Carbohydrate Quality and Antinutritional Factor Accumulation in Maize (*Zea mays* L.) Grain as Affected by Herbicide Application Rates

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Abstract

Herbicide-based weed management is widely adopted in maize (*Zea mays* L.) production, yet its influence on grain carbohydrate fractions and antinutritional factors remains poorly documented. This study investigated the effects of S-metolachlor (pre-emergence) and nicosulfuron (post-emergence) on carbohydrate composition and antinutritional profile of harvested maize grain during the 2021 and 2022 cropping seasons. Six treatments; S-metolachlor at 3 and 6 L/ha, nicosulfuron at 1.5 and 3.0 L/ha, a weed-free control, and an unweeded check were arranged in a randomised complete block design with four replications. Dietary fibre fractions (cellulose, hemicellulose, NDF, ADF, and lignin) were determined by Van Soest detergent fibre analysis; starch by enzymatic digestion; glucose and antinutritional factors (phenols, phytate, oxalate, and saponin) by standard colorimetric assays. Data were analysed by ANOVA and treatment means separated using Duncan's Multiple Range Test at $P \leq 0.05$. Nicosulfuron at 1.5 L/ha consistently recorded the highest carbohydrate values in both seasons; starch (59.03%; 71.24%), NDF

(28.30%; 28.54%), and glucose (0.15%; 1.09%); significantly exceeding all other treatments. Higher herbicide doses elevated antinutritional factors, reflecting stress-induced secondary metabolite accumulation. Recommended-rate herbicide application, particularly nicosulfuron at 1.5 L/ha, optimises maize grain carbohydrate composition while moderately influencing antinutritional factor content.

Keywords: acetolactate synthase inhibitor; chloroacetanilide herbicide; grain fibre quality; maize grain; phytate; starch biosynthesis; weed interference

Introduction

Maize (*Zea mays* L.) is a vital staple crop globally and a major source of carbohydrates, energy, and essential nutrients for millions of people, particularly in sub-Saharan Africa (Galani et al., 2022). In vast regions of Sub-Saharan Africa, maize is the staple food with consumption of up to 450 g/person/day, and is also used as a weaning food for infants as well as for special ceremonies. Beyond its role in human diets, maize also contributes significantly to livestock feed formulations and serves as an important industrial raw material (Nuss & Tanumihardjo, 2010). The major chemical component of the maize kernel is starch, which provides up to 72 to 73 percent of the kernel weight, with other carbohydrates present as simple sugars in amounts varying from 1 to 3 percent of the kernel.

Despite its nutritional and economic value, maize productivity is often constrained by heavy weed infestation, especially during the early growth stages when crop–weed competition is most severe (Sharma et al., 2022). Weed infestation is a major cause of maize yield reduction, estimated at approximately 20 to 80%, with the most critical period of competition occurring between 4 and 7 weeks after sowing. Traditional weed control practices such as manual hoeing are labour-intensive, time-consuming, and inefficient on large fields, prompting a shift toward herbicide-based weed management, which offers greater effectiveness and consistency (Ekpa et al., 2019).

Among the widely used herbicides in maize cultivation, S-metolachlor, applied as a pre-emergence herbicide, and nicosulfuron, a post-emergence sulfonylurea herbicide, have demonstrated excellent efficacy against annual grasses and broadleaf weeds (Carles et al., 2018). S-metolachlor is applied in pre-emergence, while nicosulfuron a sulfonylurea is used in post-emergence applications; nicosulfuron acts by inhibiting branched-chain amino acid biosynthesis in susceptible weeds. Although the weed-suppressive potential of these herbicides has been widely documented, limited emphasis has been placed on their influence on the biochemical composition of maize grains. In particular, effects on carbohydrate fractions and antinutritional components key indicators of grain quality remain poorly understood.

Recent evidence suggests that herbicides can influence crop metabolic pathways, sometimes leading to modifications in grain nutrient composition (Dragičević et al., 2019). Studies involving nicosulfuron and other ALS-inhibiting herbicides have reported significant variations in soluble proteins as well as phytic and inorganic phosphorus content, which are important metabolites linked to herbicide susceptibility in maize. Likewise, the physiological benefits of effective weed control such as improved light interception, enhanced nutrient uptake, and better photosynthetic performance can contribute to increased carbohydrate deposition in grains (FAO, 1992). However, other reports indicate that herbicide-induced stress may reduce carbohydrate content, disrupt photosynthesis, and modify metabolic reserves depending on dose, crop sensitivity, and environmental conditions (Singh et al., 2019). A significant increase in total carbohydrate content in maize grain over the control has been observed across all herbicide-applied treatments in tembotrione studies, suggesting that certain herbicide applications may be compatible with food quality objectives.

In addition, some herbicides indirectly affect grain quality by altering soil microbial activity and nutrient availability, which may in turn influence antinutritional compounds such as phytate, tannins, and phenolic compounds (Joly et al., 2013). Phytic acid is abundant in cereal seeds, and phytin phosphorus accounts for about 67 percent or more of the total phosphorus in cereal grains, with limited availability to monogastric animals.

