carbohydrates (16%) followed by lignin monomers (15%), N containing compounds (11%) and alkyl aromatics (10%). Sterols, a type of lipid, was the least abundant class in whole soil and macro-aggregate samples (Table 2). An earlier study showed that the organic matter in macro-aggregates of a Dark Brown Chernozem under three wheat rotations consisted of polysaccharides, polyuronides, phenols and chloroform-methanol stable organic matter (Dormaar, 1983).

Quantitative differences were clearly observed at the aggregate level (Table 2). The concentration of most classes of compounds (except carbohydrates) was higher in macro-aggregates of the CW rotation than those of the WF rotation. Lignin dimers, alkyl aromatics, sterols and the group of compounds consisting of lipids, alkanes and alkenes reflected best the differences between the two crop rotations. Macro-aggregates of the CW rotation showed greater abundance of aromatics than macro-aggregates from the WF rotation. The latter results suggest the occurrence of less processed plant material and slow rates of biological decomposition in the CW rotation. These results showed a strong influence of soil management on the amount and composition of organic matter in macro-aggregates. Macro-aggregation is therefore a mechanism for soil organic matter conservation and improvement of soil quality.

3. Organic binding agents and aggregate stability.

Macro-aggregates are stabilized by the physical structures of plant roots and fungal hyphae (Tisdall and Oades, 1982). Therefore, it is hypothesized that specific organic molecules of root and hyphae tissues may also exert and reflect the effects on aggregate stability. Figure 1 shows that linear regression models described the stability of macro-aggregates as a function of the concentration of lignin dimers, sterols, and a group of compounds that included mostly lipids and fewer alkanes and alkenes. The regression coefficients were high and significant ($0.96 \leq r^2 = 1$). One earlier study showed no correlation between

aggregate stability and several organic compounds chemically extracted from a Dark Brown Chernozem (Dormaar, 1983).

Tisdall and Oades (1982) proposed that aromatic compounds linked to polyvalent cations were persistent binders and responsible only for the stability of micro-aggregates. Results from this study show, however, that the concentration of lignin dimers was highly correlated with macro-aggregation ($r^2=0.96$, Figure 1). Examples of lignin dimers are represented by signals at m/z 246, 260, 270, 272, 286, 300, 302, 312, 314, 328, 330 (Figures 2,3). Other aromatic structures like phenols and lignin monomers were not associated with aggregation ($r^2=0.5$). This class of compounds are represented by mass signals at m/z 94, 108, 110, 122, 124, 126, 138, 150, 164, 166, 168, 178, 180, 194, 196, 208 and 210 (Figures 2,3). Correlations between alkyl aromatics and N compounds were not significant ($r^2=0.85$ and 0.13 , respectively).

Lipids have been suggested as another class of organic binding agents. The Py-FIMS spectra shows m/z signals at 396, 410 and 424, which represent -C26, -C27 and -C28 fatty acids of plant and/or insect origin (Salisbury, 1978). These signals were absent from macro-aggregates of the WF rotation (Figure 3). The loss of n-fatty acids from macro-aggregates of the WF crop rotation may be associated with metabolic processes of soil organisms and/or erosion losses after macro-aggregates are disrupted by tillage. Humic materials rich in lipids were also found effective in stabilizing soil aggregates (Dinel et al. 1991).

In this study, sterols were the least abundant class of organic structures (<1.2% of the total identified SOM). In spite of their low content, changes in sterol concentration explained 100% of the variability in macro-aggregate stability (Figure 1). These compounds were present in macro-aggregates of the CW crop rotation and almost absent in those obtained under WF. Sterols are synthesized by eukaryotic organisms and plants. Cholesterol, a sterol synthesized by fungi and plants (Hardwood and Russell, 1981; Salisbury and Ross, 1978) is represented at mass signal m/z 386. Thus, the presence of cholesterol shows the importance of fungal hyphae and plant components in stabilizing soil macro-aggregates. Ergosterol, a sterol synthesized mostly by fungi (Salisbury and Ross, 1978) is represented at mass signal m/z 396 (Figure 3). The presence of ergosterol indicates the presence of fungal hyphae in macro-aggregates of the CW rotation. Mass signals from cholesterol and ergosterol may reflect their existence as individual macromolecules of humic acids or as part of root and hyphae tissues.

