UNIWERSYTET PRZYRODNICZY w LUBLINIE

Wydział Agrobioinżynierii
Dyscyplina naukowa: Rolnictwo i ogrodnictwo

mgr inż. Paulina Elżbieta Bogusz

Rozprawa doktorska

Badania nad technologią wytwarzania zawiesinowych nawozów wieloskładnikowych na bazie odpadowego fosforanu sodowo - potasowego z produkcji polioli oraz ich wpływ na plonowanie i parametry jakościowe roślin

Research on the technology of producing multi-component suspension fertilizers based on waste sodium potassium phosphate from the production of polyols and their impact on the yield and quality parameters of plants

Rozprawa doktorska wykonana w Katedrze Chemii Rolnej i Środowiskowej
oraz w Sieci Badawczej Łukasiewicz – Instytucie Nowych Syntez Chemicznych

Promotor: dr hab. Marzena Brodowska, prof. uczelni
Promotor pomocniczy: dr hab. Piotr Rusek

Praca doktorska powstała w ramach projektu Doktorat wdrożeniowy

Lublin, 2024

„Kiedy staje się oczywiste, że cele nie mogą zostać osiągnięte,
nie dostosowuj celów, dostosuj działania”
– Konfucjusz

„Jeśli możesz sobie coś wymarzyć, możesz to zrobić”
- Walt Disney

Serdeczne podziękowania składam
Promotorom
dr hab. Marzenie Brodowskiej, prof. uczelni
oraz dr hab. Piotrowi Ruskowi
za cenne wskazówki i rady w trakcie tworzenia tej rozprawy,
życzliwość, wyrozumiałość i wszelką pomoc.

Dziękuję pracownikom Katedry Chemii Rolnej i Środowiskowej,
za miłą atmosferę i pomoc w trakcie wykonywanych badań.

Dziękuję Dyrekcji i Pracownikom
Sieci Badawczej Łukasiewicz – Instytutu Nowych Syntez Chemicznych,
którzy dzielili się swoją wiedzą i doświadczeniem oraz
umożliwili mi korzystanie z zaplecza technicznego oraz zasobów badawczych.

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oraz dr inż. Małgorzacie Wysockiej za nieocenione wsparcie i pomoc.

Serdecznie dziękuję, wszystkim tym,
dzięki którym napisanie tej pracy stało się faktem.

Dziękuję także sobie za to,
że mimo wątpliwości i chwil słabości
nie poddałam się i osiągnęłam swój cel.

Niniejszą pracę doktorską dedykuję mężowi Jakubowi i córce Alicji.

Oświadczenie promotora rozprawy doktorskiej

Oświadczam, że niniejsza rozprawa doktorska została przygotowana pod moim kierunkiem i stwierdzam, że spełnia ona warunki do przedstawienia jej w postępowaniu o nadanie stopnia naukowego.

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Świadom/a odpowiedzialności prawnej oświadczam, że:
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- niniejsza wersja rozprawy doktorskiej jest tożsama z załączoną na płycie CD wersją elektroniczną.

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Podpis autora ....

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Data ...30.09.2024r....
Podpis promotora ...Marzena G. Brodowska...

Oświadczenie autora rozprawy doktorskiej

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Data ...30.09.2024r.......
Podpis autora ....Paulina Bogusz.....

Spis treści

Wykaz prac naukowych wchodzących w skład cyklu

(zbiór opublikowanych i powiązanych tematycznie artykułów naukowych)

1. **Paulina Bogusz,** Piotr Rusek, Marzena Sylwia Brodowska**. Suspension Fertilizers: How to Reconcile Sustainable Fertilization and Environmental Protection.** Agriculture 2021, 11, 1008. https://doi.org/10.3390/agriculture11101008

Liczba punktów w roku publikacji: **MEiN 2021 = 100; IF' 2021 = 3,408**

Indywidualny wkład pracy w publikację: udział w koncepcji pracy, przygotowanie i redagowanie manuskryptu, wizualizacja, przesłanie manuskryptu do wydawnictwa i odpowiedzi na recenzje, korekta po recenzjach.

2. **Paulina Bogusz. The Possibility of Using Waste Phosphates from the Production of Polyols for Fertilizing Purposes**. Molecules 2022, 27, 5632. https://doi.org/10.3390/molecules27175632

Liczba punktów w roku publikacji: **MEiN 2022 = 140; IF' 2022 = 4,6**

Indywidualny wkład pracy w publikację: opracowanie koncepcji pracy, zaplanowanie i przeprowadzenie badań, opis i interpretacja wyników badań, przygotowanie i redagowanie manuskryptu, przesłanie manuskryptu do wydawnictwa i odpowiedzi na recenzje, korekta po recenzjach.

3. **Paulina Bogusz**, Piotr Rusek, Marzena Sylwia Brodowska. **Suspension Fertilizers Based on Waste Phosphates from the Production of Polyols**. Molecules 2022, 27, 7916.https://doi.org/10.3390/molecules27227916

Liczba punktów w roku publikacji: **MEiN 2022 = 140; IF' 2022 = 4,6**

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4. **Paulina Bogusz**, Marzena Sylwia Brodowska, Piotr Rusek. **The Impact of Suspension Fertilizers Based on Waste Phosphorus Salts from Polyol Production on the Yield of Maize Intended for Green Fodder**. Agronomy 2024, 14, 1054. https://doi.org/10.3390/agronomy14051054

Liczba punktów w roku publikacji: **MEiN 2024 = 100; IF' 2024 = 3,3**

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5. **Paulina Bogusz**, Marzena Sylwia Brodowska, Paweł Muszyński. **The Impact of Suspension Fertilizers Based on Waste Phosphorus Salts from Polyol Production on the Content of Macronutrients in Maize Grown for Green Fodder**. Agronomy 2024, 14(9), 2079; https://doi.org/10.3390/agronomy14092079

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6. **Paulina Bogusz**, Marzena Sylwia Brodowska, Paweł Muszyński**. Content of Micronutrients in Maize Grown for Green Fodder Fertilized with Suspension Fertilizers Based on Waste Phosphorus Salts from the Production of Polyols.** – w trakcie procesu recenzji

Indywidualny wkład pracy w publikację: opracowanie koncepcji pracy, zaplanowanie i przeprowadzenie badań polowych, wykonanie analiz chemicznych, opis i interpretacja wyników badań, przeprowadzenie analizy statystycznej, przygotowanie i redagowanie manuskryptu, przesłanie manuskryptu do wydawnictwa i odpowiedzi na recenzje, korekta po recenzjach

Łączna liczba punktów MEiN = 580
Sumaryczny Impact Factor = 19,208

Streszczenie

Współczesne rolnictwo musi sprostać wyzwaniu zaspokojenia rosnących potrzeb żywnościowych ludności świata. Ze względu na ograniczoną możliwość powiększania areału upraw, nawożenie jest kluczowym elementem intensyfikacji produkcji. Z drugiej strony sektor nawozowy boryka się z dostępnością surowca fosforowego, który obok azotu i potasu jest głównym składnikiem odżywczym roślin. Ponad 80% jego zasobów trafia do produkcji nawozów. Rudy fosforytowe są nieodnawialnym źródłem, a nierównomierne rozmieszczenie kopalni fosforytów, z których dwie trzecie znajduje się w Maroku, Chinach i USA, sprawia, że Europa uzależniona jest od importu fosforu blisko w 90%. Istotne zagrożenie stanowi także zanieczyszczenie kadmem, obecnym głównie w osadowych złożach Afryki i Bliskiego Wschodu. Kadm łatwo przenika do gleby i roślin, co prowadzi do narażenia ludzi przez spożywanie skażonych upraw. Nowe regulacje UE redukują ilość kadmu w nawozach, co ogranicza wykorzystanie zanieczyszczonych fosforanów. Jednocześnie wprowadzają przepisy pozwalające na przetwarzanie odpadów bogatych w fosfor, wspierając zamknięty obieg tego surowca.

W pracy przedstawiono metodę odzysku fosforu poprzez przetwarzanie odpadów z produkcji polioli z firmy PCC Rokita S.A. Firma ta generuje około 1500 ton odpadów w formie fosforanu sodowo-potasowego, które mogłyby być użyte jako składniki nawozów. Ze względu na wysoką zawartość wody ekonomiczne ich przetwarzanie jest trudne. Najlepszym rozwiązaniem jest wykorzystanie ich w formie płynnych nawozów zawiesinowych. Na bazie odpadowych fosforanów opracowano sześć formulacji nawozów zawiesinowych dedykowanych pod uprawę kukurydzy na paszę, których działanie przetestowano w 3-letnich badaniach polowych. Porównano w nich działanie nawozów zawiesinowych, w których źródłem fosforu był odpadowy fosforan, z komercyjnym granulowanym nawozem fosforowym – Fosdar 40. Porównano także działanie nawozów zawiesinowych ze względu na ich skład testując nawozy zawierające główne składniki nawozowe (NPK), nawozy z dodatkiem drugorzędnych składników pokarmowych (S, Mg) oraz wzbogacone mikroelementami (B, Zn, Mn).

Słowa kluczowe: nawozy zawiesinowe, fosfor, odpady fosforowe, gospodarka odpadami, kukurydza na paszę

Summary

Modern agriculture must rise to the challenge of meeting the growing food needs of the world's population. Due to the limited possibility of expanding the area of crops, fertilization is a key element of production intensification. On the other hand, the fertilizer sector is struggling with the availability of phosphorus, which, along with nitrogen and potassium, is the main nutrient for plants. Over 80% of its resources go to fertilizer production. Phosphorus ores are a non-renewable source and the uneven distribution of phosphate mines, two thirds of which are located in Morocco, China and the USA, means that Europe depends on phosphorus imports for almost 90%. Another significant threat is cadmium contamination, present mainly in sedimentary deposits in Africa and the Middle East. Cadmium easily penetrates soil and plants, leading to human exposure through the consumption of contaminated crops. New EU regulations reduce the amount of cadmium in fertilizers, which limits the use of contaminated phosphates. At the same time, they introduce regulations allowing the processing of waste rich in phosphorus, supporting the closed circulation of this raw material.

The paper presents a method of phosphorus recovery by processing waste from polyol production from PCC Rokita S.A. This company generates about 1500 tons of waste in the form of sodium potassium phosphate, which could be used as fertilizer components. Due to the high water content, their economic processing is difficult. The best solution is to use them in the form of liquid suspension fertilizers. On the basis of waste phosphates, six formulations of suspension fertilizers dedicated to the cultivation of maize for feed were developed, the effects of which were tested in 3-year field tests. The effects of suspension fertilizers, where the source of phosphorus was waste phosphate, were compared with commercial granulated phosphorus fertilizer - Fosdar 40. The effects of suspension fertilizers were also compared due to their composition, testing fertilizers containing the main fertilizer components (NPK), fertilizers with the addition of secondary nutrients (S, Mg) and enriched with microelements (B, Zn, Mn).

Key words: suspension fertilizers, phosphorus, phosphorus waste, waste management, corn for feed

Wstęp

Wyzwaniem dla współczesnego rolnictwa jest zaspokojenie potrzeb stale rosnącej liczby ludności na świecie dzięki wydajnej produkcji żywności (1). Ze względu na ograniczone możliwości rozszerzenia produkcji rolnej poprzez nowe grunty orne, nawożenie jest istotnym czynnikiem wspierającym i intensyfikującym produkcję rolną (1–3). Żyzna gleba jest kluczem do zrównoważonej produkcji roślinnej na skalę przemysłową, ale bardzo niewiele gleb rolniczych ma wystarczającą zawartość składników odżywczych, aby zaspokoić potrzeby upraw (4). Większość z nich wymaga regularnego stosowania nawozów, które uzupełniają niskie lub brakujące składniki odżywcze w glebie (1,2,4).

Przez wiele lat sprawdzała się prosta korelacja pomiędzy ilością produkowanych nawozów a produkcją żywności. Sprawiała ona, że głównym celem przemysłu nawozowego było dostarczenie rolnictwu odpowiednio dużej ilości nawozów. Aby sprostać tym wymaganiom uruchomiono wiele nowych wytwórni nawozowych i zwiększono zdolność produkcyjną. Wpłynęło to negatywnie na stan środowiska naturalnego ze względu na emisję toksycznych gazów, ścieków, pyłów i produkowane odpady (5–7).

Efektywne wykorzystanie składników nawozowych jest podstawą zielonej gospodarki, aby produkować więcej żywności i energii przy jednoczesnym ograniczeniu zanieczyszczenia środowiska (8). Innowacje produktowe, które spełniają te wymagania, obejmują zarówno skład chemiczny nawozów, jak i ich właściwości fizyczne oraz sposób aplikacji (1,7).

Znaczenie fosforu

Fosfor, obok azotu i potasu, odgrywa kluczową rolę w intensyfikacji produkcji rolnej. Jako budulec organizmów żywych jest jednym z najważniejszych składników odżywczych dla roślin i zwierząt (9–11). Niedobór fosforu w glebie jest często głównym czynnikiem ograniczającym wzrost i rozwój roślin. Jego niewystarczająca ilość, zwłaszcza we wczesnych stadiach rozwoju roślin jednorocznych, może skutkować zmniejszeniem plonów. Późniejsza korekta jego dawki nie jest w stanie przywrócić prawidłowego wzrostu roślin (10). Konieczne jest zatem uzupełnianie jego niedoborów w glebie (9,12,13).

Głównym źródłem fosforu w rolnictwie są fosforyty. Są to minerały osadowe zbudowane z fosforanu wapnia z domieszką kwarcu, dolomitu, glaukonitu lub glinokrzemianów. Mogą zawierać znaczne ilości substancji organicznych, żelaza, glinu, metali ciężkich i substancji radioaktywnych, co utrudnia ich przetwarzanie (12).

Rudy fosforytowe nie są równocenne pod względem zawartości fosforu i mogą zawierać od 12 do 38% P_2O_5. Obecny stan techniki pozwala na ekonomicznie opłacalną eksploatację rud o zawartości P_2O_5 powyżej 28%. Wartość surowca zależy również od jego aktywności chemicznej. Starsze fosforyty, zwane twardymi, mają niższą aktywność chemiczną w porównaniu do młodszych (miękkich) (12). Zawarty w nich fosfor jest w ograniczonym stopniu dostępny dla roślin, dlatego są przetwarzane przy użyciu kwasów (głównie kwasu siarkowego) (14).

Światowe opłacalne rezerwy fosforytów stopniowo się kurczą (12). Szacuje się, że ich zdolność wydobywcza mieści się w przedziale 165–195 mln ton · rok^{-1}. Specjaliści różnie określają czas wykorzystania takich zasobów, ale są zgodni co do jednego: są one źródłem nieodnawialnym i prędzej czy później ulegną wyczerpaniu (4,7).

Problematyczną kwestią jest również nierównomierne rozmieszczenie ważnych gospodarczo kopalni fosforytów w skali globalnej (4,15). Ponad dwie trzecie wydobywanego w nich surowca pochodzi z Maroka, Chin i Stanów Zjednoczonych (9,10). Racjonalne gospodarowanie fosforem jest szczególnie ważne dla krajów europejskich, w których ekonomicznie opłacalne zasoby tego surowca są niewielkie. W efekcie zależność Europy od importu tego surowca sięga 90% (15–18).

Aby zminimalizować wpływ rynków zewnętrznych, kraje Unii Europejskiej zwróciły się w kierunku poszukiwania alternatywnych źródeł fosforu, w tym z materiałów odpadowych. Odpowiada to celom gospodarki o obiegu zamkniętym, która zakłada minimalizację i recykling odpadów oraz wydłużenie cyklu życia produktów gospodarczych (15,19–21).

Dystrybucja i dostępność rud fosforanowych nie są jedynym problemem przemysłu nawozowego i jego beneficjenta — sektora rolniczego. Zanieczyszczenia towarzyszące złożom fosforytów budzą duże obawy. Szczególnie niebezpieczny jest kadm, którym zanieczyszczone są głównie minerały fosforanowe pochodzenia osadowego. Dotyczy to złóż zlokalizowanych w północnej i wschodniej Afryce oraz na Bliskim Wschodzie. Mniejsze zanieczyszczenie obserwuje się w minerałach pochodzenia wulkanicznego (złoża w Finlandii, Rosji i Republice Południowej Afryki) (15). Kadm przedostający się do gleby za pośrednictwem nawozów, łatwo migruje i kumuluje się w roślinach (9,10,16). Spożywanie zanieczyszczonych upraw jest główną drogą narażenia ludzi (16). Kadm jest toksyczny i mutagenny (10,16). W organizmie człowieka uszkadza nerki, powoduje choroby kości oraz anemię (16). Połączenie wysoce negatywnego wpływu kadmu na zdrowie człowieka i jego wysokiej zawartości w fosforytach wymusiło regulacje prawne ograniczające jego ilość w produktach nawozowych (9).

Nowe przepisy UE ograniczają zawartość kadmu w produktach nawozowych, co znacznie zmniejsza stosowanie zanieczyszczonych fosforanów. Z drugiej strony wprowadzają regulacje prawne umożliwiające przetwarzanie odpadów bogatych w fosfor, przekształcając jego obieg w cykl zamknięty (22).

O znaczeniu tego surowca dla produkcji rolnej świadczy fakt, że ponad 80% jego zasobów przeznaczane jest na cele nawozowe, gdzie stanowi podstawę do produkcji niemal wszystkich nawozów fosforowych (9,15). W zawiązku z tym ma możliwości zrekompensowania jego niedoborów w tym sektorze poprzez przesunięcie zasobów z innych gałęzi przemysłu (7,15). Organizacja Narodów Zjednoczonych do spraw Wyżywienia i Rolnictwa (FAO) przewiduje, że globalny popyt na nawozy będzie wzrastał wraz ze wzrostem populacji i zmianą nawyków żywieniowych (15).

Straty fosforu dotyczą nie tylko marnotrawstwa zasobów naturalnych, ale także wody, energii i innych zasobów wykorzystywanych w cyklu jego przetwarzania. Tak więc produkcja nawozów zasilanych materiałami odpadowymi przynosi korzyści zarówno ekologiczne, jak i ekonomiczne. Podjęcie takiego kierunku działania w dłuższej perspektywie umożliwi zamknięcie cyklu fosforu (15,23). Ponadto, w celu podkreślenia dużego znaczenia gospodarczego i wysokiego ryzyka dostaw, fosfor i fosforyty zostały wpisane na listę krytycznych zasobów naturalnych (14,16).