The variability in reported outcomes ranging from increases to reductions in carbohydrate levels and antinutritional constituents reflects the interplay of multiple factors such as herbicide chemistry, application rate, timing, moisture conditions, and maize genotype (Dragičević et al., 2020). Despite the extensive use of S-metolachlor and nicosulfuron in maize production, there is limited empirical evidence on how these herbicides influence grain biochemical parameters such as soluble sugars, starch composition, and key antinutritional factors including phytate, tannins, and protease inhibitors. Most existing studies have focused predominantly on yield and weed control, with minimal emphasis on biochemical quality attributes that have direct implications for human nutrition, livestock feeding, and processing industries (Mennan et al., 2020).

Given maize's importance as a major caloric and nutritional staple, assessing herbicide effects on grain quality is vital for sustainable agriculture. This study examines how S-metolachlor and nicosulfuron influence maize carbohydrate composition and antinutritional profile, shedding light on the biochemical effects of herbicide-based weed management.

MATERIALS AND METHODS

Experimental Site and Soil Characterisation

Field experiments were conducted during the 2021 and 2022 cropping seasons at the Botanical Garden of the University of Ilorin, Ilorin, Kwara State, Nigeria (8°29′N, 4°35′E; altitude 307 m a.s.l.). The site lies within the southern Guinea savannah agro-ecological zone of Nigeria, characterised by a mean annual rainfall of approximately 1,200 mm distributed in a bimodal pattern, a mean annual temperature of 26.2 °C, and a mean daily maximum and minimum temperature of 32.5 °C and 21.2 °C, respectively. Monthly meteorological data for both cropping seasons were obtained from the Lower Niger River Basin Development Authority, Ilorin, Nigeria.

Prior to the establishment of the experiments, composite soil samples were collected from a depth of 0–20 cm and characterised using standard procedures. The experimental soil was classified as a sandy loam (84.26–86.20% sand, 8.98–9.26% clay, 4.82–5.48% silt) and is taxonomically categorised as a Typic Ustipsamment (USDA Soil Taxonomy). The previous crop on the site was left fallow. Baseline soil chemical properties were determined prior to planting and are presented in Table 1.

2.2 Plant Material and Herbicide Treatments

The maize (*Zea mays* L.) variety used was SWAM-1-SR-Y, an early-maturing, quality protein maize cultivar with Striga (*Striga hermonthica*) resistance, drought tolerance, and adaptability to diverse soil conditions, obtained from the Institute for Agricultural Research (IAR), Ahmadu Bello University, Zaria, Nigeria.

Two selective herbicides were evaluated: S-metolachlor [active ingredient: S-metolachlor 960 g/L EC (emulsifiable concentrate), a chloroacetanilide pre-emergence herbicide] and nicosulfuron [active ingredient: nicosulfuron 40 g/L SC (suspension concentrate), a post-emergence acetolactate synthase (ALS)-inhibiting sulfonylurea herbicide]. S-metolachlor was applied pre-emergence at 3 and 6 L/ha in 200 L of water per hectare using a knapsack sprayer fitted with a flat-fan nozzle. Nicosulfuron was applied post-emergence at the 4–6 leaf stage of maize (21–25 days after planting, DAP), at 1.5 and 3.0 L/ha in 200 L/ha of water. Six treatments were evaluated: T0 (weed-free control — hand-weeded), T1 (S-metolachlor at 3 L/ha), T2 (S-metolachlor at 6 L/ha), T3 (nicosulfuron at 1.5 L/ha), T4 (nicosulfuron at 3.0 L/ha), and T5 (weedy check — zero weed control).

Experimental Design and Agronomic Management

The experiment was laid out in a Randomised Complete Block Design (RCBD) with six treatments replicated four times, giving a total of 24 plots. Each plot measured 3 m × 3 m (9 m^2) with a 1 m inter-plot alley and 1.5 m inter-block alley. Maize was sown at a spacing of 75 cm × 25 cm (two seeds per hole, later thinned to one plant per stand), giving a plant population density of approximately 53,333 plants/ha. Basal fertilisation was applied at planting using NPK 15:15:15 at 200 kg/ha, with a top-dress application of urea (46% N) at 100 kg/ha at 5 WAP, in line with recommended practice for the southern Guinea savannah zone of Nigeria. All other agronomic practices like irrigation, pest and disease management were kept uniform across all plots throughout both seasons.

Grain was harvested at physiological maturity, sun-dried to a moisture content of 12–13%, shelled, and further oven-dried at 60 °C to constant weight before milling to pass a 0.5 mm sieve for biochemical analyses.