Carbohydrates which represent mass signals from hexoses, pentoses and pyrolysis products of cellulose and

hemicellulose did not show a significant relation with the stability of macro-aggregates ($r^2=0.27$). These results are similar to earlier reports (Mehta et al. 1960; Webber, 1965) but differ from those of Rennie et al. (1954) and Angers and Mehuys (1989). The latter authors found a significant correlation between aggregate stability and total carbohydrates.

In our study, soil samples were taken in early spring after fall tillage, winter freeze-thaw cycles and before the start of very active plant growth. Hence, the identified chemical structures in stable aggregates must represent persistent binding agents under steady-state. Lignin dimers, sterols and other long-chain lipids control the long-term stability of soil macro-aggregates. Disruption of aggregates by tillage or abiotic processes induces the biochemical decomposition of these compounds by soil organisms. As a consequence, aggregate stability decreases and leaves the soil prone to erosion. The net result is a decline of SOM and soil fertility. Our data showed that the chemical structure of SOM, as characterized by Py-FIMS, reflected the contribution of the chemical components of roots and fungal hyphae to the stability of macro-aggregates. Py-FIMS showed to be a useful diagnostic tool for soil quality assessment.

SUMMARY AND CONCLUSIONS

1. In comparison to CW, there was a reduction in the proportion of macro-aggregates and an increase of micro-aggregates in the WF crop rotation.
2. Macro-aggregates of the CW rotation contained more organic matter and classes of organic compounds than those of the WF rotation.
3. The binding agents controlling the long-term stability of macro-aggregates were sterols, lignin dimers and lipids.
4. The latter classes of chemical compounds affect a physical attribute (aggregation) of soil quality.

ACKNOWLEDGEMENTS

The authors would like to express special thanks to the Environmental Sustainability Initiative for funding this research, and to Dr. H.R. Schulten for conducting the Py-FIMS analysis. We also gratefully acknowledge the technical assistance of D. Chao and the assistance of C. Sauder during the preparation of this manuscript.

REFERENCES

- Angers, D.A. and G.R. Mehuys. 1989. Effects of cropping on carbohydrate content and water-stable aggregation of a clay soil. *Can.J.Soil Sci.* 69: 373-380.
- Biederbeck, V.O., C.A Campbell, and R.P. Zentner. 1984. Effect of crop rotation and fertilization on some biological properties of a loam in Southwestern Saskatchewan. *Can. J. Soil Sci.* 64: 355-367.
- Bremner, J.M. and L.S. Mulvaney 1982. Total Nitrogen. In: *Methods of Soil Analysis, Part 2.* A.L. Page (ed). Agronomy Series No. 2. American Society of Agronomy, Inc. Madison, Wisconsin, USA.
- Dinel H., G.R. Mehuys and M. Levesque. 1991. Influence of humic and fibric material on the aggregation and aggregate stability of a lacustrine silty clay. *Soil Science* 151: 146-158.
- Dormaer, J.F. 1983. Chemical properties of soil and water stable aggregates after sixty-seven years of cropping to spring wheat. *Plant and Soil* 75: 51-61.
- Edwards, A.P. and J.M. Bremner. 1967. Microaggregates in soils. *J. Soil Sci.* 18: 64-73.
- Elliot, E.T. 1986. Aggregate structure and carbon, nitrogen and phosphorous in native and cultivated soils. *Soil Sci. Soc. Am. J.* 50: 627-633.
- Hardwood, J.L. and N.J. Russell. 1984. Lipids in plants and microbes. George Allen and Unwin, London, Chapter 3.
- Kemper, W.D. and W.S. Chepil. 1965. Size distribution of aggregates. In: *Methods of Soil Analysis.* Amer. Soc. Agron. Monograph 9. pp. 499-510.
- Mehta, N.C., H. Streuli, M. Muller and H. Duell. 1960. Role of polysaccharides in soil aggregation. *J. Sci. Food and Agric.* 11: 40-47.
- Monreal, C.M., R.P. Zentner, C.A. Campbell, M. Nyborg, K. Greer, E.G. Gregorich and D.W. Anderson. 1992. Simulating the dynamics of soil organic matter in long-term rotation plots of Saskatchewan and Alberta. In: *Management of Agriculture Science. Soils and Crops Workshop.* University of Saskatchewan, Saskatoon, Saskatchewan. pp. 206-234.
- Reeve, R.C. 1965. Air to water permeability ratio. In: *Methods of Soil Analysis.* Amer. Soc. Agron. Monograph 9. pp. 499-510.