Ograniczone zasoby surowców fosforowych, sytuacja polityczna na obszarach ich wydobycia, słaba jakość eksploatowanych złóż i rosnące wymagania dotyczące produktów nawozowych wymuszają opracowanie nowych technologii przetwarzania odpadów zawierających fosfor (12,15). W Unii Europejskiej istnieje duży potencjał odzyskiwania fosforu z materiałów odpadowych, w tym: ścieków komunalnych i przemysłowych, osadów ściekowych, popiołów ze spalania osadów ściekowych, mączki mięsno-kostnej, gnojowicy, biomasy i odpadów przemysłowych. Nadal trwają intensywne prace nad umożliwieniem gospodarczego przetworzenia tych odpadów, głównie na cele nawozowe, gdzie zapotrzebowanie na ten pierwiastek jest największe (9).

Odpadowy fosforan sodowo - potasowy z produkcji polioli

Ciekawą opcją odzysku fosforu ze strumienia odpadów jest przetwarzanie odpadów z produkcji polioli, które mają postać wodnej zawiesiny fosforanów sodu i potasu. W Polsce największym producentem polioli jest PCC Rokita w Brzegu Dolnym, która generuje ok. 1500 ton · rok^{-1} odpadów fosforanowych. Odpady te powstają w zakładzie produkcji polioli na etapie rozdziału faz, gdzie rozdziela się fazę organiczną (produkt), wodną fazę fosforanową i interfazę zawierającą materiał filtracyjny. Fosforany powstają w wyniku neutralizacji jonów sodu i potasu (z katalizatora polimeryzacji) kwaśnym pirofosforanem disodowym. W firmie PCC Rokita nie ma możliwości ich ponownego wykorzystania w procesie produkcji polioli. Jednak zawarte w nich sole fosforowe mogą być z powodzeniem stosowane jako składnik nawozów. Ze względu na wysoką zawartość wody w tych odpadach (ok. 49%) możliwości ich ekonomicznego przetworzenia są ograniczone i do tej pory nie były wykorzystywane. Odparowanie takiej ilości wody byłoby bardzo energochłonne, co wiąże się z wysokimi kosztami. Najlepszym rozwiązaniem jest wykorzystanie nieprzetworzonych odpadów do produkcji płynnych nawozów zawiesinowych.

Nawozy zawiesinowe

Nawozy zawiesinowe są ważnym narzędziem dla rolnictwa, spełniającym ustalone kryteria środowiskowe i agronomiczne (8). Ich płynna formuła i wysokie stężenie soli nawozowych umożliwiają skuteczne pobieranie składników odżywczych przez rośliny (5). Nawozy te stanowią element zrównoważonego gospodarowania składnikami mineralnymi, oferując możliwość zbilansowania ich dystrybucji, a także stwarzając możliwość zagospodarowania szkodliwych odpadów (8).

Nawozy zawiesinowe są definiowane jako nawozy płynne, w których składniki odżywcze są obecne w ilości przekraczającej ich rozpuszczalność (24). Oprócz składników całkowicie rozpuszczonych w wodzie, zawierają składniki nierozpuszczalne w postaci zdyspergowanej oraz stabilizator, który jest obecny w celu utrzymania jednolitości mieszanki (24–26). Nasycony wodny roztwór soli nawozowych stanowi fazę ciągłą, zaś nierozpuszczone sole w postaci drobnych kryształów stanowią fazę rozproszoną, co razem stanowi układ rozproszony (27).

Kryształy soli nawozowych utrzymywane są w roztworze za pomocą czynnika stabilizującego, który w roztworze pęcznieje przyjmując formę żelu. Zapobiega w ten sposób procesowi sedymentacji tych cząstek (5).

Nawozy zawiesinowe łączą w sobie zalety nawozów płynnych i stałych, ale również posiadają cechy unikatowe, czyniące je atrakcyjną pozycją na rynku nawozowym.

Dużą zaletą tych nawozów jest wysokie stężenie składników pokarmowych przy jednoczesnym zachowaniu płynnej formy. Koncentracja soli nawozowych w zawiesinie jest zbliżona do koncentracji nawozów stałych, a więc dużo wyższa niż możliwa do uzyskania w nawozach klarownych (5,25,26).

Z formy zawiesinowej wynikają mniejsze wymagania dotyczące czystości surowców stosowanych do ich wytwarzania (25,26). W porównaniu bowiem z nawozami klarownymi, nie jest wymagana ich całkowita rozpuszczalność (28–30). Można wykorzystać także surowce trudno rozpuszczalne w wodzie i pyliste, takie jak drobno zmielony fosforyt (30). Użyteczną cechą formy zawiesinowej nawozu jest możliwość wykorzystania w ich produkcji odpadów o dużej zawartości wody, zawierających cenne składniki nawozowe. Odpady w postaci szlamów, zawiesin i osadów ściekowych pochodzących z przemysłu chemicznego i rolno-spożywczego ze względu na dużą zawartość wilgoci i zanieczyszczenia nie nadają się do produkcji innych form nawozów (5).

Ponieważ zawartość składników pokarmowych nie jest limitowana ich rozpuszczalnością, łatwo można uzyskać zawiesiny nawozowe o niemal dowolnych proporcjach między składnikami nawozowymi (5,28). Stwarza to dużą elastyczność w zakresie doboru mieszanek nawozowych (31). Obecnie wytwarza się w formie zawiesinowej niemal wszystkie odpowiedniki klasycznych nawozów stałych (32).

Dowolność kombinacji składników w zawiesinie nawozowej daje możliwość dostosowania składu nawozu do konkretnych potrzeb uprawianych roślin (5,31). Jednocześnie zróżnicowane warianty stosunku poszczególnych komponentów nawozowych umożliwiają ich zastosowanie według zasobności gleby (32).

Ważną zaletą tego typu produktu jest możliwość wprowadzenia do gleby za ich pośrednictwem dodatkowych substancji poprawiających kondycję roślin (28). Bez przeszkód można zawrzeć w strukturze nawozu zawiesinowego mikroelementy w pożądanych stężeniach i formach (5,32). Istnieje również możliwość wykorzystania zawiesiny nawozowej jako nośnika środków ochrony roślin, witamin, inhibitorów nitryfikacji itp., niezależnie od ich postaci fizycznej (5,28).

Szerokie możliwości wzbogacania nawozów zawiesinowych o dodatkowe składniki pozwala na łączenie nawożenia z innymi zabiegami agrotechnicznymi (28). Oprócz połączenia zabiegu nawożenia i ochrony roślin dostępny jest również wariant połączony z nawadnianiem i irygacją (5).

Cechą wspólną nawozów płynnych, zarówno klarownych jak i zawiesinowych, jest duża jednorodność składu chemicznego (5). Wynikają z tego istotne korzyści użytkowe związane z równomiernością rozprowadzenia nawozu na polu (5,30,33). Nie występuje zjawisko rozdzielania składników, tak jak ma to miejsce w przypadku rozsiewu nawozów stałych (31,33). Precyzyjne dozowanie jest szczególnie istotne w przypadku mikroelementów, wprowadzanych do nawozu w niewielkich ilościach (5,31).

Na tle innych form nawozów bardzo dobrze spełniają swoją główną funkcję jaką jest zaopatrywanie roślin w substancje pokarmowe. Płynna forma zapewnia lepszą dostępność i wykorzystanie przez rośliny składników nawozowych, w porównaniu z ekwiwalentnymi dawkami nawozów stałych (33,34). Różnice w plonach na korzyść nawozów płynnych wynikają także z wysokiej równomierności rozprowadzania składników nawozowych oraz dostosowaniu jego składu do indywidualnych potrzeb uprawianych roślin. Ponadto nawozy zawiesinowe dają lepsze efekty plonotwórcze w latach o mniejszej ilości opadów (34).

Produkcja nawozów granulowanych w etapie odparowania i granulacji skutkuje emisją do atmosfery substancji szkodliwych dla środowiska. Są nimi głównie opary amoniaku, tlenków azotu, tlenków siarki oraz znaczna ilość pyłów gotowych wyrobów. Ujemne działanie takich czynników można potwierdzić naocznie w okolicy wielkich zakładów produkujących nawozy. W produkcji nawozów płynnych skrócono linię technologiczną o węzeł granulacji, suszenia, klasyfikacji i pakowania, czyli etapy najbardziej uciążliwe dla środowiska (32). Ponadto w procesie produkcji nawozów zawiesinowych emisja zanieczyszczeń jest znacznie ograniczona dzięki hermetyzacji urządzeń i przetłaczaniu przy użyciu pomp (5).

Nawozy zawiesinowe są wygodne w stosowaniu, transporcie, przeładunku i magazynowaniu (5,30). Ich wytwarzanie i obrót są mało pracochłonne, gdyż można je całkowicie zmechanizować (25,26,28,31). Ponieważ nawóz jest płynny może być transportowany za pomocą pomp przez rury i może być rozpryskiwany na glebę przez dysze. Dlatego też zmniejszona jest ilość pracy związana z aplikacją.

Dużą zaletą tych nawozów jest rezygnacja z jednorazowych opakowań, które nie podlegają degradacji oraz redukcja zbędnych substancji balastowych np. antyzbrylaczy (5).

Stosowanie nawozów zawiesinowych wpływa na polepszenie struktury gruzełkowatej gleby, za sprawą żelujących substancji ilastych. Przed zastosowaniem nawozu substancje te mają za zadanie utrzymać w rozproszeniu nierozpuszczalne elementy układu zawiesinowego, w glebie zaś zwiększają jej chłonność (28).

W przypadku nawozów płynnych wyeliminowano trudności wynikające z segregacji i zbrylania, które towarzyszą magazynowaniu nawozów w postaci stałej (30). Dzięki płynnej formie wykluczono również zagrożenie wybuchem, związane z użyciem stałej saletry amonowej (5).

Mimo licznych zalet nawozy zawiesinowe posiadają też wady, które wpływają na ograniczenia w ich stosowaniu. Główną ich wadą jest krótki czas magazynowania, ze względu na ograniczoną trwałość zawiesiny. Dlatego nawozy te są zwykle produkowane na potrzeby lokalne, a czas ich przechowywania to co najwyżej kilka dni (26). Stacje wytwarzające nawozy zawiesinowe muszą być usytuowane w pobliżu nawożonych gruntów (28). Stosowanie zawiesin nawozowych jest najkorzystniejsze w przypadku dużych gospodarstw rolnych o nierozproszonym areale (6,28). Ponadto zawiesina nawozowa może mieć korozyjny wpływ na zbiorniki magazynowe.

Popularyzacja nawozów zawiesinowych w powszechnym użytku jest odpowiedzią na bieżące i możliwe przyszłe problemy związane z rosnącą liczbą odpadów i wyczerpywaniem się zasobów naturalnych. Nawozy zawiesinowe wpasowują się w zmieniającą się strukturę gospodarstw rolnych, objawiającą się zwiększoną mechanizacją i dążeniem do dużych, nierozproszonych gruntów uprawnych.

Ze względu na duże wykorzystanie nawozów płynnych zawiesinowych w Stanach Zjednoczonych, wiele procedur jest wynikiem doświadczeń eksploatacyjnych, które w tej dziedzinie ma amerykańska firma Tennesse Valey Authority (TVA) (5).

W przypadku nawozów zawiesinowych ważne jest utrzymanie jednorodności składu w całej objętości nawozu od chwili wytworzenia do momentu aplikacji (5). Stabilna struktura w trakcie magazynowania decyduje o możliwości obrotu tymi nawozami (5,25,26). Powstawanie klarownej warstwy na powierzchni lub w środku zawiesiny, zwane synerezą, jest zjawiskiem niepożądanym (35). Może ono powodować nadmierny wzrost kryształów na granicy faz, co zaś może skutkować powstawaniem osadów zdolnych do cementowania dna zbiornika (5,35). Kryształy mogą również powstawać w wyniku wibracji generowanych w procesie transportowym. Ilość osadzanych kryształów nie powinna przekraczać 2% objętości produktu (5). Aby zawiesina mogła być dopuszczona do użytku powstałe kryształy powinny przechodzić przez sito 0,246 mm (60 mesh) lub 0,850 mm (20 mesh). Jednakże, jeśli obecne w zawiesiny kryształy można rozdrobnić przez recyrkulację zawiesiny lub barbotujący gaz, zawiesina nadal kwalifikuje się do użytku (35).

Ze względów aplikacyjnych ważnym parametrem nawozów zawiesinowych jest możliwość swobodnego, grawitacyjnego wylewu. Wartość ta określana wskaźnikiem wylewności według norm amerykańskich powinna wynosić 98% w temperaturze 27°C (5).

Pożądanymi właściwościami reologicznymi jest duża lepkość pozorna przy małych siłach ścinających oraz mała lepkość pozorna przy dużych siłach ścinających (5,24,35,36). Preferowane wartości lepkości to nie większa niż 1000 mPa·s w temp. 27°C i 1500 mPa·s w temp. 30°C (5,35). Produkty o takich parametrach nie ulegają sedymentacji, a zarazem wykazują zdolność tworzenia kropelek w dyszach rozpryskowych, umożliwiając bezproblemową aplikację (5,35,36). Parametr ten jest więc niezbędny do określenia technicznych parametrów sprzętu przeznaczonego do aplikacji nawozów zawiesinowych (25,26). Dopuszczalny zakres gęstości mieści się w przedziale 1,200 – 1,400 g · cm^{-3}, natomiast lejność określana przy użycia kubka wypływowego - 10 – 15 s (37).

Stabilność jest podstawowym czynnikiem decydującym o jakości zawiesiny [143]. W roli środka stabilizującego najlepiej sprawdzają się minerały ilaste (5,25). Mają one dużą powierzchnię właściwą, co skutkuje dobrymi właściwościami sorpcyjnymi [144]. Ich dodatek, poza działaniem pęczniejącym i jonowymiennym w nawozie, po wprowadzeniu do gleby polepsza jej strukturę (32,38). Negatywny wpływ na stabilność zawiesiny może mieć również temperatura (39). Pod wpływem zmian temperatury w czasie magazynowania mogą z nasyconego roztworu wykrystalizować duże belkowate kryształy. Ich obecność w zawiesinie utrudnia przetłaczanie produktu, a także powoduje zarastanie zbiorników i dysz rozpryskowych, zakłócając proces nawożenia (5).

W przemyśle do stabilizacji zawiesin nawozowych najczęściej stosowane są minerały ilaste w ilości 0,5 – 3% (5). Są to zwykle minerały z grupy smektytu, takie jak atapulgity i bentonity (5,25,39). W tym celu można również wykorzystać związki organiczne, np. sorbit, skrobię, hydrolizaty białkowe i hydrolizaty keratynowe (33,40).

Kukurydza

W odpowiedzi na rosnącą populację zwiększenie produkcji roślinnej stało się jednym z głównych celów zapewnienia wystarczającej ilości żywności. W tym kontekście zboża odgrywają kluczową rolę (41). Trzy podstawowe zboża na świecie — pszenica, ryż i kukurydza — są kluczowymi składnikami diety człowieka, stanowiąc około 42% globalnego spożycia kalorii i 37% spożycia białka (41–44).

Kukurydza (*Zea mays L.*) pochodzi z Ameryki Środkowej, gdzie została udomowiona około 7000 lat temu, a od osadnictwa europejskiego szybko rozprzestrzeniła się na całym świecie. Od tego czasu odgrywała coraz większą i bardziej zróżnicowaną rolę w systemie rolno-spożywczym (42,43,45–47).

Przewagą kukurydzy nad innymi zbożami jest jej wysoki potencjał plonowania zarówno ziarna, jak i elementów paszowych (41). Co więcej, może być uprawiana w szerokim zakresie warunków klimatycznych i glebowych. Dostarcza więcej składników odżywczych w porównaniu do innych zbóż i roślin strączkowych (47–49). Kukurydza zawiera około 72% skrobi, 10% białka i 4% tłuszczu, zapewniając gęstość energetyczną 365 Kcal·100 g^{-1}, ale ma niższą zawartość białka w porównaniu do ryżu i pszenicy (48).

Kukurydza jest bardzo wszechstronnym zbożem o wielu potencjalnych zastosowaniach. Może być wykorzystywana jako roślina spożywcza, pasza dla zwierząt, surowiec przemysłowy i do produkcji energii (48,50,51).

W przemyśle spożywczym kukurydza jest wykorzystywana do produkcji różnych produktów, takich jak skrobia kukurydziana, dekstroza, syrop kukurydziany i płatki kukurydziane (42,48,52). W gospodarkach rozwiniętych spożycie większej ilości produktów zwierzęcych prowadzi do zwiększonego wykorzystania kukurydzy w produkcji paszy dla zwierząt gospodarskich (42). Jest to jedna z najcenniejszych i najbardziej wydajnych roślin pastewnych uprawianych na skalę globalną (53–55). Jest wykorzystywana do produkcji pasz objętościowych, wykorzystywanych głównie zimą, ale coraz częściej również przez cały rok do karmienia zwierząt przeżuwających. Najpopularniejszą formą jest kiszonka z całych roślin kukurydzy (54).

Rozwój produkcji pasz z kukurydzy wynika z jej potencjału do wysokich plonów, wysokiej strawności i większej odporności na wyleganie w porównaniu ze zbożami drobnoziarnistymi, takimi jak jęczmień i owies (53). W uprawie zapewnia stabilne plony w różnych warunkach środowiskowych i agrotechnicznych. Charakteryzuje się wysoką wartością energetyczną i doskonałymi właściwościami do kiszenia (49).

Kukurydza stwarza możliwość zwiększenia produkcji mięsa i mleka bez konieczności rozszerzania użytkowania gruntów rolnych (56). W diecie krów mlecznych zwiększa spożycie paszy, wydajność mleczną i zawartość białka (48). W gospodarstwach kiszonka paszowa jest zazwyczaj tańsza niż suche koncentraty i może być produkowana przy niższym nakładzie energii, takim jak energia potrzebna do suszenia i transportu (57,58).