Carbohydrate Composition Analysis

Dietary Fibre Fractions

Neutral detergent fibre (NDF), acid detergent fibre (ADF), and acid detergent lignin (ADL) were determined sequentially following the procedures of Van Soest et al. (1991), as adapted for cereal grain analysis. For NDF, 0.5 g of dried, defatted sample was placed in a heat-resistant vessel and treated with 100 mL of neutral detergent solution (pH 7.0) containing sodium lauryl sulfate, ethylenediaminetetraacetic acid disodium salt, sodium tetraborate decahydrate, disodium hydrogen phosphate, and triethylene glycol, with 50 µL of heat-stable α-amylase (Sigma A3306) added to eliminate starch interference. The mixture was refluxed for 60 min, filtered through pre-weighed sintered glass crucibles (porosity 2, 1.5 µm), washed sequentially with hot distilled water and acetone, and oven-dried at 105 °C for 8 h. NDF was expressed as a percentage of dry matter. For ADF, 0.5 g of sample was refluxed in 100 mL of acid detergent solution (0.5 M H_2SO_4 containing 20 g/L cetyltrimethylammonium bromide [CTAB]) for 60 min, filtered, washed, and dried as described for NDF. ADF was expressed as a percentage of dry matter. ADL (lignin) was determined by treating the ADF residue with 72% (w/w) H_2SO_4 for 3 h at room temperature with occasional stirring. The residue was filtered, washed to neutrality, dried at 105 °C, and ashed at 500 °C for 3 h; ADL was calculated as the difference between dried and ashed residues. Hemicellulose was calculated as NDF − ADF, and cellulose was calculated as ADF − ADL, following Van Soest et al. (1991). All analyses were conducted in triplicate and expressed as percentage of dry matter (% DM).

Total Starch Determination

Total starch content was determined using the enzymatic method of McCleary et al. (1997), corresponding to AOAC Official Method 996.11 (AOAC, 2005) and AACC Method 76-13.01.

Briefly, 100 mg of milled sample was dispersed in 0.2 mL of aqueous ethanol (80%, v/v) and then gelatinised and solubilised by incubation with thermostable α-amylase (1 mL, pH 7.0, 100 °C, 6 min). After cooling and pH adjustment to 4.5, amyloglucosidase (0.1 mL, Sigma A7420) was added and the mixture incubated at 50 °C for 30 min to hydrolyse dextrins to glucose. The reaction was stopped by adding 10 mL of absolute ethanol, centrifuged at 1,000 × g for 10 min, and the supernatant collected. Glucose concentration in the hydrolysate was quantified using glucose oxidase–peroxidase (GOPOD) reagent (Megazyme, Bray, Ireland), measured spectrophotometrically at 510 nm. Total starch content was calculated using the formula: Starch (%) = Glucose (mg) × 0.9 / sample weight (mg) × 100. Values were expressed as percentage of dry matter.

Free Glucose Determination

Free glucose content was determined colorimetrically using the glucose oxidase–peroxidase (GOPOD) reagent (Megazyme), as described in AOAC Official Method 923.09, following aqueous extraction of 0.5 g of ground sample in 25 mL of distilled water at 40 °C for 30 min with continuous agitation. An aliquot of the clear filtrate was reacted with GOPOD reagent and absorbance read at 510 nm against a glucose standard curve. Results were expressed as percentage of dry matter.

Antinutritional Factor Determination

Total Phenol Content

Total phenolic content was determined using the Folin-Ciocalteu colorimetric method of Singleton & Rossi (1965) as modified by Vinson et al. (1998). Briefly, 0.1 g of dried, powdered maize was extracted with 15 mL of 1.2 N HCl in 50% aqueous methanol at 90 °C for 2 h in a water bath to quantify both conjugated and free phenolic compounds. The extract was centrifuged at 10,000 rpm for 30 min and the supernatant evaporated to dryness. The residue was reconstituted, reacted with Folin-Ciocalteu reagent under alkaline conditions (Na_2CO_3, 20% w/v), and absorbance measured at 650 nm after 30 min. Results were expressed as mg gallic acid equivalent per gram dry matter (mg GAE/g DM) using a gallic acid standard curve ($R^2 \geq 0.999$).

Phytate Content

Phytate was determined following AOAC Official Method 986.11 (AOAC, 2005) using the colorimetric procedure of Haug & Lantzsch (1983). A 0.5 g sample was extracted with 0.5 M HNO_3 for 1 h with agitation, clarified by centrifugation, and an aliquot digested with perchloric acid. Phosphorus liberated from phytic acid was measured colorimetrically after reaction with vanadium molybdate reagent at 460 nm using a spectrophotometer (UV/Vis, P7 model). Phytate content was calculated from a phytic acid standard curve and expressed as mg/100 g dry matter.

Oxalate Content

Oxalate content was determined by the permanganate titration method as described by Day & Underwood (1986). One gram of sample was dissolved in 75 mL of 3 M H_2SO_4 and agitated on a magnetic stirrer for 1 h before filtering through Whatman No. 1 filter paper. A 25 mL aliquot of the clear filtrate was titrated while warm against 0.05 M $KMnO_4$ solution until a faint pink endpoint persisted for at least 30 s. Oxalate content was calculated using the equation: Oxalate (mg/100 g) = titre (mL) $\times$ 0.05 $\times$ 88.02 $\times$ 4 $\times$ (100/sample weight in g), and expressed as mg/100 g dry weight.