- Rennie, D.A., E. Truog and O.N. Allen, 1954. Soil aggregation as affected by microbial gums, level of fertility and kind of crop. *Soil Sci. Am. Proc.* 18: 339-403.
- Salisbury, F.B. and G.R. Mehuys. 1989. Effects of cropping on carbohydrate content and water-stable aggregation of a clay soil. *Can. J. Soil Sc.* 69: 373-380.
- Schulten, H.-R. and M. Schnitzer. 1990. Aliphatics in soil organic matter in fine-clay fractions. *Soil Sci. Soc. Am. J.*, 54: 98-105.
- Tiessen, H., J.R. Bettany and J.W.B. Stewart. 1981. An improved method for the determination of carbon in soils and soil extracts by dry combustion. *Commun. Soil Sci. Plant Anal.* 12: 211-218.
- Strickling, E. 1950. The effect of soy beans on volume weight and water stability of soil aggregates, soil organic matter content, and crop yield. *Soil Sci. Soc. Am. Proc.* 15: 30-34.
- Tisdall, J.M. and J.M. Oades. 1980. The effect of crop rotation on aggregation in a red-brown earth. *Australian Journal of Soil Research* 18: 423-434.
- Weber, L.R. 1965. Soil polysaccharides and aggregation in crop sequences. *Soil Sci. Soc. Amer. Proc.* 29: 39-42.

Table 1. The soil organic matter concentration in whole soil and aggregate fractions of a Brown Chernozem under wheat-fallow (WF) and continuous wheat (CW).

Aggregate size (μm)	Stable aggregates (As % of soil weight)		Carbon (%)		Nitrogen (%)		C/N	
	WF	CW	WF	CW	WF	CW	WF	CW
	Whole	-	-	1.83 (.14) ¹	2.18 (.12)	0.19 (.01)	.22 (.01)	9.6
>250	19.1 (.8)	30.0 (1.8)	2.30 (.14)	2.62 (.03)	0.22 (.008)	.25 (.004)	10.5	10.5
50-250	44.1 (.5)	40.8 (0.6)	1.74 (.08)	2.10 (.03)	0.17 (.008)	.21 (.003)	10.2	10.0
<50	36.8 (.6)	28.7 (2.2)	1.65 (.06)	1.94 (.02)	0.17 (.008)	.20 (.001)	9.7	9.7

1. Standard deviation values are shown in parenthesis.

Table 2. The concentration (%) of organic compound classes in whole soils and macro-aggregates of the 0-7.5 cm depth.

Aggregate size (μm)	Rotation	Carbohydrates	Lignin ¹ monomers	Lignin dimers	Lipids ²	Sterols	Alkyl aromatics	Nitrogen compounds	Identified (%) ³
Whole	WF	15.3	13.6	3.6	4.2	0.2	9.9	10.2	62
	CW	16.2	14.8	3.3	4.2	0.2	10.8	10.9	66
>250 (Macro-aggr.)	WF	15.6	10.0	1.6	2.2	0.08	6.1	7.8	48
	CW	13.0	13.6	5.4	6.1	1.2	10.6	9.1	64

1. Class includes phenolic structures.
2. Class includes a few alkanes and alkenes.
3. Expressed as % of total ion counts.