W ciągu ostatnich kilku dekad produkcja kukurydzy na całym świecie gwałtownie wzrosła. Uprawa kukurydzy obejmuje ponad 170 krajów, w tym gospodarki wschodzące i rozwinięte. Obszar jej uprawy jest skoncentrowany głównie w obu Amerykach i Azji, przy czym największy udział przypada na Amerykę Północną (głównie w USA) i Azję Wschodnią (szczególnie w Chinach). Regiony te dostarczają ponad połowę światowej produkcji kukurydzy (42,46). Głównymi krajami eksportującymi kukurydzę są Stany Zjednoczone, Brazylia, Argentyna i Ukraina. W latach 2020–2021 skumulowany eksport kukurydzy z tych czterech krajów stanowił 88,12% światowego eksportu. Oznacza to, że chociaż Chiny są głównym producentem kukurydzy, nie są jej głównym eksporterem. USA i Chiny są dwoma największymi konsumentami kukurydzy (47).

W ostatnich latach nastąpił znaczny wzrost udziału kukurydzy w strukturze zasiewów, co powoduje konieczność uprawy tego gatunku na glebach mniej urodzajnych.

Szczególnie w tych warunkach istotne jest odpowiednie zbilansowanie nawożenia mineralnego w celu maksymalizacji potencjału plonowania nowoczesnych odmian kukurydzy (59). Jest ona zaliczana do roślin intensywnych o wysokich wymaganiach odżywczych i nawozowych, znacznie wyższych niż inne rośliny zbożowe (60,61). Generuje dużą ilość biomasy w krótkim czasie. Optymalne nawożenie mineralne i efektywna fotosynteza przyczyniają się do jej szybkiego wzrostu, co bezpośrednio przekłada się na wyższe plony zarówno ziarna, jak i części wegetatywnych (59).

Aby zapewnić prawidłowe odżywienie kukurydzy uprawianej na kiszonkę, niezbędne jest dostarczenie odpowiednich ilości niezbędnych składników odżywczych, takich jak azot, fosfor, potas, siarka, magnez, a z mikroelementów głównie cynk i bor. Do wyprodukowania jednej tony zielonej masy kukurydzy na kiszonkę roślina potrzebuje około 3,5–4,1 kg azotu (N), 1,3–1,5 kg fosforu (P_2O_5), 6,3–7,7 kg potasu (K_2O) i 0,7–0,9 kg magnezu (MgO) [13].

Potrzeby odżywcze kukurydzy rosną w miarę rozwoju rośliny, szczególnie w przypadku azotu, którego większość pobierana jest w fazie rozwoju generatywnego (60). Kluczowym okresem w rozwoju kukurydzy jest etap przechodzenia rośliny z etapu odżywiania z ziarna na odżywianie przez system korzeniowy, który jest jeszcze niewystarczająco rozwinięty (faza 4–8 liści). W tym okresie roślina napotyka na trudności w pobieraniu wody i składników pokarmowych, co wpływa na osłabienie jej wzrostu i rozwoju. Szczególnie przy niskich temperaturach panujących w okresie wiosennym można zaobserwować problemy z pobieraniem fosforu (59). Ponadto dobre odżywienie kukurydzy w fazie 4–10 liści zapewnia odpowiedni plon, ponieważ w tym okresie ustala się maksymalny potencjał plonowania, czyli liczba rzędów ziaren w kolbie i ich długość. W początkowych fazach rozwoju roślina szczególnie potrzebuje azotu, łatwo przyswajalnego fosforu i cynku. Inne składniki odżywcze, takie jak potas, magnez, siarka, wapń i bor, są pobierane przez kukurydzę w późniejszych fazach wzrostu (59).

Kukurydza, choć ma umiarkowane wymagania glebowe, nie oznacza, że powinna być uprawiana na słabszych stanowiskach. Optymalne warunki dla kukurydzy to gleby z kompleksami pszennymi o bardzo dobrej i dobrej jakości. Jednak w praktyce takie stanowiska są rzadko dostępne. Zazwyczaj najlepsze działki w gospodarstwie są przeznaczone pod uprawę rzepaku ozimego i pszenicy. W rezultacie, kukurydza często jest uprawiana na przypadkowych stanowiskach na glebach o mniejszej żyzności – od klasycznego w zmianowaniu, po wymarznięte oziminy (np. jęczmienia, rzepaku), świeżo wydzierżawione pola, a często tam, gdzie nie udają się inne uprawy (59).

Kukurydza nie toleruje gleb, które są zimne, ciężkie, nadmiernie zbite i zbyt wilgotne. Na słabszych stanowiskach należy szczególnie zadbać o zasobność gleby w niezbędne składniki odżywcze. Kukurydza należy do roślin, które tolerują lekko kwaśny odczyn gleby. Optymalny zakres pH dla wzrostu kukurydzy mieści się w przedziale 5,5-6,5. Tylko w takim od-czynie zapewnione są optymalne warunki rozwoju rośliny. Nawet gdy gleba jest dobrze zaopatrzona w składniki odżywcze, nieodpowiedni odczyn gleby utrudnia skuteczne pobieranie składników pokarmowych a szczególnie fosforu (59).

Problem badawczy

Problem badawczy polega na zweryfikowaniu czy odpadowy fosforan sodowo – potasowy z produkcji polioli może posłużyć jako surowiec w produkcji wieloskładnikowych nawozów zawiesinowych, charakteryzujących się korzystnymi właściwościami reologicznymi oraz wysoką koncentracją składników nawozowych, o pozytywnym działaniu rolniczym.

Cel pracy

Główne cele pracy:

- Ocena możliwości wykorzystania fosforanów odpadowych z produkcji polioli z PCC Rokita S. A. do celów nawozowych na podstawie analizy fizykochemicznej odpadów.
- Ocena możliwości wytwarzania nawozów zawiesinowych na bazie odpadowego fosforanu z produkcji polioli.
- Ocena wpływu nawozów zawiesinowych na bazie odpadów z polioli na plonowanie i parametry jakościowe roślin kukurydzy.

Cele szczegółowe pracy:

- Ocena odpadu z polioli pod kątem zawartości składników nawozowych i substancji szkodliwych dla roślin.
- Ocena możliwości wykorzystania odpadu z polioli jako surowca nawozowego w odniesieniu do przepisów nawozowych.
- Ocena postaci fizycznej odpadu pod kątem wykorzystania w produkcji nawozów.
- Dobór odpowiedniego typu nawozu dla wykorzystania odpadu z polioli jako surowca.
- Ocena nawozów zawiesinowych na tle innych typów nawozów.
- Ocena środków stabilizujących nawozy zawiesinowe.
- Analiza uwarunkowań prawnych wprowadzenia do obrotu tego typu nawozów.
- Ocena wpływu nawozów zawiesinowych na bazie odpadu z polioli na plonowanie kukurydzy uprawianej na paszę.

- Ocena wpływu nawozów zawiesinowych na bazie odpadu z polioli na jakość kukurydzy uprawianej na paszę.
- Ocena wpływu nawozów zawiesinowych na bazie odpadu z polioli na podstawowe parametry glebowe oraz na zawartość w glebie metali ciężkich.

Materiały i metody

1. Odpad z produkcji polioli (Publikacja nr 2)

1.1. Zawartość węgla organicznego

Odpadowy fosforan z produkcji polioli ma postać niestabilnej zawiesiny (część fazy stałej opada na dno podczas magazynowania), dlatego do analizy zawartości węgla organicznego pobrano próbki uśrednione podczas intensywnego mieszania strumieniem sprężonego powietrza. Zawartość węgla organicznego analizowano przy użyciu analizatora TOC serii InnovOx przy użyciu technologii utleniania wody nadkrytycznej.

1.2. Analiza chemiczna

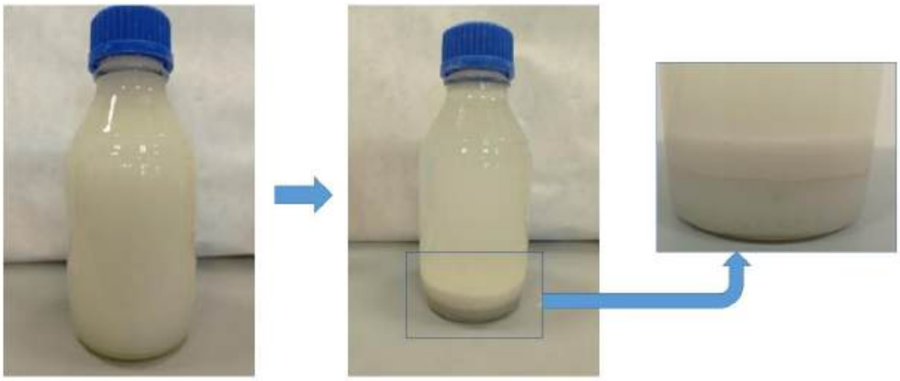
Kluczowym zagadnieniem decydującym o przydatności odpadów do celów nawozowych jest zawartość składników odżywczych dla roślin oraz poziom zanieczyszczeń. Dlatego określono zawartość oczekiwanych składników w odpadach: fosforu (P), potasu (K), sodu (Na) oraz zanieczyszczeń w postaci: kadmu (Cd), chromu (Cr VI), rtęci (Hg), niklu (Ni), ołowiu (Pb), arsenu (As), miedzi (Cu), cynku (Zn), żelaza (Fe) i glinu (Al.). Do badań zastosowano standardowe metody i procedury wymienione w tabeli 1.

Tabela 1. Metody badawcze stosowane w analizie odpadu

Badana cecha	Metoda	Procedura
Fosfor rozpuszczalny w kwasach mineralnych (P_2O_5)	Metoda wagowa	PN-EN 15956:2011 PN-EN 15959:2011
Potas (K_2O)	Metoda wagowa	PN-EN 15477:2009
Sód (Na) Miedź (Cu) Żelazo (Fe) Cynk (Zn) Kadm (Cd) Ołów (Pb) Nikiek (Ni) Glin (Al)	Atomowa spektrometria emisyjna ze wzbudzeniem plazmą sprzężoną indukcyjnie (ICP-OES)	PB 35 ed. III of 02/03/2020 PN-EN 16319 + A1: 2016-02 z wyjątkiem punktu 8.2
Arsen (As)	Atomowa spektrometria emisyjna ze wzbudzeniem plazmą sprzężoną indukcyjnie (ICP-OES)	PB 35 ed. II of 02/03/2020 PN-EN 16317 + A1: 2017-04 z wyjątkiem punktu 8.2
Rtęć (Hg)	Atomowa spektrometria absorpcji z techniką amalgamacji	RMG załącznik 3, p. 4*
Chrom (VI)	Chromatografia jonowa	PN-EN 16318+A1:2016-03

1.3. Analiza osadów w odpadzie z polioli

Odpadowy fosforan sodowo-potasowy jest białą zawiesiną, która łatwo ulega rozwarstwieniu podczas magazynowania (rysunek 1).



Rysunek 1. Opadowy fosforan z produkcji polioli z firmy PCC Rokita S.A.

Po dłuższym magazynowaniu na dnie odpadu powstają trzy warstwy osadu o różnych rozmiarach kryształów. Osady z poszczególnych warstw były w formie półpłynnej i zostały rozdzielone przez dekantację. Aby uniknąć mieszania się kryształów z poszczególnych warstw, osad na styku warstw został wylany oddzielnie i nie był używany do dalszych badań. Poszczególne warstwy osadu zostały następnie wysuszone i poddane analizie fluorescencji rentgenowskiej (XRF) w celu określenia ich składu. Pomiary XRD przeprowadzono na dyfraktometrze proszkowym PANalytical Empyrean pracującym w geometrii Bragga–Brentano.

2. Surowce nawozowe (Publikacja nr 3)

Nawozy na bazie odpadowych fosforanów mają być dobrym zamiennikiem dla komercyjnych nawozów fosforowych, wśród których jednym z bardziej popularnych na naszym rynku nawozowym jest – Fosdar 40. Dlatego w testach wykorzystano typowe surowce nawozowe najczęściej stosowane w produkcji nawozów zawiesinowych, z wyjątkiem surowca, który był źródłem fosforu.

Źródłami azotu i potasu dla wszystkich nawozów (zawiesin i kontroli) był roztwór saletrzano-mocznikowy (RSM) oraz sól potasowa (60% K_2O). Drugorzędne składniki pokarmowe wprowadzono do nawozów wraz siarczanem magnezu natomiast surowcami mikroelementowymi był kwas borowy, siarczany cynku i manganu. Źródłem fosforu w nawozach zawiesinowych był płynny fosforan sodowo-potasowy z produkcji polioli, natomiast w próbach kontrolnych granulowany nawóz Fosdar 40.

Do stabilizacji zawiesin nawozowych najczęściej stosowanym surowcem ze względu na cenę i dostępność są bentonity. W badaniach przetestowano cztery bentonity z Zakładów Górniczo-Metalowych „ZĘBIEC” w Zębcu S.A. : bentonit GM, Specjal, Specjal 45, SN. Bentonity GM, Special i Special 45 o zawartości montmorylonitu 75% aktywowano kationami sodu, natomiast bentonit SN stanowiący mielony i suszony bentonit wapniowy, nie podlegał procesowi aktywacji.

3. Opracowanie formulacji nawozów zawiesinowych (Publikacja nr 3)

Przedstawione w pracy nawozy zawiesinowe dedykowane są do uprawy kukurydzy na kiszonkę ze względu na jej duże znaczenie w produkcji żywności i pasz. Skład nawozów opracowano na podstawie zaleceń dotyczących uprawy kukurydzy na zieloną masę opracowanych przez Instytut Uprawy Nawożenia i Gleboznawstwa – Państwowy Instytut Badawczy w Puławach (IUNG) (62).

Kukurydza pobiera z gleby duże ilości składników odżywczych i wody. Przy plonie 10 ton paszy zużywa średnio: 38 kg azotu (N), 16 kg fosforu (P_2O_5), 45 kg potasu (K_2O), 20 kg wapnia (CaO), 12 kg magnezu (MgO), 5 kg siarki (S) lub przeliczonej na SO_3—12,5 kg oraz 17 g boru (B), 13 g miedzi (Cu), 150 g manganu (Mn), 1,5 g molibdenu (Mo) i 150 g cynku (Zn). Roślina ta wykazuje dużą wrażliwość na niedobór cynku i średnią wrażliwość na niedobór boru, manganu i miedzi. Na podstawie potrzeb pokarmowych rośliny testowej ustalono stosunek głównych składników odżywczych N:P:K taki jak: 38:16:45 = 2,4:1:2,8.

Dla testowanych w badaniach nawozów zawiesinowych z dodatkiem składników mikroelementowych wybrano trzy mikroelementy o kluczowym znaczeniu w uprawie kukurydzy, takie jak bor, mangan i cynk. Ilość tych składników w nawozach zawiesinowych została dobrana jako minimalna ilość jaką można zadeklarować w nawozie zawierającym podstawowe i/lub drugorzędne składniki pokarmowe z dodatkiem mikroelementów stosowanych doglebowo w uprawach polowych wg Rozporządzenia Ministra Gospodarki z dnia 8 września 2010 r. w sprawie sposobu pakowania nawozów mineralnych, umieszczania informacji o składnikach nawozowych na tych opakowaniach, sposobu badania nawozów mineralnych oraz typów wapna nawozowego. Ilość ta dla zastosowanych w nawozach mikroelementów wynosi: Zn – 0,01% (m/m), Mn – 0,1% (m/m), B – 0,01% (m/m).

Według nowego Rozporządzenia Parlamentu Europejskiego i Rady (UE) 2019/1009, uchylającego rozporządzenie (WE) nr 2003/2003, które ma zastosowanie od dnia 16 lipca

2022 r., mangan i cynk w płynnych nieorganicznych nawozach mogą być deklarowane przy niższych zawartościach: Mn – 0,01% (m/m), Zn – 0,002% (m/m). Nowe unijne przepisy nie stwarzają konieczności zmian w przyjętych składach dla nawozów zawiesinowych.

Do badań polowych przygotowano dwie serie nawozów. W pierwszej serii zaproponowano trzy nawozy o procentowej zawartości głównych składników NPK: 9,5-4-11. Nawóz 1 zawiera tylko główne składniki odżywcze (N, P, K), nawóz 2 jest dodatkowo wzbogacony o składniki drugorzędne (Mg, S), a nawóz 3 jest poza tym wzbogacony o mikroelementy (tabela 2).

Tabela 2. Składy nawozów I serii o zawartości procentowej NPK: 9,5 – 4 – 11

Nr	**Typ nawozu**	**Zawartość składników nawozowych, %**							
		N	**P_2O_5**	**K_2O**	**MgO**	**S**	**Zn**	**Mn**	**B**
1	NPK	9.5	**4**	11	-	-	-	-	-
2	NPK + MgO + S	9.5	**4**	11	3	6	-	-	-
3	NPK + MgO + S + mikro	9.5	**4**	11	3	6	0.01	0.1	0.01

W drugiej serii nawozów zwiększono dawkę fosforu o 2% przy takiej samej zawartości azotu, potasu, składników drugorzędnych i mikroelementów jak w nawozach z pierwszej serii. Skład nawozów serii II (nawóz 4, 5 i 6) przedstawiono w tabeli 3.

Tabela 3. Składy nawozów II serii o zawartości procentowej NPK: 9,5 – 6 – 11

Nr	**Typ nawozu**	**Zawartość składników nawozowych, %**							
		N	**P_2O_5**	**K_2O**	**MgO**	**S**	**Zn**	**Mn**	**B**
4	NPK	9.5	**6**	11	-	-	-	-	-
5	NPK + MgO + S	9.5	**6**	11	3	6	-	-	-
6	NPK + MgO + S + mikro	9.5	**6**	11	3	6	0.01	0.1	0.01

Skład nawozów zawiesinowych dobrano w taki sposób, aby porównać efektywność plonotwórczą kukurydzy w odniesieniu do ilości składnika fosforowego oraz w stosunku do dodatku składników drugorzędnych i mikroelementów.

4. Wytwarzanie nawozów zawiesinowych (Publikacja nr 3)

Nawozy zawiesinowe wytwarzano przy użyciu szybkoobrotowego mieszalnika Dispermat z mieszadłem typu dissolwer. Odpowiednie ilości płynnych surowców dozowano do reaktora i mieszano z prędkością 800 obr./min przez 5 min. Następnie stopniowo dozowano stałe surowce, zwiększając prędkość mieszadła do 1500 obr./min. Po zakończeniu dozowania wszystkich surowców zawiesinę mieszano przez około 15 min.