Saponin Content

Total saponin content was determined using the spectrophotometric method of Harborne (1973), as adapted by Obadoni & Ochuko (2001). Five grams of sample were extracted in 20 mL of 1 N HCl by boiling for 4 h, cooled, filtered, and the filtrate partitioned against 50 mL of petroleum ether (40–60 °C). The ether layer was evaporated to dryness and the residue dissolved in acetone–ethanol (1:1, v/v). A 0.4 mL aliquot was reacted with 6 mL of ferrous sulfate reagent and 2 mL of concentrated H_2SO_4, mixed thoroughly, and absorbance measured at 490 nm after 10 min. Saponin content was quantified from a diosgenin standard curve and expressed as mg/100 g dry matter.

Statistical Analysis

All data were subjected to one-way analysis of variance (ANOVA) using IBM SPSS Statistics version 26.0 (IBM Corp., Armonk, NY, USA). Treatment means were separated using Duncan's Multiple Range Test (DMRT) at a significance level of $P \leq 0.05$. Data are presented as mean ± standard deviation (SD) of four replications. Cropping seasons (2021 and 2022) were analysed separately to account for year-specific environmental variation. Pearson's correlation analysis was performed to assess relationships between carbohydrate fractions and antinutritional factors across all treatments.

Results

Soil Physicochemical Characteristics

Results of the mechanical analysis of the soil sample showed that it has 84.26 -86.2% of sand, 8.98-9.26% of clay and 4.82-5.48% of silt. The soil of the experimental site is therefore, a sandy loam soil (Table 1).

Carbohydrate Profile of the Harvested Maize

Cellulose

In 2021 cropping season, cellulose content of the harvested maize grains was significantly ($P \leq 0.05$) increased when subjected to 1.5L / ha of Nicosulfuron (Table 2). This was followed by plot treated with 3 L/h of S-metolachlor, and the control while the least cellulose content was recorded in the weedy check plot. However, these results followed the same pattern in the 2022 cropping season where by plot treated with 1.5L / ha of Nicosulfuron recorded the highest cellulose content and the least was observed in the weedy check plot.

Hemicellulose

In 2021/2022 cropping season, significantly ($P \leq 0.05$) highest hemicellulose content was observed in plot subjected to 1.5L / ha of Nicosulfuron when compared to the control plot (Table 2). This was followed by 6.0 L/ha of S-metolachlor and 3 L/ha of Nicosulfuron which were found to be statistically the same. However, the least hemicellulose content was observed in the weedy check plot.

Neutral Detergent Fibre (NDF)

In 2021 cropping season, significantly ($P \leq 0.05$) highest Neutral Detergent Fibre (NDF) content was observed in plot treated with 1.5L / ha of Nicosulfuron. This was followed by plot treated with 3 L/ha of Nicosulfuron while the least NDF content was observed in the weedy check plot. However, in the 2022 cropping season, 1.5L / ha of Nicosulfuron recorded the highest NDF, followed by plot treated with 3L/ha of S-metolachlor while the least NDF was recorded in the weedy check plot (Table 2).

Acid Detergent Fibre (ADF)

Significantly (P≤0.05) highest Acid Detergent Fibre (NDF) content was observed in plot treated with 1.5L / ha of Nicosulfuron, followed by 3 L/h of Nicosulfuron while the least ADF content was observed in the weedy check plot (Table 2). In the 2022 cropping season, significantly highest ADF was recorded in plot treated with 1.5L /ha of Nicosulfuron and this was followed by plot treated with 3L/ha of S-metolachlor, while the least ADF was observed in the weedy check plot (Table 2).

Lignin

In 2021 cropping season, Table 2. showed lignin contents of maize grains as influenced by herbicide treatment. Significantly highest lignin content was observed in plots subjected to 3.0 L/ha of Nicosulfuron, followed by 1.5 L/ha of Nicosulfuron, while the weedy check had the least (Table 2). In the 2022 cropping season, all herbicides treated plot showed higher lignin contents than the control. Significantly highest lignin content was observed in 3.0 L/ha of Nicosulfuron, followed by 1.5 L/ha of Nicosulfuron while the weedy check had the least lignin content.

Starch

Table 3 showed starch contents of maize grains as affected by different herbicides treatments during the 2021 and 2022 cropping seasons. Significantly highest starch contents were observed in plots subjected to 1.5 L/ha of Nicosulfuron. This was followed by 3.0 L/ha of S-metolachlor and the least starch content was observed in the weedy check plot.

Glucose

Table 3 showed glucose contents of maize grains as affected by different herbicide treatments during the 2021/2022 cropping seasons. Significantly highest glucose contents were observed in plots subjected to 1.5 L/ha of Nicosulfuron which was statistically the same with 3.0 L/ha of Nicosulfuron while the least was recorded in weedy check.