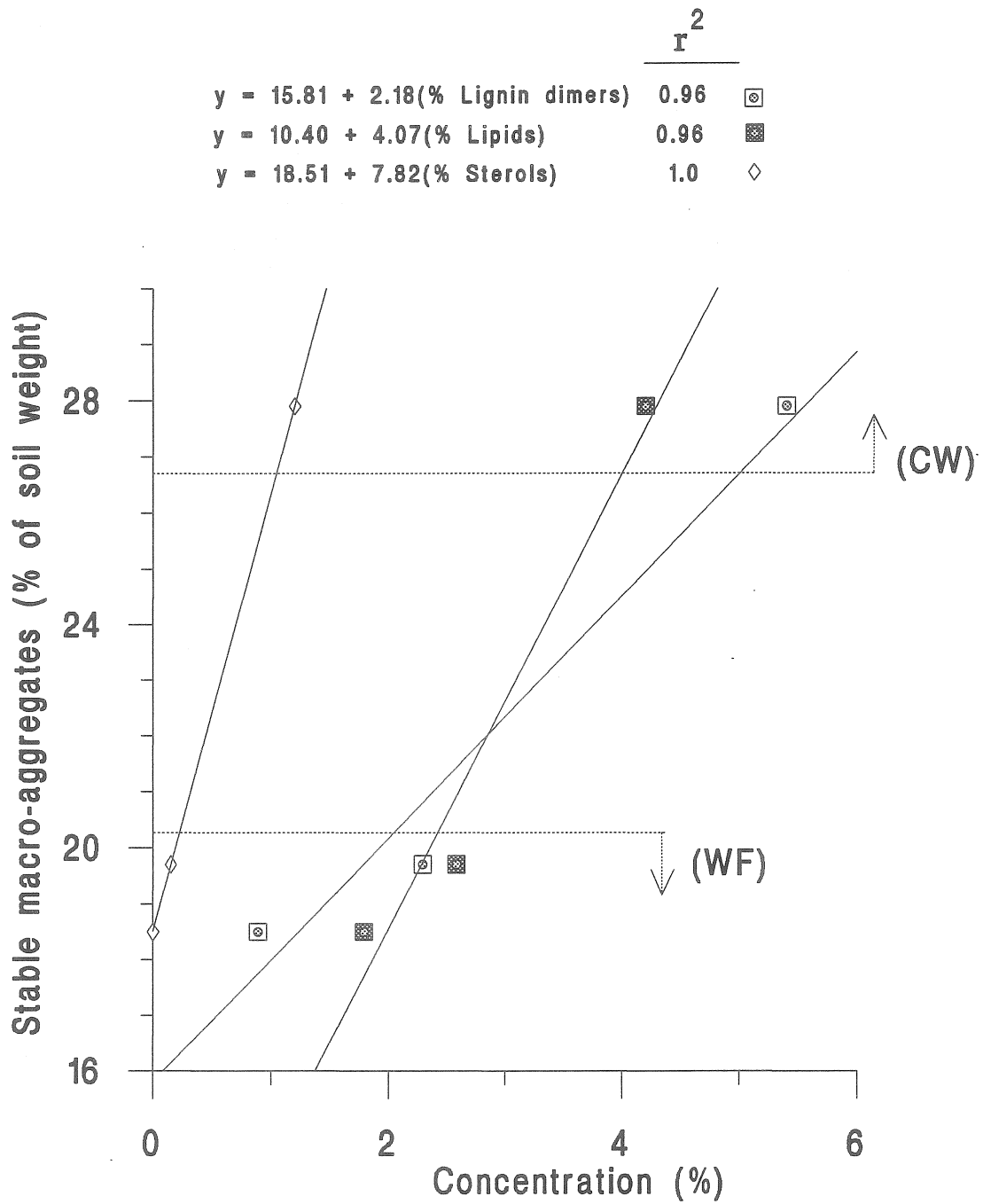


Figure 1. The effect of sterols, lignin dimers and lipids on water stable macro-aggregates.

WF=wheat-fallow, two data points per chemical class;
 CW=contin. wheat, one data point per chemical class.