5. Badania jakości nawozów zawiesinowych (Publikacja nr 3)

5.1. Badanie stabilności

Trwałość przygotowanych zawiesin nawozowych oznaczono przez badania sedymentacyjne. Badania prowadzono przez 48 godzin aby zaobserwować zjawiska zachodzące w zawiesinach nawozowych od ich wytworzenia do aplikacji lub całkowitej degradacji. Za zadowalający czas na utrzymanie zawiesiny w stabilnej formie uważa się 48 godzin. Jest to minimalny czas, który pozwala na transport i aplikację nawozu w tej formie. W celu wykonania pomiaru badane nawozy zawiesinowe bezpośrednio po wytworzeniu umieszczono w cylindrach miarowych z korkiem o pojemności 100 ml, średnicy 30 mm i oznaczono zachodzące w czasie zmiany poprzez pomiar wysokości rozwarstwienia.

5.2. Badanie lejności

Badanie lejności wykonano w temperaturze 20°C przy użyciu kubka Forda o pojemności 100 ml i średnicy dyszy wypływowej 4 mm. Po napełnieniu kubka do pełna badaną zawiesiną zmierzono czas swobodnego wypływu całości płynu przez dyszę znajdującą się na dnie pojemnika. Pomiary lejności wykonano bezpośrednio po wytworzeniu zawiesin oraz po upływie 48 godzin po wcześniejszym jej wymieszaniu.

5.3. Badanie gęstości

Pomiar gęstości wykonano w temperaturze 20°C przy użyciu aerometru. Nawóz zawiesinowy bezpośrednio po wytworzeniu przelano do cylindra miarowego i umieszczono w nim aerometr, w taki sposób aby nie dotykał ścianek cylindra. Po ustabilizowaniu się poziomu aerometru w zawiesinie odczytano i zapisano wynik pomiaru.

6. Metodyka badań polowych (Publikacja nr 4)

W doświadczeniu polowym testowano 6 nawozów zawiesinowych na bazie odpadowego fosforanu. Badania obejmowały dwie kontrole, w których zastosowano nawozy NPK o składzie takim samym jak w nawozie zawiesinowym nr 1 oraz nr 4, z tym że surowiec fosforowy zastąpiono granulowanym nawozem – Fosdar 40 oraz kontrolę bez nawożenia. Każdy nawóz został zastosowany na polu w ilości odpowiadającej dwóm dawkom azotu: a—180 $kg \cdot ha^{-1}$; b—135 $kg \cdot ha^{-1}$.

Tabela 1. Plan nawożenia w doświadczeniu polowym

Główne składniki nawozowe - NPK	Zawartość fosforu w nawozie, %	Źródło fosforu w nawozie	Drugorzędne składniki pokarmowe	Mikroelementy	Dawka N, kg · ha^{-1}	Ilość powtórzeń
9.5-4-11	4	Odpadowe fosforany z produkcji polioli	0	0	180	3
					135	3
			Mg, S	0	180	3
					135	3
			Mg, S	Z, B, Mn	180	3
					135	3
		Fosdar 40	0	0	180	3
					135	3
9.5-6-11	6	Odpadowe fosforany z produkcji polioli	0	0	180	3
					135	3
			Mg, S	0	180	3
					135	3
			Mg, S	Z, B, Mn	180	3
					135	3
		Fosdar 40	0	0	180	3
					135	3
0	0	0	0	0	0	3
Ilość poletek doświadczalnych						51

Badania polowe przeprowadzono w Gospodarstwie Doświadczalnym Uniwersytetu Przyrodniczego w Lublinie w miejscowości Czesławice (51°18′24″N 22°16′04″E) w sezonach wegetacyjnych 2021, 2022 i 2023. Rośliną testową była nowa odmiana kukurydzy uprawianej na kiszonkę firmy Pioneer P8244. Jest to odmiana średnio wczesna o FAO: K240, mieszaniec pojedynczy S.C., typ ziarna – dent. Doświadczenie polowe wykonano metodą losowych bloków w trzech powtórzeniach, co dało łącznie 51 poletek doświadczalnych. Poletka miały powierzchnię 25 m^2 i składały się z 8 rzędów oddalonych od siebie o 75 cm (co wynikało z rozstawu dysz siewnika).

Siew wykonano w optymalnym dla kukurydzy terminie tj. 12.05 w 2021 r., 15.06 w 2022 r. i 09.05 w 2023 r. Termin siewu kukurydzy w drugim roku badań był późniejszy w stosunku do pozostałych lat trwania eksperymentu ze względu na zniszczenia spowodowane przez dziki i konieczność powtórzenia siewu. Gęstość siewu wynosiła 80 tys. ziaren · ha^{-1}. W okresie wzrostu rośliny chroniono przed chwastami przez wykonanie oprysku insektycydem Lumax 537,5SE. Nawozy aplikowano przedsiewnie w ilości odpowiadającej 70% całkowitej dawki nawozu, a pozostałą część pogłównie w fazie 5-6 liścia.

Kukurydzę zbierano w fazie dojrzałości mleczno-woskowej, gdy zawartość suchej masy była na poziomie 30-35%. Parametry plonu określono na podstawie zbioru 2 m^2 roślin pobranych z dwóch centralnych rzędów z każdego poletka doświadczalnego. Nadziemne części roślin zebrano poprzez ręczne przycięcie roślin 10 cm nad powierzchnią gleby. Zważono plon części nadziemnej jako sumę plonu ziarna i części wegetatywnej i osobno masę kolb.

Z każdego poletka doświadczalnego wybrano losowo 8 roślin, w których zmierzono wysokość, zliczono ilość kolb oraz ilość rzędów ziarniaków w kolbie. Następie wybrane losowo rośliny z każdego poletka pocięto w sieczkarni na kawałki, z których po mechanicznym wymieszaniu pobrano 500 g próbki do oznaczeń laboratoryjnych. Po zważeniu próbki umieszczono w piecu z obiegiem powietrza nastawionym na 70°C, aż biomasa roślinna osiągnęła stałą masę, w celu oszacowania wartości suchej masy. Wysuszone próbki zmielono i część poddano mineralizacji „na mokro" w stężonym kwasie siarkowym(VI) w celu przygotowania do dalszych badań.

7. Analiza chemiczna kukurydzy (Publikacja nr 5 i 6)

Oznaczenie azotu ogólnego w roślinie przeprowadzono metodą Kjeldahla po mineralizacji materiału roślinnego w stężonym kwasie siarkowym (VI) (H_2SO_4) z dodatkiem 30% H_2O_2. Oznaczenie fosforu przeprowadzono metodą molibdenowo-wanadową również po wcześniejszej mineralizacji materiału roślinnego, natomiast oznaczenie siarki siarczanowej (VI) wykonano metodą nefelometryczną po ekstrakcji materiału roślinnego 2% CH_3COOH z dodatkiem węgla aktywnego. Potas, sód, wapń i magnez oznaczono metodą atomowej spektrometrii absorpcyjnej (ASA) po uprzedniej mineralizacji.

8. Analiza gleby (dane niepublikowane)

Badania gleby wg metod akredytowanych:

- Oznaczenie pH gleby w chlorku potasu wg normy PN-ISO 10390:1997;
- Oznaczenie zawartości przyswajalnego fosforu (P_2O_5) wg normy PN-R-04023:1996;
- Oznaczenie zawartości przyswajalnego potasu (K_2O) wg normy PN-R-04022:1996+Az1:2002;
- Oznaczenie zawartości przyswajalnego magnezu wg normy PN-R-04020:1994+Az1:2004;

- Oznaczenie zawartości siarki siarczanowej ($S-SO_4$) metodą nefelometryczną;
- Oznaczenie zawartości przyswajalnego cynku wg normy PN-R-04016:1992;
- Oznaczenie zawartości przyswajalnego manganu wg normy PN-R-04019:1993 p.1, 2, 5;
- Oznaczenie zawartości przyswajalnego żelaza wg normy PN-R-04021:1992 p. 1, 2, 4;
- Oznaczenie zawartości przyswajalnej miedzi wg normy PN-R-04017:1992 p. 1, 2, 4;
- Oznaczenie zawartości metali ciężkich (Cd, Pb, Hg, As) wg normy PN-ISO 11047:2001.

9. Analiza statystyczna (Publikacja nr 4, 5, 6)

Analizę statystyczną wyników przygotowano przy użyciu programu Statistica 13. W tym celu zastosowano analizę wariancji (ANOVA) dla układów czynnikowych, a istotność różnic określono przy użyciu testu Tukeya (HSD) przy poziomie istotności $\alpha = 0{,}05$ dla każdego roku badań oddzielnie. Założenia dla testu ANOVA sprawdzono przy użyciu testu Levene'a (jednorodność wariancji) i testu Shapiro–Wilka (normalność rozkładu).

Dla każdego zmierzonego parametru w poszczególnych latach przedstawiono wpływ poszczególnych czynników oraz wpływ ich efektów interakcji. Miarę tego wpływu określono poprzez obliczenie współczynnika: cząstkowego eta kwadrat (η^2_p) — określającego, który czynnik w większym stopniu wyjaśnia zmienność mierzonego parametru.

Analiza statystyczna wyników została podzielona na dwie części:

Część I — Porównano działanie nawozów w zależności od surowca fosforowego (czynnik nadrzędny, 2 poziomy: odpadowy fosforan lub Fosdar 40). Czynnikami drugorzędnymi w tej analizie były dawka fosforu (2 poziomy: 4% lub 6%) i dawka azotu (2 poziomy: 135 lub 180 kg $N \cdot ha^{-1}$). Uzyskane wyniki porównano z obiektem kontrolnym bez nawożenia. Za pomocą testu Tukeya wyznaczono grupy jednorodne dla średnich wartości badanych parametrów (oznaczone małymi literami) oraz grupy jednorodne dla średnich grupowych (oznaczone dużymi literami).

Część II — Porównano działanie wytworzonych nawozów zawiesinowych pod względem typu nawozu (czynnik nadrzędny, 3 poziomy: NPK, NKP+Mg+S oraz NPK+Mg+S+mikro). Czynnikami drugorzędnymi w tej analizie były dawka fosforu

(2 poziomy: 4% lub 6%) i dawka azotu (2 poziomy: 135 lub 180 kg N·ha^{-1}). Za pomocą testu Tukeya wyznaczono grupy jednorodne dla średnich wartości badanych parametrów (oznaczone małymi literami) oraz grupy jednorodne dla średnich grupowych (oznaczone dużymi literami).

Omówienie wyników badań

1. Odpadowy fosforan sodowo-potasowy z produkcji polioli (Publikacja nr 2)

1.1. Zawartość węgla organicznego w odpadzie

Średnia zawartość węgla organicznego (TOC) w odpadowym fosforanie była na niskim poziomie i wynosiła 586 ppm w próbce homogenizowanej przez mieszanie sprężonym powietrzem. W nawozach wytworzonych przez zmieszanie tych odpadów z innymi surowcami nawozowymi zawartość węgla organicznego będzie jeszcze niższa. Zgodnie z Rozporządzeniem UE 2019/1009 nawóz o zawartości węgla organicznego poniżej 3% (m/m) jest klasyfikowany jako nawóz nieorganiczny. Zawartość węgla organicznego na poziomie niższym niż 1% (m/m) dodatkowo eliminuje konieczność badania zawartości patogenów w nawozie (*Salmonella spp.* i *Escherichia coli* czy *Enterococcaceae*) (22).

1.2. Analiza chemiczna odpadu

Odpadowe fosforany z produkcji polioli zawierały dużą ilość wody, dlatego najbardziej ekonomiczne jest wykorzystanie ich do produkcji nawozów zawiesinowych (63). W związku z tym w tabeli 4 podsumowano wyniki analiz chemicznych odpadów wraz z wymaganiami dla tego typu nawozu przewidzianymi w nowym Rozporządzeniu Parlamentu Europejskiego i Rady (UE) 2019/1009 z dnia 5 czerwca 2019 r.: PFC 1 (C)(I)(b)(ii): wieloskładnikowy płynny nieorganiczny nawóz makroelementowy (22).

Tabela 4. Wyniki analizy chemicznej odpadów

Badana cecha	Jednostka	Wynik y ± U[1]	Wymagania dla nawozów zawiesinowych według Rozporządzenia UE Nr 2019/1009
Fosfor rozpuszczalny w kwasach mineralnych (P_2O_5)	%	18,9 ± 0,3	min. 1,5% mas. P_2O_5
Potas (K_2O)	%	7,79 ± 0,16	min. 1,5% mas. K_2O
Sód (Na)	%	4,72	min. 0.5% - max. 20% mas. Na_2O
Miedź (Cu)	$mg \cdot kg^{-1}$	≥ 1,0	600[2]
Żelazo (Fe)	$mg \cdot kg^{-1}$	46,0	-
Cynk (Zn)	$mg \cdot kg^{-1}$	≥ 1,0	1500[2]
Kadm (Cd)	$mg \cdot kg^{-1}$	≥ 1,0	60
Ołów (Pb)	$mg \cdot kg^{-1}$	≥ 8,0	120
Nikiel (Ni)	$mg \cdot kg^{-1}$	≥ 1,0	100
Glin (Al)	$mg \cdot kg^{-1}$	74,7	-
Arsen (As)	$mg \cdot kg^{-1}$	≥ 4,0	40
Rtęć (Hg)	$mg \cdot kg^{-1}$	≥ 0,002	1
Chrom (VI)	$mg \cdot kg^{-1}$	≥ 0,3	2

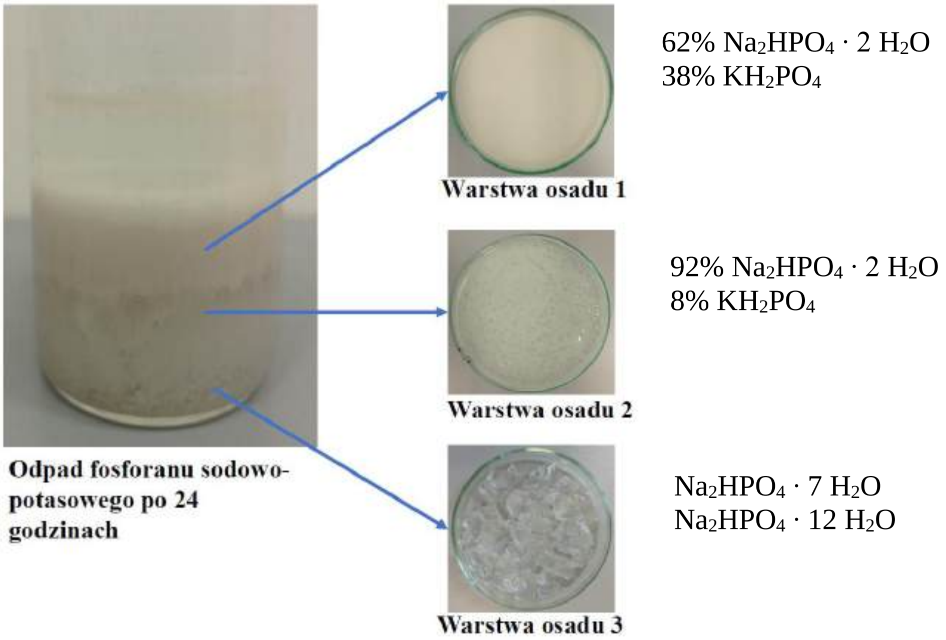
[1] Podana rozszerzona niepewność (U) opiera się na niepewności standardowej pomnożonej przez współczynnik pokrycia k = 2, co daje poziom ufności 95%. Niepewność pobierania próbek nie została uwzględniona w obliczeniach (U).

[2] Wartości te nie mają zastosowania, jeśli składnik został celowo dodany do nawozu w celu uzupełnienia niedoborów w glebie.

Wysoka zawartość fosforu w odpadowym fosforanie na poziomie blisko 19% czyni go atrakcyjnym surowcem nawozowym i potwierdza ekonomikę jego wykorzystania w produkcji nawozów. Zawartość zanieczyszczeń w wyprodukowanym nawozie zawiesinowym jest znacznie niższa od wartości progowych ustalonych przez Komisję Europejską w nowych przepisach. Dzięki temu badane odpady stanowią konkurencyjny surowiec nawozowy w stosunku do fosforytów często zanieczyszczonych kadmem (16,64).

1.3. Wyniki analizy składu osadów w odpadach

Podczas magazynowania odpadowych fosforanów na ich dnie tworzą się trzy wyraźnie oddzielone warstwy osadu (rysunek 2). Różnią się one składem i wielkością kryształów. Wielkość kryształów utworzonych w osadzie ma znaczenie przy aplikacji nawozów na ich bazie. Drobne kryształy, które osiadają na dnie, można z powodzeniem ponownie wymieszać natomiast duże kryształy zatykają dysze wytryskowe w urządzeniach aplikacyjnych/dozujących (63).



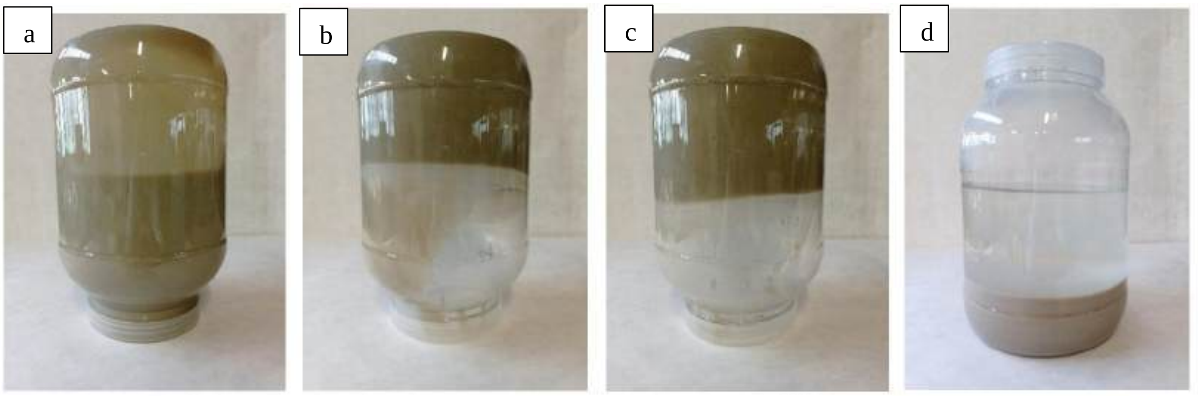
Rysunek 2. Warstwy osadu w odpadowym fosforanie o różnej wielkości kryształów

W próbce z osadem 1 występują dwie fazy krystaliczne $Na_2HPO_4 \cdot 2H_2O$ i faza KH_2PO_4. Faza $Na_2HPO_4 \cdot 2H_2O$ stanowi około 62%, a KH_2PO_4 około 38% faz krystalicznych. W próbce z osadem 2 występują dwie fazy krystaliczne $Na_2HPO_4 \cdot 2H_2O$ oraz faza KH_2PO_4. Faza $Na_2HPO_4 \cdot 2H_2O$ jest szacowana na 92%, a KH_2PO_4 na ok. 8% faz krystalicznych. W próbce z osadem 3 można wyróżnić fazę krystaliczną $Na_2HPO_4 \cdot 7H_2O$. Drugą fazą krystaliczną jest $Na_2HPO_4 \cdot 12H_2O$. Są to główne fazy krystalograficzne zarejestrowane na dyfraktogramie. Ze względu na brak odpowiednich informacji w bazie danych dla tej próbki nie jest możliwe oszacowanie zawartości faz w niej obecnych.