Anti-nutritional Factor of the Harvested Maize

Phenol

Phenol concentration in 2021 cropping season was significantly ($P \leq 0.05$) influenced by different herbicides application as shown in Table 4. All the weed control subjected to double the recommended rate of application (6 and 3 L/ha of S-metolaclor and Nicosulfuron respectively) significantly ($P \leq 0.05$) increased the phenol content of the maize. This was followed by the control and was found to be at par with plot subjected to 3.0 L/ha of S-metolachlor and the weedy check, while the least concentration of phenol in the maize grains was obtained in plot subjected to 1.5 L/ha of Nicosulfuron. In 2022 cropping season, the concentrations of phenol recorded in all the treatments were found to be statistically ($P \leq 0.05$) the same in comparison to the weed free plot. However, plot subjected to 6.0 and 3.0 L/ha of S-metolaclor and Nicosulfuron respectively recorded the highest value (Table 4).

Phytate

Phytate concentration in 2021 cropping season was significantly ($P \leq 0.05$) affected by different herbicides treatment as shown in Table 4. Significantly ($P \leq 0.05$) highest phytate concentration was observed in plot treated with 6 L/ha of S-metolaclor and this was followed by plot treated with 3 L/ha of Nicosulfuron, while the least concentration of phytate was observed in the control plot and was found to be statistically ($P \leq 0.05$) the same with 3 L/ha of S-metolaclor, 1.5 L/ha of Nicosulfuron and the weedy check, while the least concentration of phytate in the maize grains was obtained in plot subjected to 1.5 L/ha of Nicosulfuron.

In 2022 cropping season, significantly highest phytate content was recorded in plot treated with 6 L/ha of S-metolaclor and this was followed by plot treated with 3 L/ha of Nicosulfuron, while the least concentration of phytate was observed in the control plot (Table 4).

Oxalate

In the 2021 cropping season, oxalate concentration of the maize was influenced by the application of herbicides. Plot subjected to 3.0 and 6.0 L/ha of S-metolachlor significantly ($P \leq 0.05$) influenced oxalate content of the maize. This was followed by plot treated with 3.0 L/ha of Nicosulfuron with the least recorded in control and weedy check plot. However, in 2022 cropping season significantly highest oxalate concentration was observed in plot treated with 3 and 6 L/ha of S-metolachlor while the least was observed in control and was found to be statistically the same with the weedy check and plot subjected to 1.5 and 3.0 L/ha of Nicosulfuron (Table 4).

Saponin

In 2021 cropping season, Saponin content of the maize was found to be highest in plot subjected to 1.5 and 3 L/ha of Nicosulfuron, this was followed by plot treated with S-metolachlor and was found to be statistically the same with the control, and weedy check plot (Table 4). However, during the 2022 cropping season, significant highest Saponin content was observed in plot treated with 3 L/ha of Nicosulfuron while the least was recorded in the control and weedy check plot (Table 4).

Discussion

Dietary Fibre Fractions

Cellulose serves as the primary structural reinforcement of the plant cell wall, providing rigidity and mechanical strength that enables plants to cope with biotic and abiotic stresses (Appenzeller et al., 2004). Cell wall composition particularly the content of cellulose, hemicellulose, and lignin is key in determining the quality of maize biomass and is directly influenced by genotypic background, agronomic management, and environmental pressures. The significant increase in cellulose content recorded under nicosulfuron at 1.5 L/ha across both 2021 and 2022 cropping seasons can primarily be attributed to the alleviation of weed-imposed stress on the maize plant. By effectively suppressing weed competition, nicosulfuron at its recommended rate freed the crop from resource depletion, allowing greater allocation of photosynthate and mineral nutrients toward grain structural carbohydrate biosynthesis (Sharma et al., 2022). Weed competition depletes soil nutrients particularly macronutrients such as nitrogen and phosphorus that are essential for normal grain development and cell wall biogenesis. When these nutrients are adequately available following herbicide-mediated weed removal, maize plants channel more resources into cellulose synthesis, thereby increasing grain cellulose content (Galani et al., 2022).

Photosynthesis serves as the primary pathway for carbon fixation, producing non-structural carbohydrates essential for plant survival and growth; these serve as precursors for the biosynthesis of structural polysaccharides such as cellulose and hemicellulose during grain development. The lowest cellulose content consistently recorded in the weedy check plot across both seasons reflects the combined effects of reduced light interception and chronic nutrient depletion under uncontrolled weed pressure. Weed infestation is a major cause of maize yield and quality reduction, estimated at approximately 20 to 80%, with the most critical competition occurring between 4 and 7 weeks after sowing. This shading and resource competition suppresses photosynthetic efficiency, thereby reducing the energy supply and carbon substrate needed for cellulose deposition in developing grain tissues.

The significant increase in hemicellulose content under 1.5L / ha of Nicosulfuron follows a similar mechanistic pathway. Hemicellulose, the matrix polysaccharide interwoven with cellulose microfibrils in the cell wall, is synthesised from UDP-sugar precursors derived from primary carbon metabolism (Appenzeller et al., 2004). When weed pressure is removed and nutrient uptake is optimised, the maize plant has adequate substrate for glucuronoarabinoxylan which is the dominant hemicellulose in grass cell walls to be deposited alongside cellulose. Competition from weeds for vital resources including water, nutrients, light, and space can deplete these resources in unmanaged plots, negatively affecting the development and maturation of maize plants and consequently impairing the synthesis and deposition of structural cell wall components. The lowest hemicellulose values in weedy check plot are therefore consistent with impaired carbon and nutrient availability under heavy weed infestation.