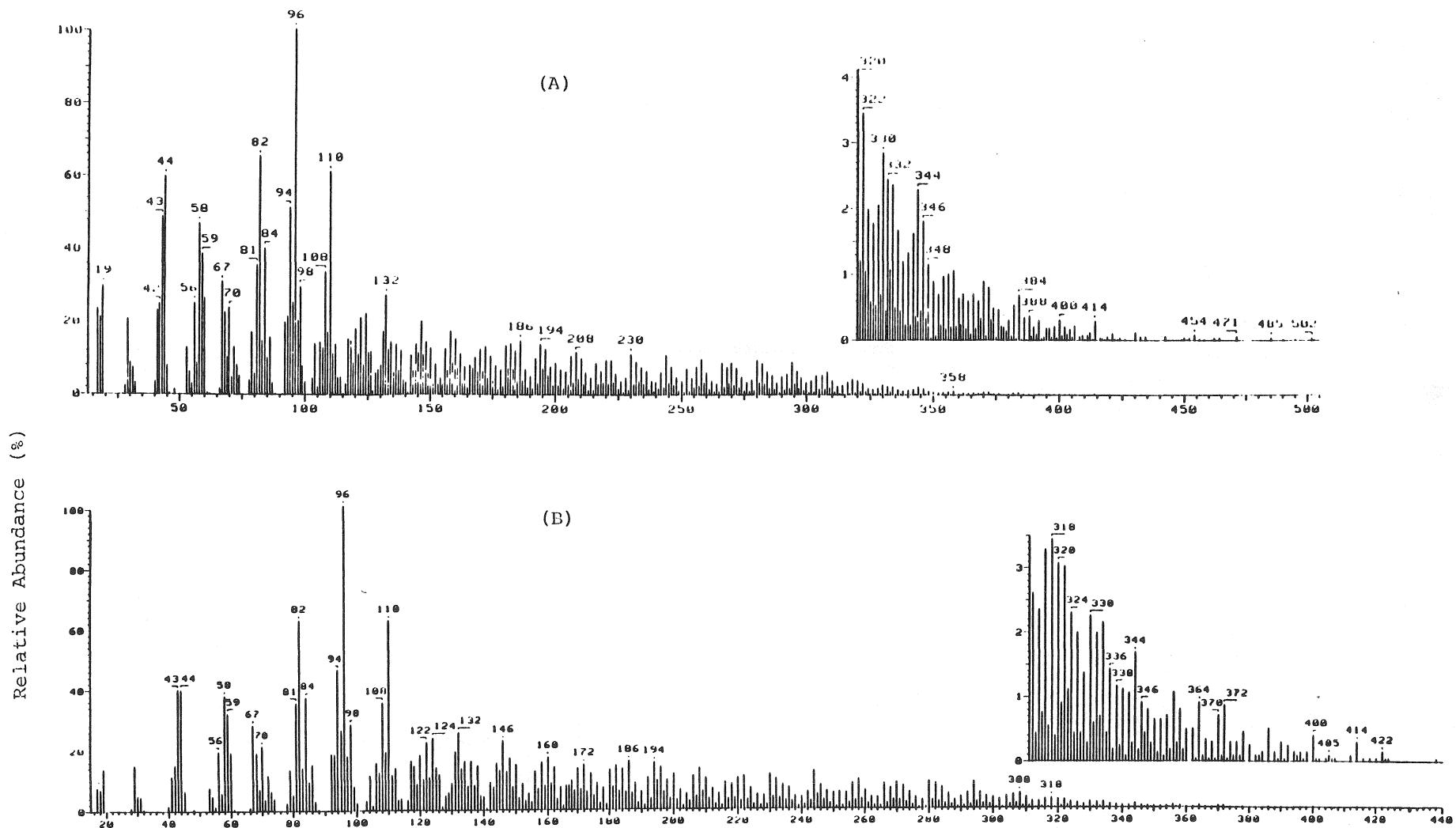


Figure 2. Py-FIMS spectra of whole samples from the 0-7.5 cm depth of a Brown Chernozem at Swift Current. A = wheat-fallow, B = continuous wheat.