2. Ocena przydatności bentonitów do stabilizacji zawiesin nawozowych (Publikacja nr 3)

Aby określić przydatność różnego typu bentonitów do stabilizacji zawiesin nawozowych, przygotowano ich 12% roztwory wodne i po 30 minutach oceniono wizualnie ich stopień spęcznienia.

Największe spęcznienie zaobserwowano w roztworach bentonitów Specjal i Specjal 45. Przyjęły one postać galaretowatej substancji, która nie zmieniała położenia nawet po odwróceniu pojemnika do góry dnem (rysunek 3 b, c). Bentonit GM utworzył stabilną i płynną zawiesinę (rysunek 3 a). Natomiast roztwór bentonitu SN w ogóle nie pęczniał. Po 30 minutach rozwarstwił się na warstwę wody i osad bentonitu (rysunek 3 d). Dlatego też nie był on stosowany w dalszych badaniach mających na celu stabilizację nawozów zawiesinowych.



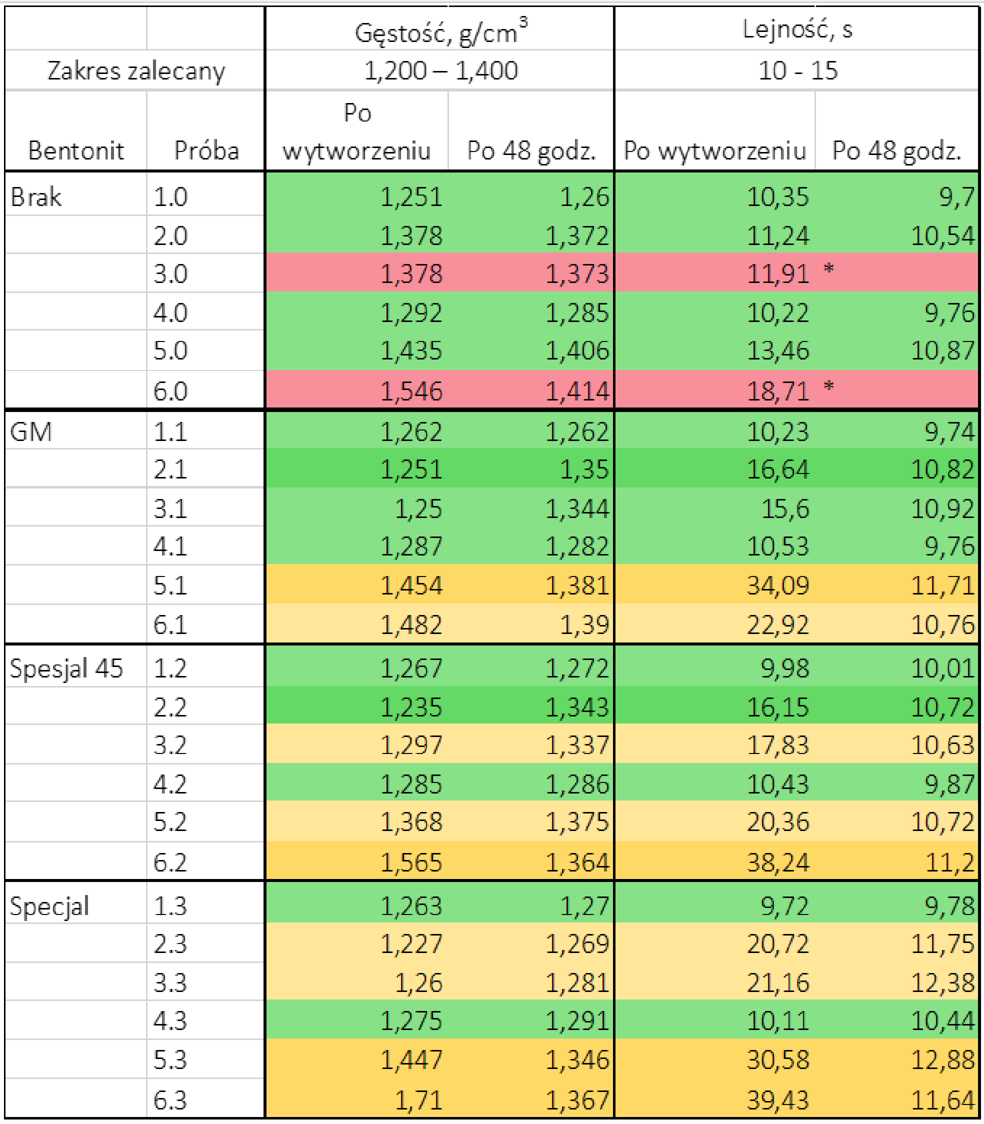
Rysunek 3. 12% wodny roztwór bentonitu (a) GM (b) Specjal (c) Specjal 45 (d) SN 30 minut od jego wytworzenia

3. Ocena parametrów fizycznych prób nawozów zawiesinowych (Publikacja nr 3)

3.1. Ocena gęstości i lejności nawozów zawiesinowych

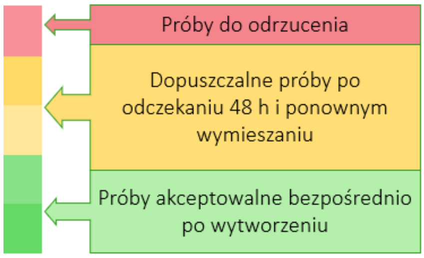
Sporządzono próby nawozów zawiesinowych bez dodatku bentonitu: próby 1.0 - 6.0 oraz z dodatkiem 3% wybranych typów bentonitów w formie 12% roztworu: z bentonitem GM próby 1.1 – 6.1, z bentonitem Specjal 45 próby 1.2 – 6.2, z bentonitem Specjal próby 1.3 – 6.3. W tabeli 5 dla podanych prób nawozów zestawiono wyniki badań gęstości i lejności. Badanie przeprowadzono bezpośrednio po wytworzeniu oraz po upływie 48 godzin po wcześniejszym wymieszaniu przez potrząsanie butelki z nawozem.

Tabela 5. Parametry fizyczne wytworzonych prób nawozów zawiesinowych



		Gęstość, g/cm^3		Lejność, s	
Zakres zalecany		1,200 – 1,400		10 - 15	
Bentonit	Próba	Po wytworzeniu	Po 48 godz.	Po wytworzeniu	Po 48 godz.
Brak	1.0	1,251	1,26	10,35	9,7
	2.0	1,378	1,372	11,24	10,54
	3.0	1,378	1,373	11,91	*
	4.0	1,292	1,285	10,22	9,76
	5.0	1,435	1,406	13,46	10,87
	6.0	1,546	1,414	18,71	*
GM	1.1	1,262	1,262	10,23	9,74
	2.1	1,251	1,35	16,64	10,82
	3.1	1,25	1,344	15,6	10,92
	4.1	1,287	1,282	10,53	9,76
	5.1	1,454	1,381	34,09	11,71
	6.1	1,482	1,39	22,92	10,76
Spesjal 45	1.2	1,267	1,272	9,98	10,01
	2.2	1,235	1,343	16,15	10,72
	3.2	1,297	1,337	17,83	10,63
	4.2	1,285	1,286	10,43	9,87
	5.2	1,368	1,375	20,36	10,72
	6.2	1,565	1,364	38,24	11,2
Specjal	1.3	1,263	1,27	9,72	9,78
	2.3	1,227	1,269	20,72	11,75
	3.3	1,26	1,281	21,16	12,38
	4.3	1,275	1,291	10,11	10,44
	5.3	1,447	1,346	30,58	12,88
	6.3	1,71	1,367	39,43	11,64

*zatkanie dyszy przez duże kryształy szybko opadające



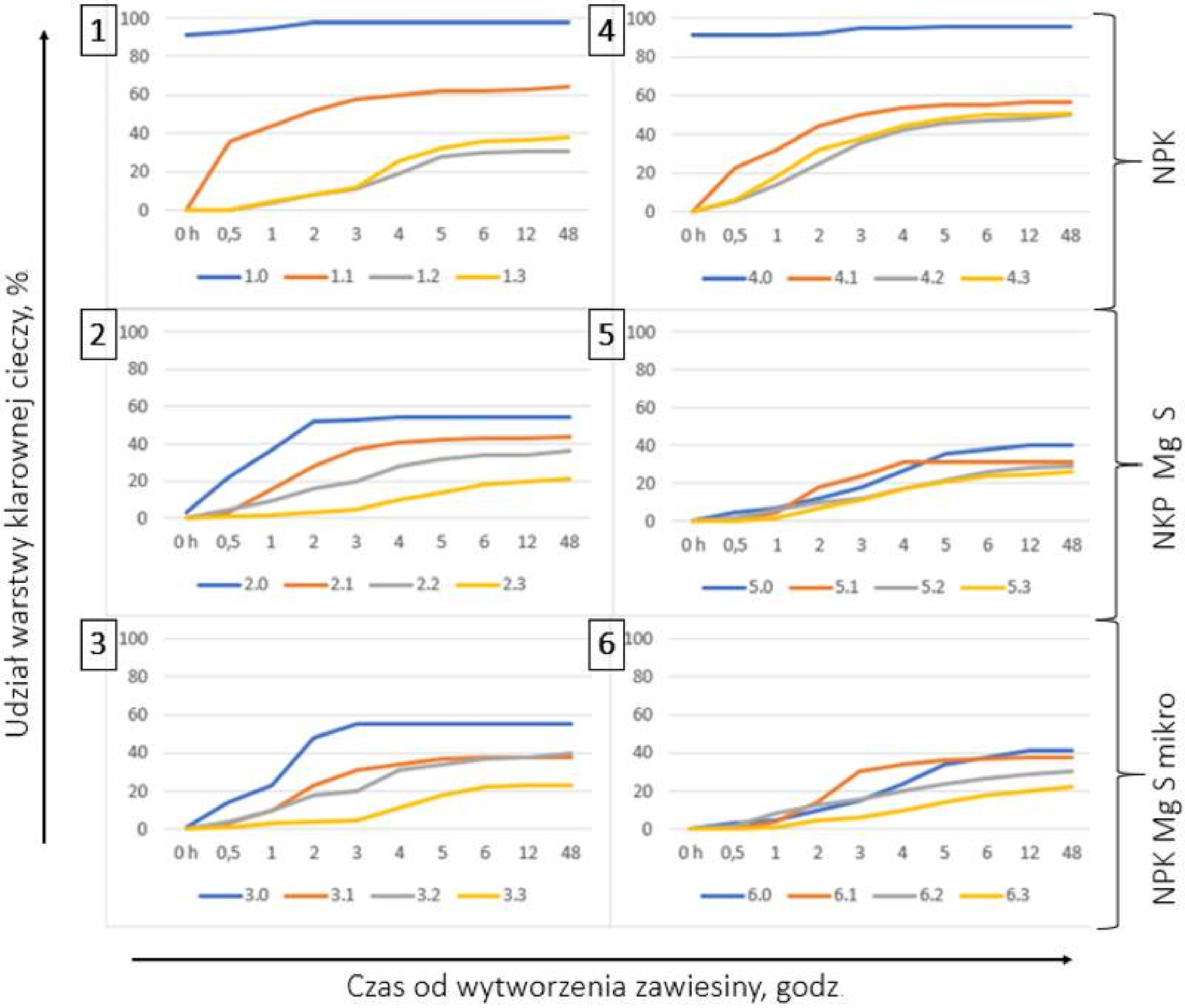
Gęstość w nawozach bez dodatku bentonitu po upływie 48 godz. nie uległa znaczącej zmianie. Ponadto w nawozach bez bentonitu o wyższym stężeniu (próby 3.0 i 6.0) wytworzyły się grubsze kryształy, które zatykały dyszę wypływową kubka Forda. Może to powodować kłopoty przy aplikacji nawozów.

W nawozach z dodatkiem bentonitu po 48 godz. poprawiła się lejność nawozów. W próbach tych skrócił się czas wypływu z kubka Forda, który bezpośrednio po wytworzeniu w próbach o wyższym stężeniu był poza zalecanym zakresem. Ma to związek z wytwarzaną przez bentonit wraz z upływem czasu strukturą, która rozdziela ziarna fazy rozproszonej. Z tego względu też dodatek bentonitu ułatwia ponowne rozmieszanie nawozu. Próbki bez dodatku bentonitu wymagały dłuższego czasu potrząsania, w celu poruszenia zgromadzonego na dnie osadu.

3.2. Stabilność nawozów zawiesinowych

Na wykresach na rysunku 4 przedstawiono zmiany stabilność wytworzonych prób nawozów zawiesinowych, której miarą jest ilość klarownej warstwy cieczy u góry w miarę upływu czasu. Natomiast w tabeli 6 zestawiono wyniki stabilności dla badanych nawozów zawiesinowych po upływie 48 godz. od wytworzenia jako procentowy udział warstwy klarownej cieczy wraz z skalą kolorystyczną.

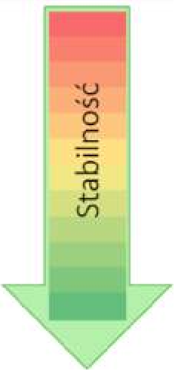
W każdym przypadku próby z dodatkiem bentonitów miały lepszą stabilność niż próby bez ich dodatku. Najlepsze parametry stabilności wykazały próby z bentonitem Specjal, w których wytworzyła się najmniejsza warstwa klarownej cieczy. Największe rozwarstwienie zaobserwowano w próbach bez dodatku bentonitu, szczególnie w przypadku tych o mniejszym stężeniu. Ponadto próby zawierające w składzie siarczan magnezu wykazywały mniejsze rozwarstwienie: poniżej 60% dla prób nawozów 2 i 3 oraz poniżej 40% dla prób 5 i 6, w porównaniu do prób zawierających jedynie główne składniki pokarmowe (próby 1 i 4). Próby z dodatkiem bentonitów łatwo ulegały wymieszaniu (2-3 krotne wstrząśnięcie cylindrem) i odzyskiwały swoją początkową stabilność.



Rysunek 4. Zestawienie wykresów przedstawiających stabilność nawozów zawiesinowych w zależności od czasu upływającego od momentu ich wytworzenia

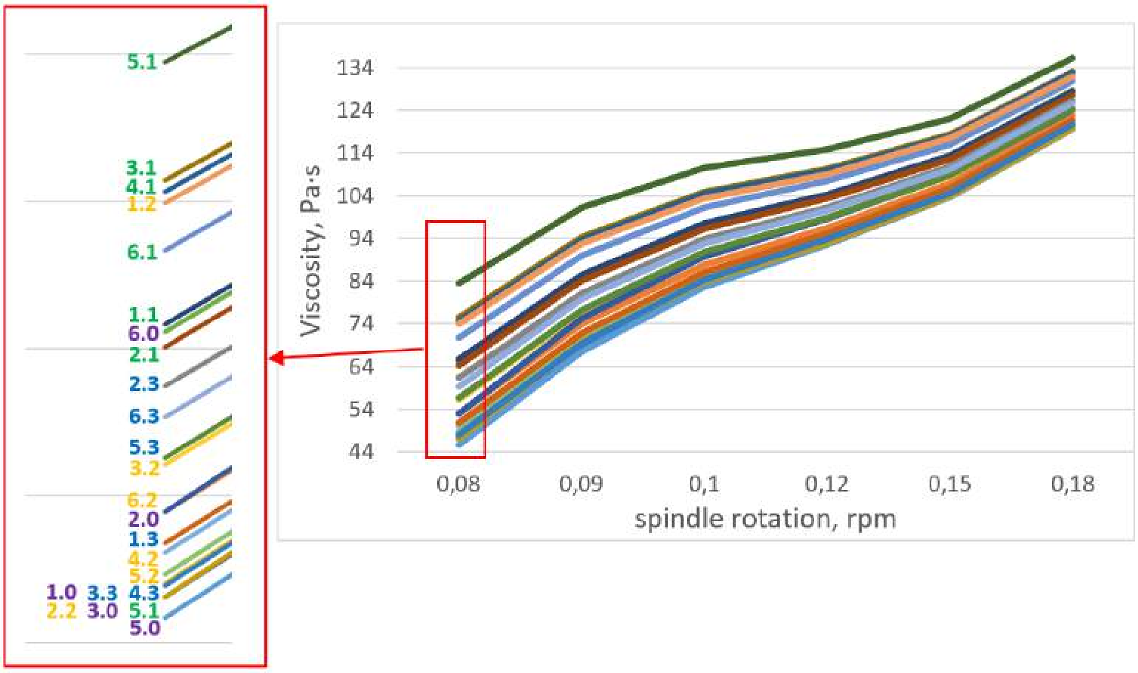
Tabela 6. Stabilność nawozów zawiesinowych po 48 godz. od wytworzenia

Bentonit	Próba	Stabilność po 48 h –udział warstwy klarownej cieczy, %
brak	1.0	98
	2.0	54
	3.0	55
	4.0	96
	5.0	40
	6.0	41
GM	1.1	64
	2.1	44
	3.1	38
	4.1	57
	5.1	31
	6.1	38
Specjal 45	1.2	31
	2.2	36
	3.2	40
	4.2	50
	5.2	29
	6.2	30
Specjal	1.3	38
	2.3	21
	3.3	23
	4.3	51
	5.3	26
	6.3	22



3.3. Lepkość nawozów zawiesinowych

Lepkość wpływa na stabilność zawiesiny i jej zdolność do wylewania. Gdy lepkość środowiska dyspersyjnego rośnie to faza zdyspergowana opada wolniej i pozostaje dłużej zdyspergowana, co daje stabilniejsza zawiesinę. Jednak wraz ze wzrostem lepkości układu maleje jej lejność i powstaje problem przy dozowaniu.