The elevated NDF and ADF values in plot treated with 1.5L / ha of Nicosulfuron across both seasons are logical consequences of increased cellulose and hemicellulose, given that NDF = cellulose + hemicellulose + lignin, while ADF = cellulose + lignin. These parameters reflect the total structural fibre content of the grain and are important quality indicators for livestock feed and human digestive health (Slavin et al., 1981). The elevated NDF and ADF under 1.5L / ha of Nicosulfuron therefore indicate richer grain fibre architecture resulting from superior crop establishment and unhindered vegetative growth during the critical developmental period.

The markedly high lignin content under plot treated with (nicosulfuron at 3 L/ha) 10.40% in 2021 and 6.31% in 2022 compared to all other treatments, including 1.5L / ha of Nicosulfuron, is particularly noteworthy and suggests a dose-dependent phytostress response. Lignin is a complex aromatic polymer biosynthesised primarily through the phenylpropanoid pathway, and its upregulation under biotic or chemical stress is a well-established plant defence mechanism (Appenzeller et al., 2004). Nicosulfuron inhibits ALS activity in a dose-dependent manner, with increasing doses causing deeper biochemical perturbations including disruption of branched-chain amino acid biosynthesis, oxidative stress, and metabolic reorientation in treated plants. At the higher dose in 3 L/ ha of Nicosulfuron, herbicide-induced oxidative stress may have upregulated the phenylpropanoid pathway, diverting carbon flux away from starch and structural polysaccharides toward lignin as a protective biochemical response. Nicosulfuron at elevated doses destroys chloroplast structure and diminishes photosynthetic capacity, reducing ATP and NADPH synthesis, which fundamentally alters carbon partitioning in the treated plant. This photosynthetic impairment, combined with stress-induced lignification, explains the abnormal lignin elevation in 1.5L / ha of Nicosulfuron; relative to 3 L/ ha of Nicosulfuron.

For S-metolachlor treatments, (3 L/ha) showed modest improvements in cellulose and NDF over weed free , reflecting the indirect benefit of pre-emergence weed suppression during the early, weed-susceptible growth stages. S-metolachlor at 6 L/ha, however, showed reduced cellulose and ADF relative to weed free alongside elevated hemicellulose, a pattern that may indicate disruption of normal cell wall assembly under excessive herbicide load. Herbicides can inhibit the incorporation of glucose into cell wall components, with cellulose and hemicellulose fractions being differentially sensitive to chemical stress in maize root and grain tissues. The imbalance in cellulose-to-hemicellulose ratio at the higher S-metolachlor dose is consistent with compensatory upregulation of hemicellulose as a cell wall adaptation to partial cellulose deficiency, a pattern documented in herbicide-habituated maize cell cultures (Largo-Gosens et al., 2014).

Non-Fibre Carbohydrates: Starch and Glucose

The highest starch content recorded under nicosulfuron at 1.5 L/ha in both seasons (59.03% in 2021 and 71.24% in 2022) confirms that effective post-emergence weed control at recommended herbicide rates substantially enhances maize grain starch accumulation. Starch is the major chemical component of the maize kernel, providing up to 72 to 73 percent of the kernel weight; its accumulation during grain filling is directly dependent on photosynthetic productivity and the efficiency of carbon partitioning from source leaves to the developing grain. Removal of weed competition under plot treated with 1.5L / ha of Nicosulfuron ensured unimpeded canopy development, maximising light interception and photosynthetic carbon assimilation during the critical grain-filling period, which in turn supplied abundant substrate primarily in the form of sucrose for ADP-glucose pyrophosphorylase (AGPase)-mediated starch biosynthesis in the endosperm (Xu et al., 2022).

The significantly elevated free glucose content under 1.5L / ha of Nicosulfuron, particularly in 2022 (1.09%), compared to all other treatments (0.01%–0.04%), is a biochemically distinctive finding. Nicosulfuron treatment significantly alters sugar metabolism in maize, with the activities of sucrose phosphate synthase and sucrose synthase increasing differentially across lines under herbicide stress, and sucrose content rising markedly reflecting metabolic modulation of the glycolytic and TCA pathways in tolerant maize genotypes. The accumulation of free glucose in 1.5L / ha of Nicosulfuron grain may therefore represent a metabolic signature of nicosulfuron's interaction with sucrose hydrolysis pathways: as the crop mounts a biochemical adaptation to herbicide exposure at the recommended dose, increased invertase activity or altered sucrose synthase flux may result in transient accumulation of free hexoses, consistent with the stress-resistance sugar accumulation mechanisms reported by Xu et al. (2022).