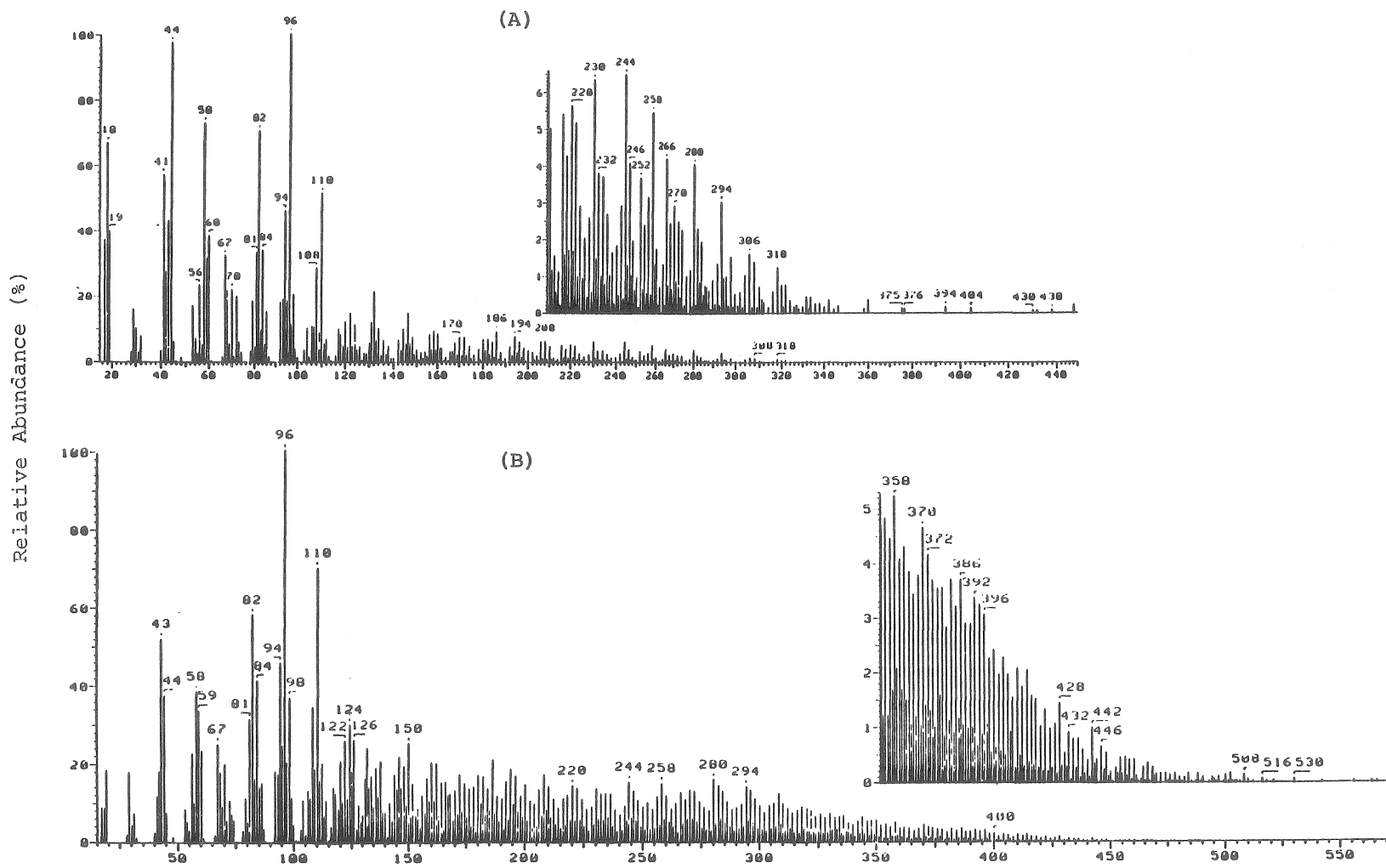


Figure 3. Py-FIMS spectra of macro-aggregates from the 0-7.5cm depth depth of a Brown Chernozem at Swift Current. A = wheat-fallow, B = continuous wheat.