Rysunek 5. Zależność lepkości zawiesin nawozowych od prędkości obrotowej wrzeciona pomiarowego

Lepkość wszystkich prób nawozów zawiesinowych wrastała wraz z ze zwiększającą się szybkością obrotu wrzeciona pomiarowego. Ogólnie stwierdzono, że próby z bentonitem GM (1.1 – 6.1) mają wyższą lepkość w stosunku do pozostałych prób. Natomiast wartość lepkości prób bez dodatku bentonitu (1.0 – 6.0) plasuje się na najniższym poziomie.

4. Badania gleby przed założeniem doświadczenia (Publikacja nr 4)

Gleba na stanowisku przeznaczonym do badań polowych charakteryzowała się bardzo wysoką zawartością fosforu (350 mg·kg^{-1} gleby P_2O_5), potasu (291 mg·kg^{-1} gleby K_2O) i magnezu (92 mg·kg^{-1} gleby) oraz średnią zawartością siarki (10,4 mg·kg^{-1} gleby SO_3) i azotu (30,3 kg·ha^{-1}). Mikroelementy ważne dla uprawy kukurydzy, takie jak cynk i mangan, były na średnim poziomie (10,6 mg·kg^{-1} gleby Zn, 260 mg·kg^{-1} gleby Mn), natomiast zawartość boru była niska (0,99 mg·kg^{-1} gleby). Odczyn gleby był lekko kwaśny (pH 6,3 w 1 mol KCl · dm^{-3}).

5. Warunki meteorologiczne podczas eksperymentu terenowego (Publikacja nr 4)

Warunki meteorologiczne podczas eksperymentu terenowego były różne w poszczególnych latach badań (tabele 7 i 8).

Tabela 7. Średnie miesięczne temperatury powietrza (°C) podczas trwania eksperymentu polowego

Rok	Miesiąc						Średnia
	IV	V	VI	VII	VIII	IX	
I	6.4	12.6	19.7	22.3	17.3	12.8	15.2
II	5.9	12.8	19.4	19.4	20.5	10.8	13.1
III	8.2	12.9	17.4	20.0	21.0	17.6	16.1
Średnia	6.8	12.8	18.8	20.6	19.6	13.7	
Średnia 2011–2020	9.5	14.4	18.5	20.1	19.7	14.7	

Tabela 8. Miesięczne sumy opadów deszczu (mm) podczas trwania eksperymentu polowego

Rok	Miesiąc						Średnia
	IV	V	VI	VII	VIII	IX	
I	49.1	55.7	43.2	43.0	231.7	62.1	80.7
II	53.2	36.3	38.7	111.8	52.3	112.3	67.4
III	57.9	66.0	60.0	84.7	46.4	28.5	57.3
Średnia	53.4	52.7	47.3	79.8	110.1	67.6	
Średnia 2011–2020	40.8	80.3	64.3	91.3	54.9	60.2	

Najwyższą średnią temperaturę w sezonie wegetacyjnym odnotowano w trzecim roku badań polowych (16,1°C), a najniższą w drugim roku (13,1°C). Natomiast najwyższe średnie opady odnotowano w pierwszym roku badań (80,7 mm), a najniższe w trzecim roku (57,3 mm). Trzeci rok badań polowych był najkorzystniejszy w okresie wschodów roślin - charakteryzował się najwyższą temperaturą i opadami w kwietniu i maju. Aby pełniej scharakteryzować warunki meteorologiczne występujące w trakcie eksperymentu polowego obliczono wskaźnik hydrotermiczny Sielianinowa (k) (65):

$$k = \frac{P}{0.1 \cdot \Sigma t}$$

gdzie:
P—miesięczna suma opadów atmosferycznych (mm);
Σt—miesięczna suma temperatur powietrza > 0 ◦C.

Współczynnik Sielianinowa określa zaopatrzenie roślin w wodę w okresie wegetacji i dzieli się na klasy przedstawione w tabeli 9.

Tabela 9. Podział współczynnika Sielianinowa na klasy

Oznaczenie	Zakres współczynnika k	Opis
🟥	$k \leq 0,4$	Warunki ekstremalnie suche
🟧	$0,4 < k \leq 0,7$	Warunki bardzo suche
🟨	$0,7 < k \leq 1,0$	Warunki suche
🟨	$1,0 < k \leq 1,3$	Warunki dość suche
🟩	$1,3 < k \leq 1,6$	Warunki optymalne
🟦	$1,6 < k \leq 2,0$	Warunki dość wilgotne
🟦	$2,0 < k \leq 2,5$	Warunki wilgotne
🟦	$2,5 < k \leq 3,0$	Warunki bardzo wilgotne
🟦	$k > 3,0$	Warunki ekstremalnie wilgotne

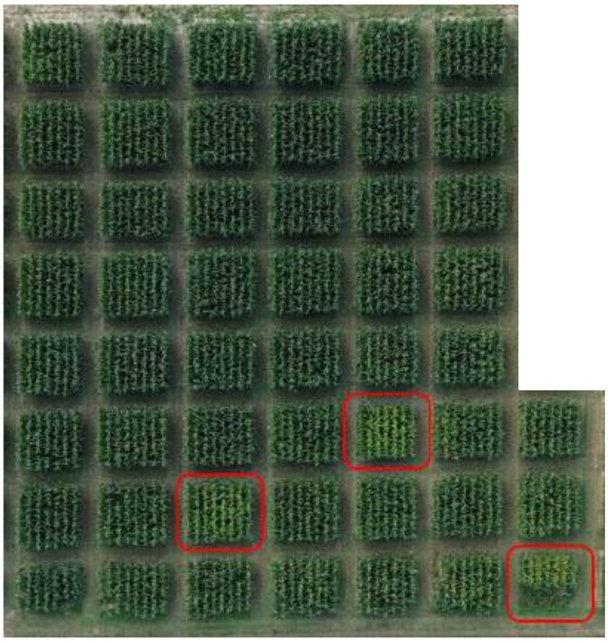
Tabela 10. Wartości współczynnika Sielininova w całym okresie badań polowych

Rok	Miesiąc					
	IV	V	VI	VII	VIII	IX
I	2,56	1,43	0,73	0,62	4,32	1,62
II	3,01	0,91	0,66	1,86	0,82	3,47
III	2,35	1,65	1,15	1,37	0,71	0,54

Analizując współczynnik Sielianinowa (tabela 10) można stwierdzić, że w każdym roku badań polowych siew kukurydzy poprzedzał miesiąc o korzystnych warunkach wilgotnościowych (k: 2,35–3,01). Najlepsze warunki siewu występowały w maju w pierwszym roku badań (k: 1,43), a najgorsze w czerwcu w drugim roku badań (k: 0,66). Kolejnym etapom rozwoju kukurydzy towarzyszyły różne warunki w poszczególnych latach. Etap zbioru we wrześniu był bardzo zróżnicowany każdego roku. Najbardziej optymalne warunki odnotowano w pierwszym roku badań (k: 1,62), w drugim roku warunki były skrajnie wilgotne (k: 3,47), a w trzecim roku były bardzo suche (k: 0,54).

6. Wyniki doświadczeń polowych (Publikacja nr 4)

Na rysunku 6 przedstawiono widok z góry na poletka doświadczalne z kukurydzą wykonane w III roku badań polowych. Zaznaczone poletka o wyraźnie jaśniejszym odcieniu zieleni przedstawiają obiekty bez nawożenia.



Rysunek 6. Zdjęcie poletek doświadczalnych wykonane z dronem w trzecim roku badań polowych- zaznaczone poletka przedstawiają obiekty bez nawożenia

6.1. Plon suchej masy

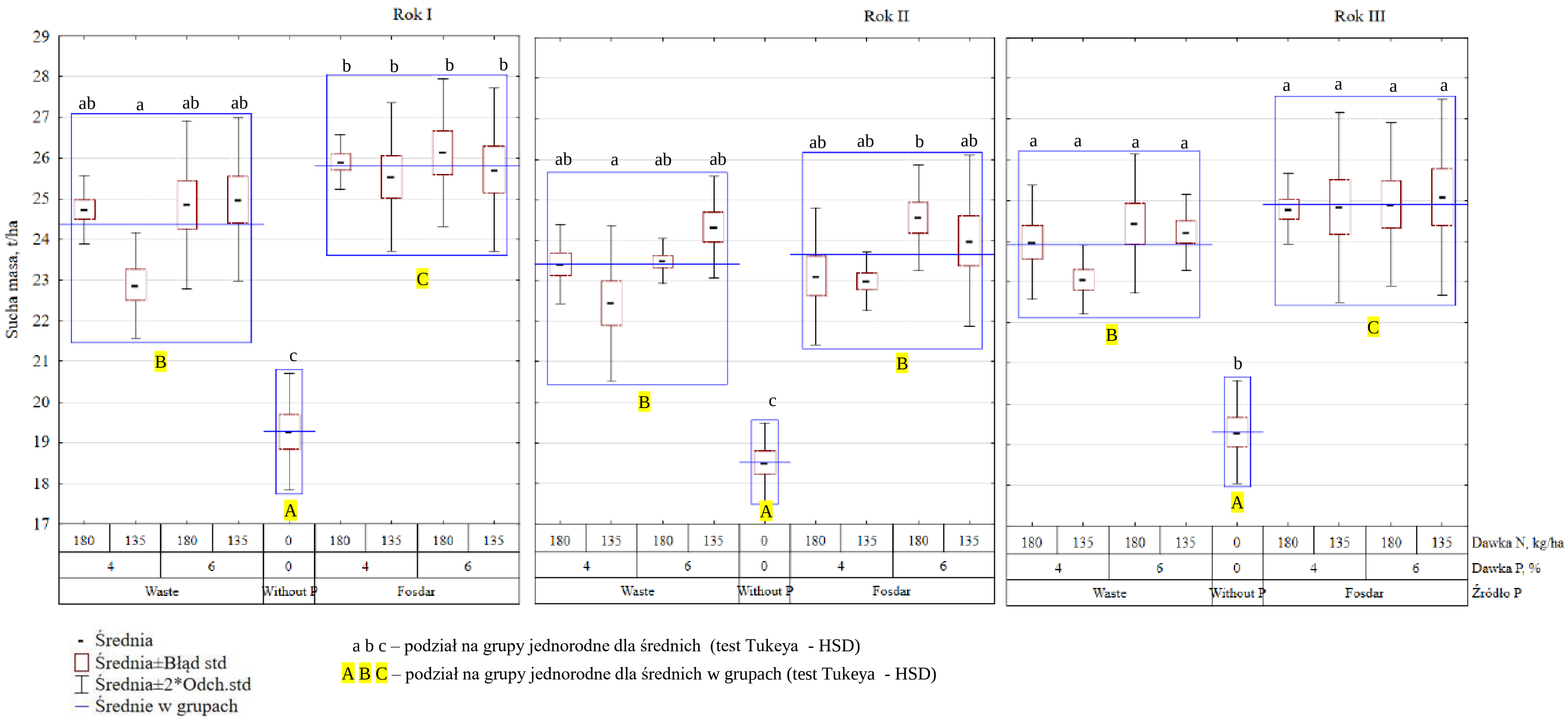
Termin zbioru kukurydzy ustalono na podstawie zawartości suchej masy tak, aby jej wartość mieściła się w przedziale 30–35%. W pierwszym roku badań średnia zawartość suchej masy wynosiła 33,49%, w drugim roku 32,49%, a w trzecim roku badań 33,06%.

Na rysunku 7 zestawiono średnie plony suchej masy roślin kukurydzy w zależności od rodzaju źródła fosforu w nawozie i jego udziału procentowego, w podziale na poszczególne lata badań i zastosowaną dawkę azotu.

W pierwszym i trzecim roku badań źródło fosforu stosowane w nawozach miało istotny wpływ na ilość uzyskanej suchej masy. W każdym przypadku wyższy plon suchej masy uzyskano na poletkach, na których źródłem fosforu w nawozie był Fosdar 40. Jednak niezależnie od rodzaju źródła fosforu w nawozie, średni plon suchej masy przekroczył 22 $t \cdot ha^{-1}$, podczas gdy plon na poletkach bez nawożenia wynosił około 19 $t \cdot ha^{-1}$. W drugim roku badań przyczyną istotnej zmienności ilości uzyskanej suchej masy była zawartość fosforu w nawozie. Dla nawozów zawierających 6% fosforu uzyskano wyższy średni plon suchej masy (24,09 $t \cdot ha^{-1}$) niż dla nawozów zawierających 4% fosforu (22,99 $t \cdot ha^{-1}$). Zastosowana dawka azotu nie miała istotnego wpływu na ten parametr.

Na rysunku 8 zestawiono średni plon suchej masy roślin kukurydzy w zależności od rodzaju nawozu zawiesinowego i procentowej zawartości fosforu, w podziale na poszczególne lata badań i zastosowaną dawkę azotu.

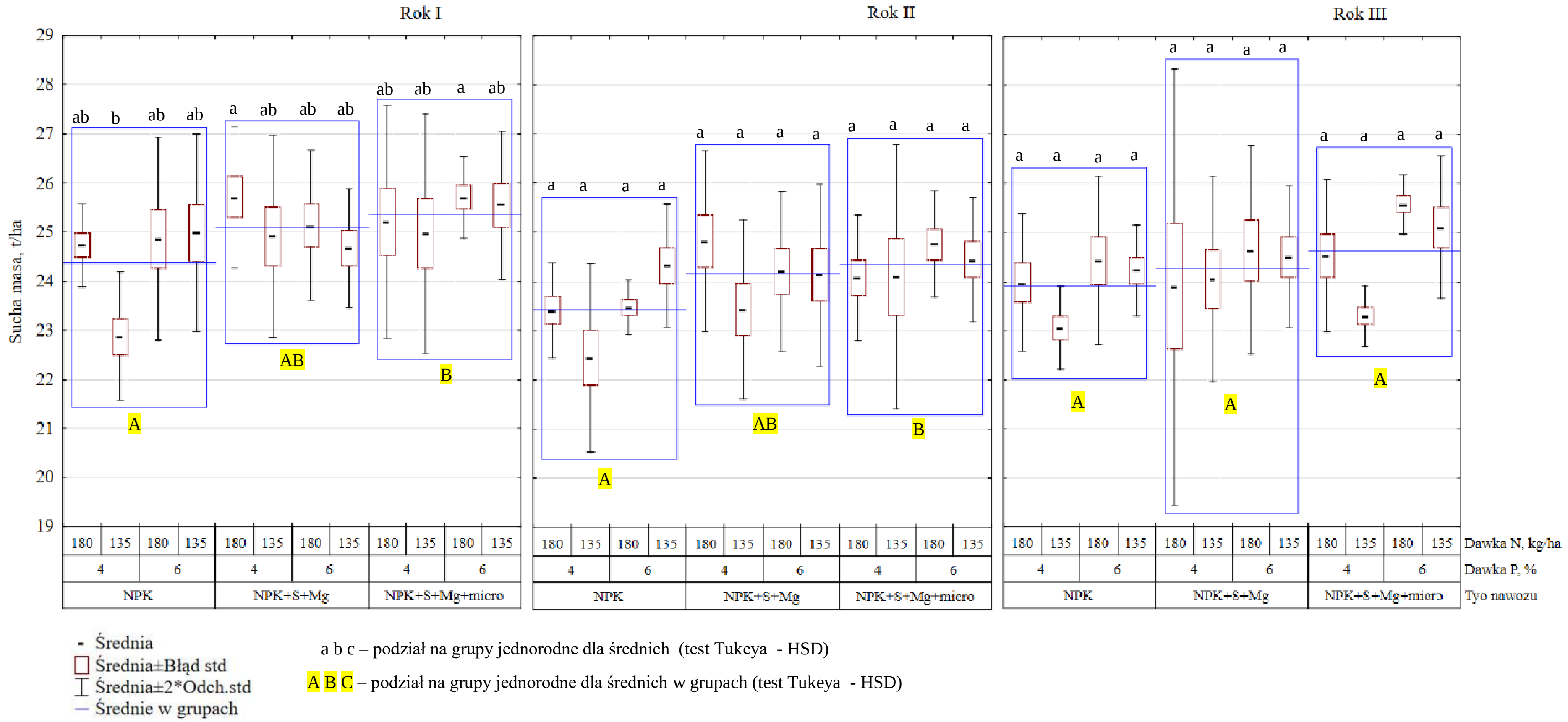
Rodzaj nawozu zawiesinowego istotnie różnicował średni plon suchej masy kukurydzy w pierwszym i drugim roku badań polowych. W obu latach istotne różnice odnotowano pomiędzy nawozami NPK i nawozami z dodatkiem mikroelementów, dla których plon suchej masy rośliny testowej był istotnie wyższy. W trzecim roku badań przyczyną zmienności średniego plonu suchej masy okazała się zawartość fosforu w nawozie. W tym przypadku nawozy o wyższej zawartości fosforu dały średni plon suchej masy istotnie wyższy o 0,95 $t \cdot ha^{-1}$. W doświadczeniu dawka azotu nie miała istotnego wpływu na plon kukurydzy niezależnie od rodzaju zastosowanego nawozu.



a b c – podział na grupy jednorodne dla średnich (test Tukeya - HSD)

A B C – podział na grupy jednorodne dla średnich w grupach (test Tukeya - HSD)

Rysunek 7. Średnia ilość suchej masy (t·ha^{-1}) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na źródło fosforu w nawozie i jego zawartość procentową w nawozie



a b c – podział na grupy jednorodne dla średnich (test Tukeya - HSD)

A B C – podział na grupy jednorodne dla średnich w grupach (test Tukeya - HSD)

Rysunek 8. Średnia ilość suchej masy (t·ha^{-1}) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na rodzaj nawozu zawiesinowego i procentową zawartość fosforu