The reduced starch content under nicosulfuron at 3 L/ha relative to 1.5L / ha of Nicosulfuron further substantiates the dose-dependent phytostress hypothesis. At elevated concentrations, nicosulfuron disrupts photosynthetic pigment composition and chloroplast structural integrity, reducing the plant's ability to synthesise ATP and NADPH, and consequently limiting the photosynthate supply available for starch deposition in grain endosperm. This is compounded by the diversion of carbon toward lignin synthesis and stress-responsive metabolites at supraoptimal doses. Similarly, S-metolachlor at 6 L/ha produced lower starch than both 3 L/ha of S-metolachlor and weed free, consistent with dose-dependent phytotoxic impairment of carbon metabolism at the higher chloroacetanilide application rate.

The weedy check consistently recorded the lowest starch values across both seasons (46.90% in 2021; 59.10% in 2022), confirming that uncontrolled weed competition is severely detrimental to maize grain carbohydrate quality. Weeds reduce the amount of available sunlight and compete with maize plants for light and nutrients, thereby reducing photosynthetic efficiency and leading to a decrease in glucose production, which in turn depresses starch synthesis and accumulation in the grain. The findings of the present study are consistent with the conclusion that the nutritional quality of maize grain not merely its yield is profoundly compromised under conditions of unmanaged weed infestation.

The higher absolute starch and fibre values recorded across all treatments in 2022 compared to 2021 likely reflect more favourable growing season conditions, including temperature regimes and rainfall distribution during the grain-filling period, which are well-established modulators of starch deposition rate and duration in maize (Landau et al., 2021).

Conclusion

This study demonstrates that Both S-metolachlor and nicosulfuron significantly affected the dietary fibre and non-fibre carbohydrate composition of maize grains in a dose-dependent manner, with nicosulfuron at its recommended rate (1.5 L/ha) producing the most favourable carbohydrate profile due to effective weed suppression. However, higher herbicide doses induced phytostress and reduced carbohydrate quality, while uncontrolled weed competition consistently resulted in the poorest grain composition.

Appendix

Table 1. Physico-chemical properties of soil used in the experimental site

Chemical properties	2021	2022
pH (H_2O)	5.80	5.65
Exchangeable acidity (cmol(+) kg^{-1})	1.72	1.67
Electrical conductivity (dS m^{-1})	1.70	1.73
Moisture content (%)	1.06	1.18
Organic carbon (%)	2.31	2.33
Total nitrogen (g kg^{-1})	0.24	0.25
Available phosphorus (mg kg^{-1})	3.68	3.87
Exchangeable Ca^{2+} (cmol(+) kg^{-1})	4.50	4.50
Exchangeable Mg^{2+} (cmol(+) kg^{-1})	1.32	1.16
Exchangeable Na^{+} (cmol(+) kg^{-1})	1.70	1.73
Exchangeable K^{+} (cmol(+) kg^{-1})	2.0	2.33
Mechanical Analysis		
Sand (%)	86.2	84.26
Clay (%)	8.98	9.26
Silt (%)	4.82	5.48
Textural class	Sandy loam	Sandy loam

Table 2: Effects of S-metolachlor and Nicosulfuron on Dietary Fibres Content of Harvested Maize Grains During 2021 and 2022 Cropping Seasons (% of Dry matter)

	2021 Cropping Season					2022 Cropping Season				
Treatment	Cellulose	Hemicellulose	NDF	ADF	Lignin	Cellulose	Hemicellulose	NDF	ADF	Lignin
T$_0$	6.20±0.06^{c}	5.60±0.02^{c}	15.90±0.02^{d}	10.30±0.02^{d}	4.10±0.18^{c}	6.40±0.05^{c}	5.66±0.03^{c}	12.25±0.02^{d}	6.59±0.02^{e}	4.19±0.05^{d}
T$_1$	7.90±0.02^{b}	4.70±0.07^{d}	16.7±0.02^{c}	12.00±0.03^{c}	4.10±0.03^{c}	8.01±0.09^{b}	4.72±0.09^{d}	17.82±0.04^{b}	13.1±0.01^{b}	5.09±0.05^{c}
T$_2$	4.00±0.08^{d}	8.40±0.12^{b}	15.60±0.02^{e}	7.20±0.10^{e}	3.20±0.07^{d}	4.11±0.08^{d}	8.52±0.09^{b}	16.85±0.02^{c}	8.33±0.10^{d}	4.22±0.13^{d}
T$_3$	12.20±0.06^{a}	10.80±0.23^{a}	28.30±0.02^{a}	17.50±0.05^{a}	5.30±0.12^{b}	12.31±0.05^{a}	10.86±0.03^{a}	28.54±0.02^{a}	17.68±0.02^{a}	5.37±0.03^{b}
T$_4$	3.10±0.10^{e}	8.20±0.23^{b}	21.70±0.01^{b}	13.50±0.18^{b}	10.40±0.01^{a}	3.23±0.12^{e}	8.26±0.06^{b}	17.80±0.03^{c}	9.54±0.03^{c}	6.31±0.02^{a}
T$_5$	2.60±0.03^{f}	3.20±0.06^{e}	8.50±0.01^{f}	5.30±0.04^{f}	2.70±0.01^{e}	2.67±0.03^{f}	3.13±0.18^{e}	9.10±0.02^{f}	5.97±0.10^{f}	3.30±0.09^{e}
Mean	6.00±0.81	6.82±0.62	17.78±1.47	10.97±0.98	4.97±0.62	6.12±0.81	6.86±0.63	17.06+1.46	17.06±1.47	4.75±0.24