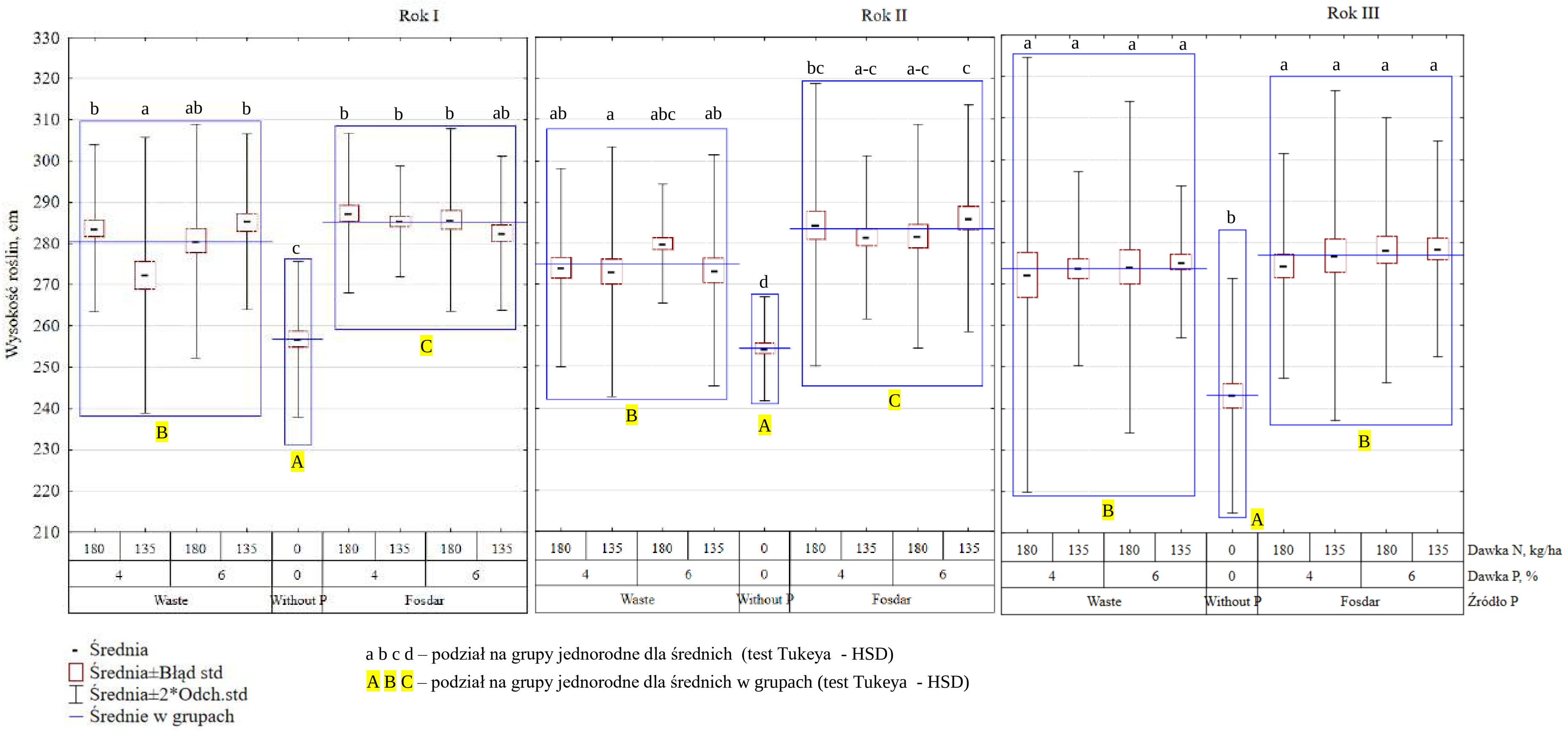
6.2. Wysokość roślin kukurydzy

Na rysunku 9 zestawiono średnią wysokość roślin kukurydzy w zależności od rodzaju źródła fosforu w nawozie i jego procentowej zawartości, w podziale na poszczególne lata badań i zastosowaną dawkę azotu.

W pierwszym i drugim roku badań zaobserwowano nieznacznie istotne różnice w wysokości roślin kukurydzy w zależności od źródła fosforu zastosowanego w nawożeniu. Najwyższą średnią wysokość roślin w obu latach eksperymentu polowego odnotowano dla roślin nawożonych nawozami zawierającymi Fosdar 40 (odpowiednio: 285,26 cm i 283,39 cm). Wysokość roślin nawożonych nawozami zawiesinowymi na bazie odpadów z polioli była niższa średnio o 4,77 cm i 8,31 cm odpowiednio w pierwszym i drugim roku badań. W każdym roku najniższe wartości średniej wysokości roślin uzyskano dla roślin na poletkach bez nawożenia. Udział fosforu w nawozie nie różnicował istotnie wysokości roślin, podobnie jak dawka azotu.

Na rysunku 10 zestawiono średnią wysokość roślin kukurydzy w zależności od typu nawozu, procentowej zawartości fosforu w nawozie, w podziale na poszczególne lata badań i zastosowaną dawkę azotu.

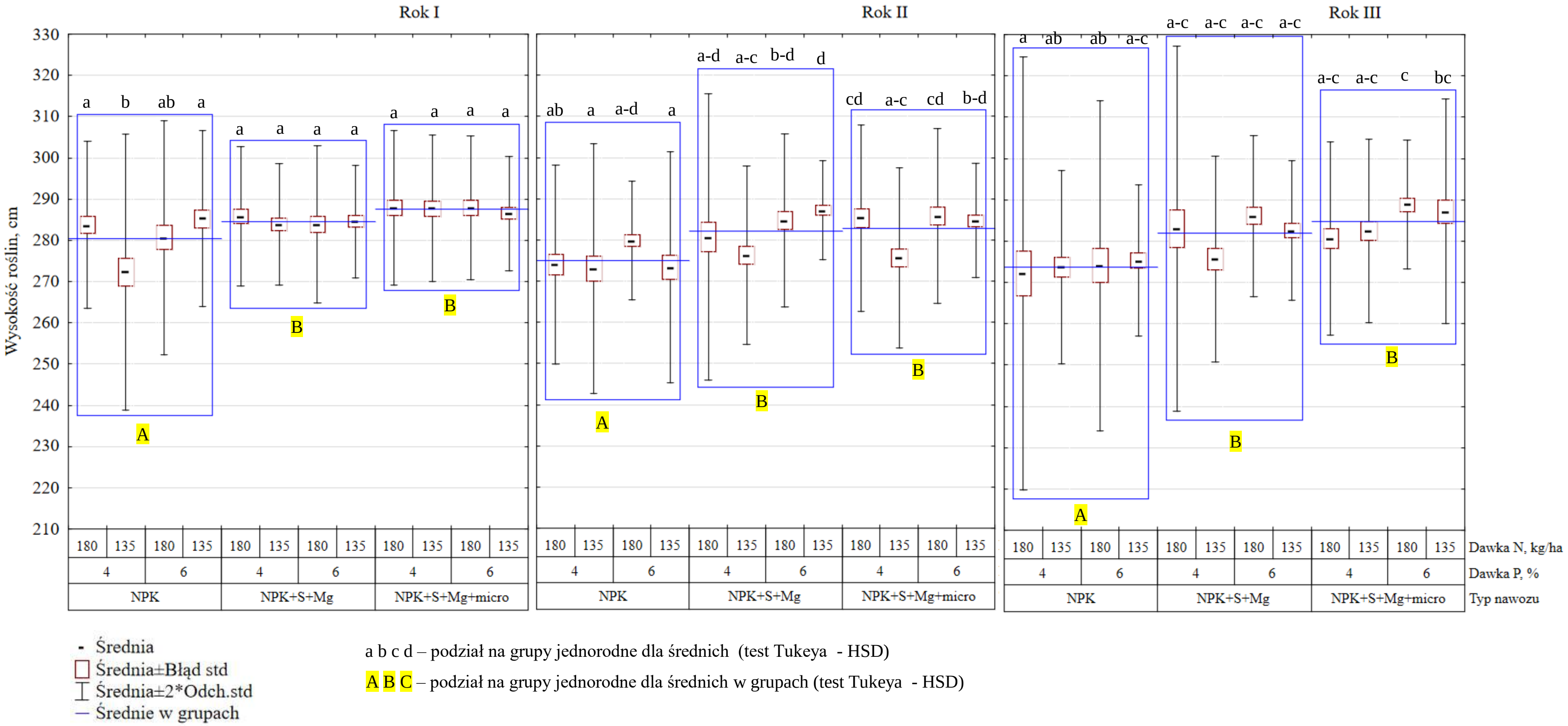
Analiza wariancji wykazała istotny wpływ rodzaju zastosowanego nawozu w formie zawiesiny na średnią wysokość roślin w każdym roku badań. Niezależnie od procentowej zawartości P, nawozy o podstawowym składzie NPK istotnie wpływały na niższą wysokość roślin w porównaniu do nawozów z dodatkiem składników drugorzędnych i mikroelementów. W drugim i trzecim roku badań polowych odnotowano również istotny wpływ procentowej zawartości fosforu na ten parametr, na korzyść nawozów o wyższej zawartości fosforu.



a b c d – podział na grupy jednorodne dla średnich (test Tukeya - HSD)

A B C – podział na grupy jednorodne dla średnich w grupach (test Tukeya - HSD)

Rysunek 9. Średnia wysokość roślin (cm) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na źródło fosforu w nawozie i jego zawartość procentową w nawozie



Rysunek 10. Średnie wysokości roślin (cm) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na rodzaj nawozu zawiesinowego i procentową zawartość fosforu

6.3. Stosunek masy kolby do masy zielonki

Średni udział kolb w całkowitej biomasie istotnie różnił się jedynie w porównaniu do roślin z poletek bez nawożenia. Dla poletek nawożonych mieścił się w zakresie 44 – 47%, a dla poletek bez nawożenia 36 – 38%.

6.4. Ilość kolb kukurydzy

W badaniu polowym nie stwierdzono istotnych różnic w ilości kolb na roślinach ze względu na źródło fosforu w stosowanych nawozach. Liczba kolb na poszczególnych roślinach zwykle wahała się od jednej do dwóch sztuk; sporadycznie zdarzały się rośliny z trzema kolbami. W trzecim roku badań zawartość fosforu w nawozach miała nieznacznie istotny wpływ, różnicując liczbę kolb na poletkach nawożonych nawozami zawierającymi 6% fosforu i na działkach bez nawożenia. W ostatnim roku większy był udział roślin z jedną kolbą. Ze względu na typ nawozu nie odnotowano istotnych różnic w liczbie kolb na poszczególnych roślinach. Zastosowana dawka azotu nie wpłynęła istotnie na liczbę kolb na roślinach.

7. Analiza kukurydzy – zawartość makroelementów (Publikacja nr 5)

7.1. Azot ogółem

Na rysunku 11 przedstawiono średnią zawartość azotu ogółem w kukurydzy w zależności od rodzaju źródła fosforu w nawozie i jego procentowej zawartości, w podziale na poszczególne lata badań i zastosowaną dawkę azotu.

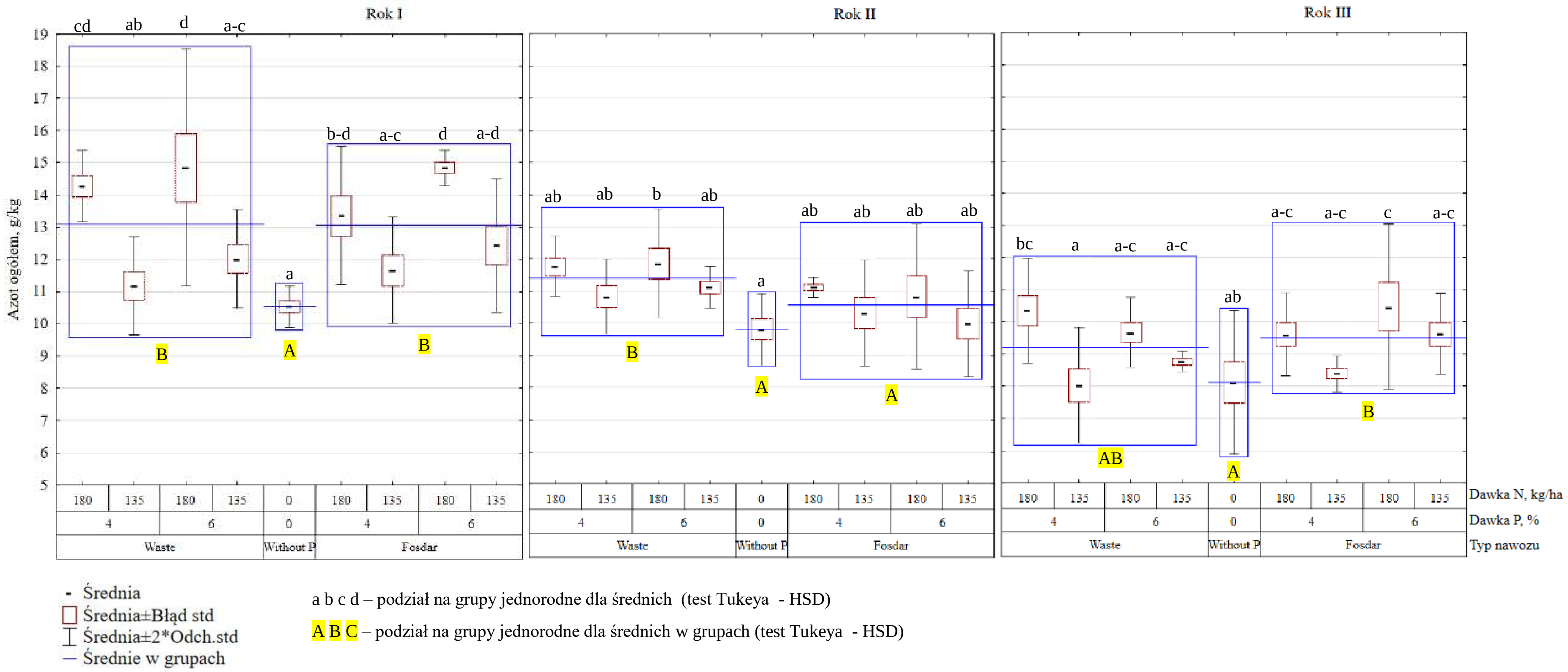
Istotne różnice w zawartości azotu ogółem w roślinach kukurydzy w zależności od źródła fosforu użytego do nawożenia odnotowano w drugim roku badań. Różnice te były widoczne między średnimi, niezależnie od zawartości fosforu w nawozie. W pierwszym i trzecim roku badań odnotowano istotnie niższe zawartości azotu ogółem w roślinach uprawianych na poletkach bez nawożenia, natomiast nie zaobserwowano różnic w stosunku do zastosowanego nawożenia fosforem, zarówno pod względem dawki fosforu, jak i rodzaju nawozu fosforowego.

W każdym roku badań polowych dawka azotu miała istotny wpływ na zawartość azotu ogółem w kukurydzy. Największy wpływ tego czynnika odnotowano w pierwszym roku badań (η^2_p = 70,37%), gdzie średnia zawartość azotu ogółem w roślinie testowej przy dawce 135 kg $N \cdot ha^{-1}$ wynosiła 11,82 $g \cdot kg^{-1}$ s.m. rośliny, natomiast przy dawce 180 kg $N \cdot ha^{-1}$ wynosiła 14,33 $g \cdot kg^{-1}$ s.m. rośliny. W drugim roku badań zawartość azotu ogółem w kukurydzy wykazywała tendencję wzrostową zgodnie ze wzrastającą dawką azotu, przy czym statystycznie istotne różnice odnotowano między roślinami z poletek kontrolnych bez nawożenia i roślinami nawożonymi najwyższą dawką azotu (180 kg N·ha^{-1}). W trzecim roku badań polowych odnotowano podobne zależności, przy czym wpływ nawożenia azotem był wyższy niż w drugim roku badań (η^2_p = 48,28%).

Na rysunku 12 przedstawiono średnią zawartość azotu ogółem w kukurydzy w zależności od rodzaju nawozu zawiesinowego i udziału fosforu w podziale na poszczególne lata badań i zastosowaną dawkę azotu.

W pierwszym roku badań polowych na zmienność zawartości azotu ogółem w roślinie testowej miał wpływ rodzaj nawozu (η^2_p = 31,56%). Zależność ta dotyczyła jedynie różnicy między nawozem mikroelementowym o zawartości 4% P (12,23 g·kg^{-1} s.m.) a nawozem o składnikach drugorzędnych o zawartości 6% P (14,15 g·kg^{-1} s.m.).