Mean with the same superscripts down the column are not significantly different at $P \leq 0.05$; T$_0$= Control (weed free); T$_1$= 3 L/ha of S-metolachlor; T$_2$= 6 L/ha of S-metolachlor; T$_3$ = 1.5L / ha of Nicosulfuron; T$_4$= 3 L/ ha of Nicosulfuron; T$_5$= Weedy check

Table 3: Effects of S-metolachlor and Nicosulfuron on Non-fibres Carbohydrate of Harvested Maize Grains During 2021 and 2022 Cropping Seasons (% of dry matter)

Treatment	2021 Cropping Season		2022 Cropping Season	
	Starch	Glucose	Starch	Glucose
T_0	56.50 ± 0.02^c	0.01 ± 0.00^b	68.53 ± 0.05^c	0.03 ± 0.00^b
T_1	58.04 ± 0.20^b	0.02 ± 0.00^b	70.26 ± 0.16^b	0.03 ± 0.01^b
T_2	49.11 ± 0.03^d	0.03 ± 0.00^b	61.31 ± 0.05^d	0.04 ± 0.01^b
T_3	59.03 ± 0.03^a	0.15 ± 0.00^a	71.24 ± 0.05^a	1.09 ± 0.05^a
T_4	48.62 ± 0.03^e	0.03 ± 0.00^{ab}	60.86 ± 0.02^e	0.03 ± 0.01^b
T_5	46.90 ± 0.03^f	0.01 ± 0.00^b	59.10 ± 0.09^f	0.01 ± 0.00^b
Mean	53.03±1.20	0.04±0.01	65.22±1.19	0.21±0.09

Mean with the same superscripts down the column are not significantly different at $P \leq 0.05$; T_0= Control (weed free); T_1= 3 L/ha of S-metolachlor; T_2= 6 L/ha of S-metolachlor; T_3 = 1.5L / ha of Nicosulfuron; T_4= 3 L/ha of Nicosulfuron; T_5= Weedy check

Table 4: Effects of S-metolachlor and Nicosulfuron on Anti-nutritional Composition of Maize During 2021 and 2022 Cropping Seasons

	2021 Cropping Season				2022 Cropping Season			
Treatment	Phenol (mg/100g)	Phytate (mg/100g)	Oxalate (mg/100g)	Saponin (mg/100g)	Phenol (mg/100g)	Phytate (mg/100g)	Oxalate (mg/100g)	Saponin (mg/100g)
T_0	0.06 ± 0.01^{b}	2.00 ± 0.05^{c}	0.36 ± 0.01^{c}	0.17 ± 0.00^{b}	0.06 ± 0.02^{a}	1.95 ± 0.06^{b}	0.36 ± 0.02^{b}	0.17 ± 0.02^{c}
T_1	0.06 ± 0.00^{b}	2.18 ± 0.27^{c}	1.25 ± 0.02^{a}	0.19 ± 0.01^{b}	0.06 ± 0.00^{a}	1.97 ± 0.06^{b}	1.23 ± 0.03^{a}	0.19 ± 0.01^{bc}
T_2	0.10 ± 0.01^{a}	4.96 ± 0.07^{a}	1.28 ± 0.01^{a}	0.19 ± 0.04^{b}	0.10 ± 0.02^{a}	3.67 ± 0.12^{a}	1.26 ± 0.01^{a}	0.23 ± 0.01^{b}
T_3	0.03 ± 0.01^{c}	2.10 ± 0.05^{c}	0.42 ± 0.02^{bc}	0.17 ± 0.01^{b}	0.05 ± 0.00^{a}	1.96 ± 0.02^{b}	0.40 ± 0.03^{b}	0.17 ± 0.02^{c}
T_4	0.10 ± 0.01^{a}	4.03 ± 0.09^{b}	0.46 ± 0.02^{b}	0.90 ± 0.03^{a}	0.10 ± 0.03^{a}	3.62 ± 0.01^{a}	0.43 ± 0.01^{b}	0.98 ± 0.02^{a}
T_5	0.06 ± 0.01^{b}	2.15 ± 0.03^{c}	0.38 ± 0.03^{c}	0.16 ± 0.02^{b}	0.06 ± 0.02^{a}	1.95 ± 0.02^{b}	0.36 ± 0.02^{b}	0.16 ± 0.00^{c}
Mean	0.07±0.01	2.90±0.01	0.69±0.09	0.30±0.70	0.07±0.01	2.52±0.19	0.67±0.09	0.32±0.07

Mean with the same superscripts down the column are not significantly different at $P \leq 0.05$; T_0= Control (weed free); T_1= 3 L/ha of S-metolachlor; T_2= 6 L/ha of S-metolachlor; T_3 = 1.5L / ha of Nicosulfuron; T_4= 3 L/ha of Nicosulfuron; T_5= Weedy check

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