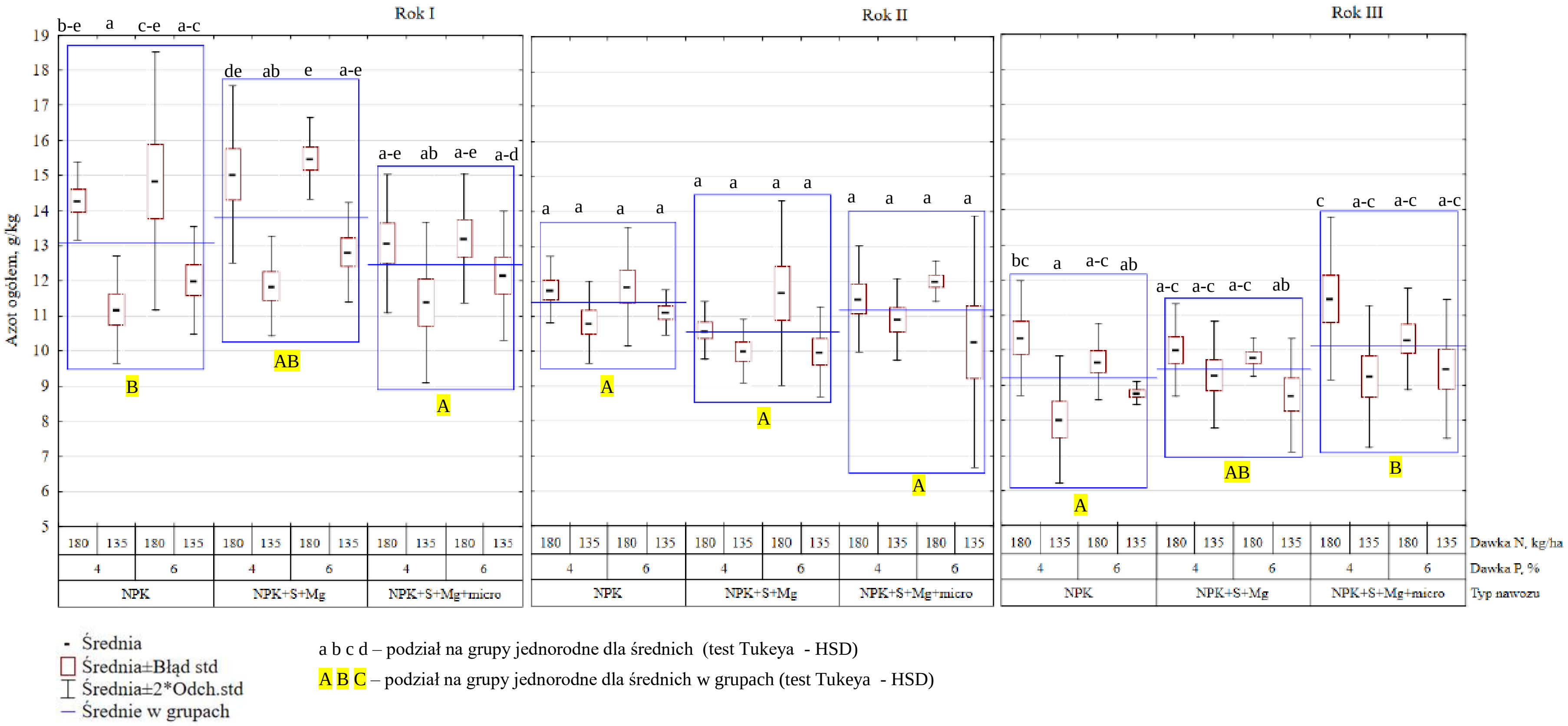
Zastosowana dawka fosforu w nawozach zawiesinowych nie miała istotnego wpływu na zawartość azotu całkowitego. We wszystkich latach doświadczenia polowego odnotowano istotny wpływ dawki azotu ogółem w nawożeniu na zawartość azotu ogółem w kukurydzy. Zwiększenie dawki tego makroelementu skutkowało wzrostem stężenia azotu w roślinach testowych. W pierwszym roku badań średnia zawartość azotu ogółem w kukurydzy z poletek, na których zastosowano nawożenie azotem w dawce 135 kg N·ha^{-1} wyniosła 11,90 g·kg^{-1} s.m. roślin, natomiast przy dawce 180 kg N·ha^{-1} wyniosła 14,35 g·kg^{-1} s.m. roślin, co stanowi różnicę 20,59%. W drugim roku badań wpływ zastosowanej dawki azotu był mniejszy w porównaniu z pierwszym i trzecim rokiem badań (η^2_p = 37,61%), a różnica w zawartości azotu ogółem pomiędzy roślinami nawożonymi dawkami azotu 180 kg N·ha^{-1} i 135 kg N · ha^{-1} wyniosła 9,88%. W trzecim roku badań zawartość azotu ogółem w kukurydzy zebranej z poletek nawożonych wyższą dawką azotu (180 kg N·ha^{-1}) była większa o 15,13% w porównaniu do kukurydzy nawożonej dawką 135 kg N·ha^{-1}.



a b c d – podział na grupy jednorodne dla średnich (test Tukeya - HSD)

A B C – podział na grupy jednorodne dla średnich w grupach (test Tukeya - HSD)

Rysunek 11. Średnia zawartość azotu ogółem w kukurydzy (g · kg^{-1} s.m.) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na rodzaj nawozu zawiesinowego i procentową zawartość fosforu



a b c d – podział na grupy jednorodne dla średnich (test Tukeya - HSD)

A B C – podział na grupy jednorodne dla średnich w grupach (test Tukeya - HSD)

Rysunek 12. Średnia zawartość azotu ogółem w kukurydzy (g · kg^{-1} s.m.) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na rodzaj nawozu zawiesinowego i procentową zawartość fosforu

7.2. Fosfor

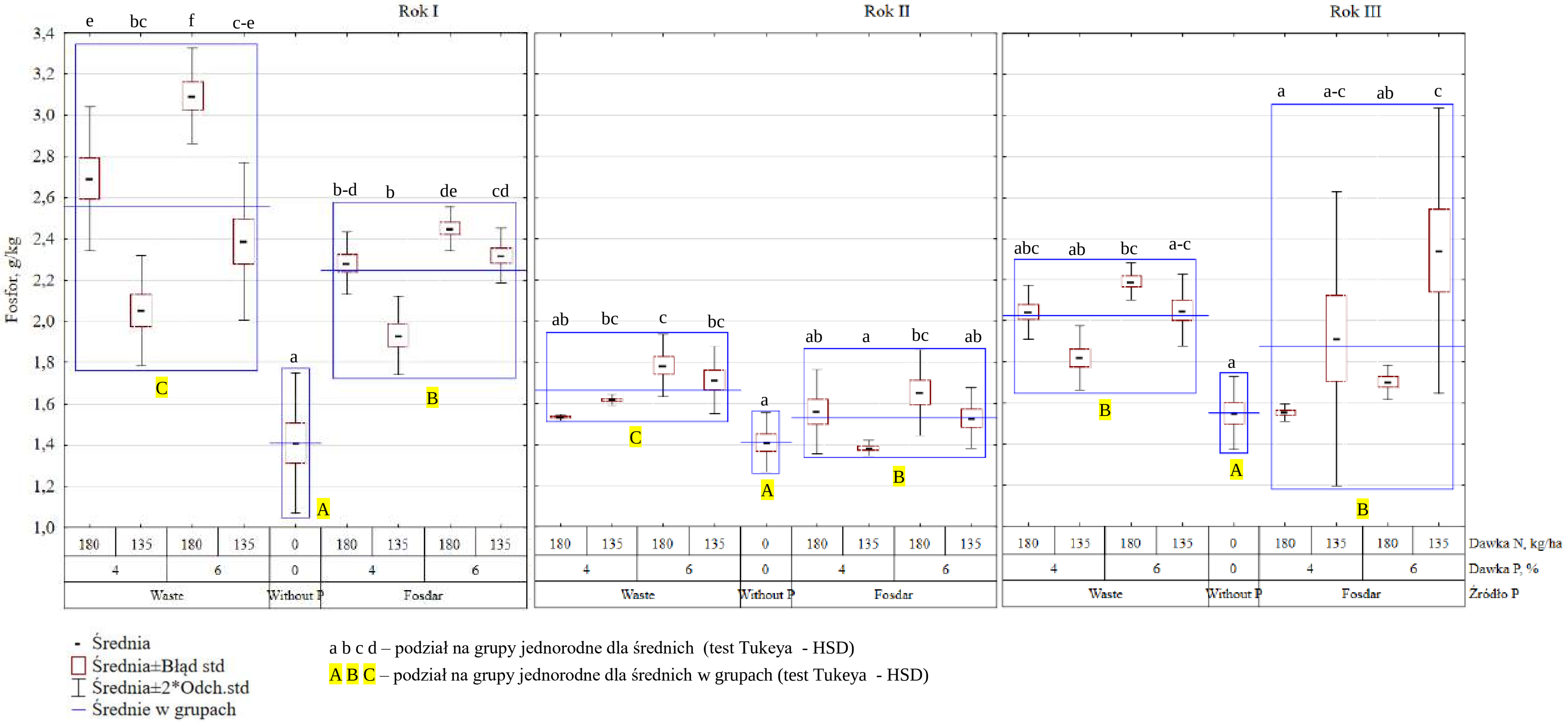
Na rysunku 13 przedstawiono średnią zawartość fosforu w biomasie kukurydzy w zależności od rodzaju źródła fosforu w nawozie i jego procentowej zawartości, w podziale na poszczególne lata badań i zastosowaną dawkę azotu.

W pierwszym i drugim roku badań polowych zastosowanie odpadowego fosforu w nawożeniu istotnie wpłynęło na zawartość fosforu w kukurydzy. W pierwszym roku przyczyniło się to do wzrostu zawartości fosforu o 13,78%, a w drugim roku o 8,5% w porównaniu z nawożeniem roślin Fosdarem 40. We wszystkich latach badań na obiektach bez nawożenia odnotowano istotnie niższe zawartości fosforu w porównaniu z roślinami z poletek nawożonych zarówno Fosdarem 40, jak i odpadowym fosforanem. Wyższa dawka fosforu, zarówno w przypadku nawożenia Fosdarem 40 jak i odpadowym fosforanem, istotnie zwiększyła zawartość tego składnika w roślinach testowych w każdym roku badań polowych.

W pierwszym roku badań zaobserwowano wyraźny wpływ wyższej dawki azotu na zawartość fosforu w roślinach testowych. Najwyższy wskaźnik uzyskano na poletkach nawożonych odpadowym fosforanem i azotem na poziomie 180 kg · ha^{-1} (2,89 g · kg^{-1} s.m.), natomiast najniższy uzyskano przy nawożeniu Fosdarem 40 i przy dawce azotu wynoszącej 135 kg · ha^{-1} (2,13 g · kg^{-1} s.m.). W kolejnych latach tendencja ta nie była już tak wyraźna. W drugim i trzecim roku badań dawka azotu istotnie różnicowała zawartość fosforu tylko w przypadku nawożenia kukurydzy Fosdarem 40, natomiast wyższą zawartość fosforu uzyskano w drugim roku przy zastosowaniu azotu na poziomie 180 kg N · ha^{-1}, a w trzecim roku przy dawce 135 kg N · ha^{-1}.

Na rysunku 14 zestawiono średnią zawartość fosforu w kukurydzy w zależności od rodzaju nawozu zawiesinowego i procentowej zawartości fosforu, w podziale na poszczególne lata badań i zastosowaną dawkę azotu.

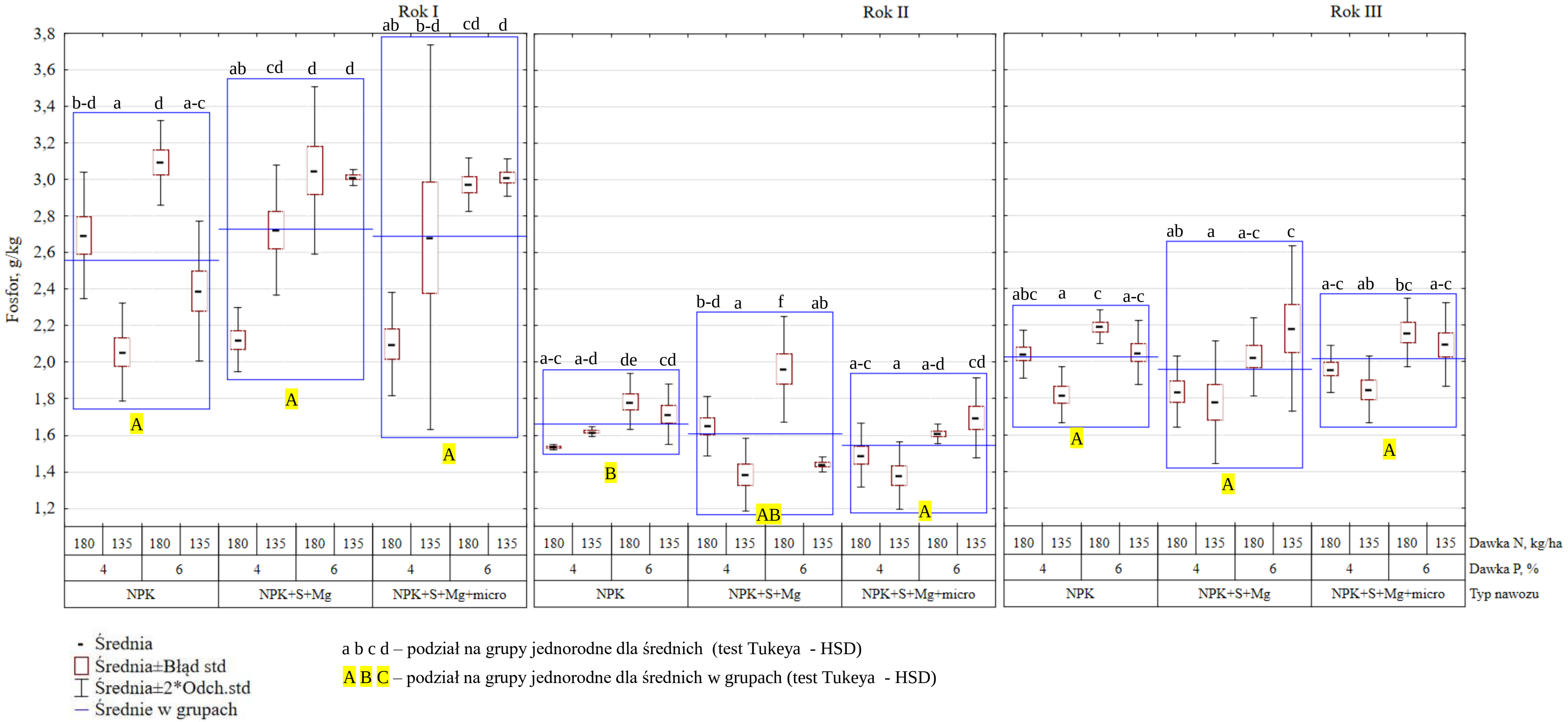
Rodzaj zastosowanego nawozu istotnie różnicował zawartość fosforu w kukurydzy tylko w drugim roku badań. Statystycznie wyższą zawartość fosforu odnotowano w roślinach, w przypadku których zastosowano nawóz NPK w porównaniu z roślinami nawożonymi nawozem z mikroelementami. We wszystkich latach doświadczenia polowego potwierdzono istotną zależność dotyczącą wzrostu zawartości fosforu w kukurydzy i wzrostu ilości fosforu w nawozie.



a b c d – podział na grupy jednorodne dla średnich (test Tukeya - HSD)

A B C – podział na grupy jednorodne dla średnich w grupach (test Tukeya - HSD)

Rysunek 13. Średnia zawartość fosforu w kukurydzy (g · kg^{-1} s.m.) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na rodzaj nawozu zawiesinowego i procentową zawartość fosforu



a b c d – podział na grupy jednorodne dla średnich (test Tukeya - HSD)

A B C – podział na grupy jednorodne dla średnich w grupach (test Tukeya - HSD)

Rysunek 14. Średnia zawartość fosforu w kukurydzy (g · kg^{-1} s.m.) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na rodzaj nawozu zawiesinowego i procentową zawartość fosforu

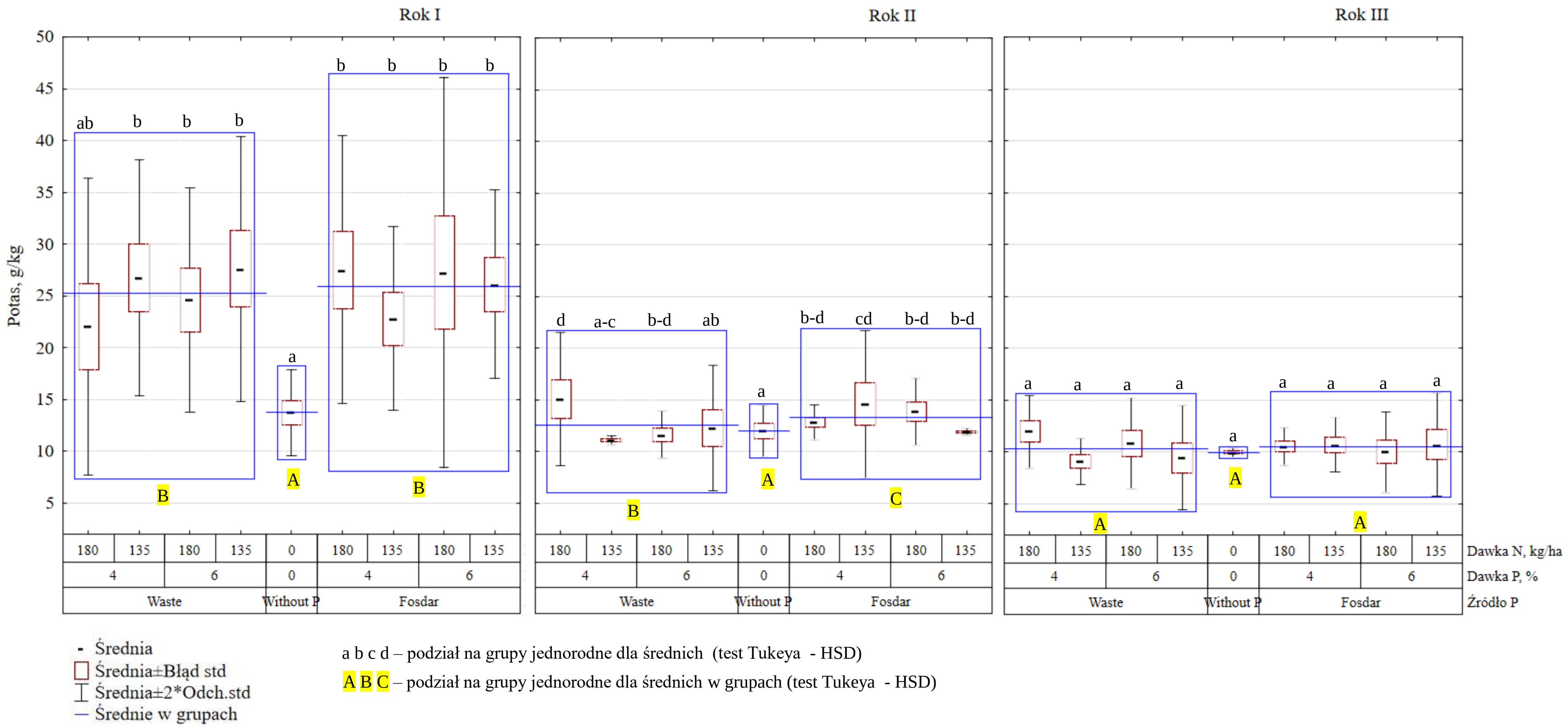
7.3. Potas

Na rysunku 15 zestawiono średnią zawartość potasu w kukurydzy w zależności od rodzaju źródła fosforu w nawozie i jego udziału procentowego, w podziale na poszczególne lata badań i zastosowaną dawkę azotu.

Źródło fosforu zastosowane w nawozie istotnie różnicowało zawartość potasu w roślinie testowej tylko w drugim roku badań polowych, gdzie w przypadku nawożenia Fosdarem 40 jego zawartość była wyższa o 7,66% w porównaniu z kukurydzą nawożoną nawozem opartym na odpadowym źródle fosforu. W badaniu polowym dawka fosforu i azotu w nawozie nie miała istotnego wpływu na zawartość potasu w roślinach testowych.

Na rysunku 16 przedstawiono średnią zawartość potasu w kukurydzy w zależności od rodzaju nawozu zawiesinowego i udziału procentowego fosforu, w podziale na poszczególne lata badań i zastosowaną dawkę azotu.

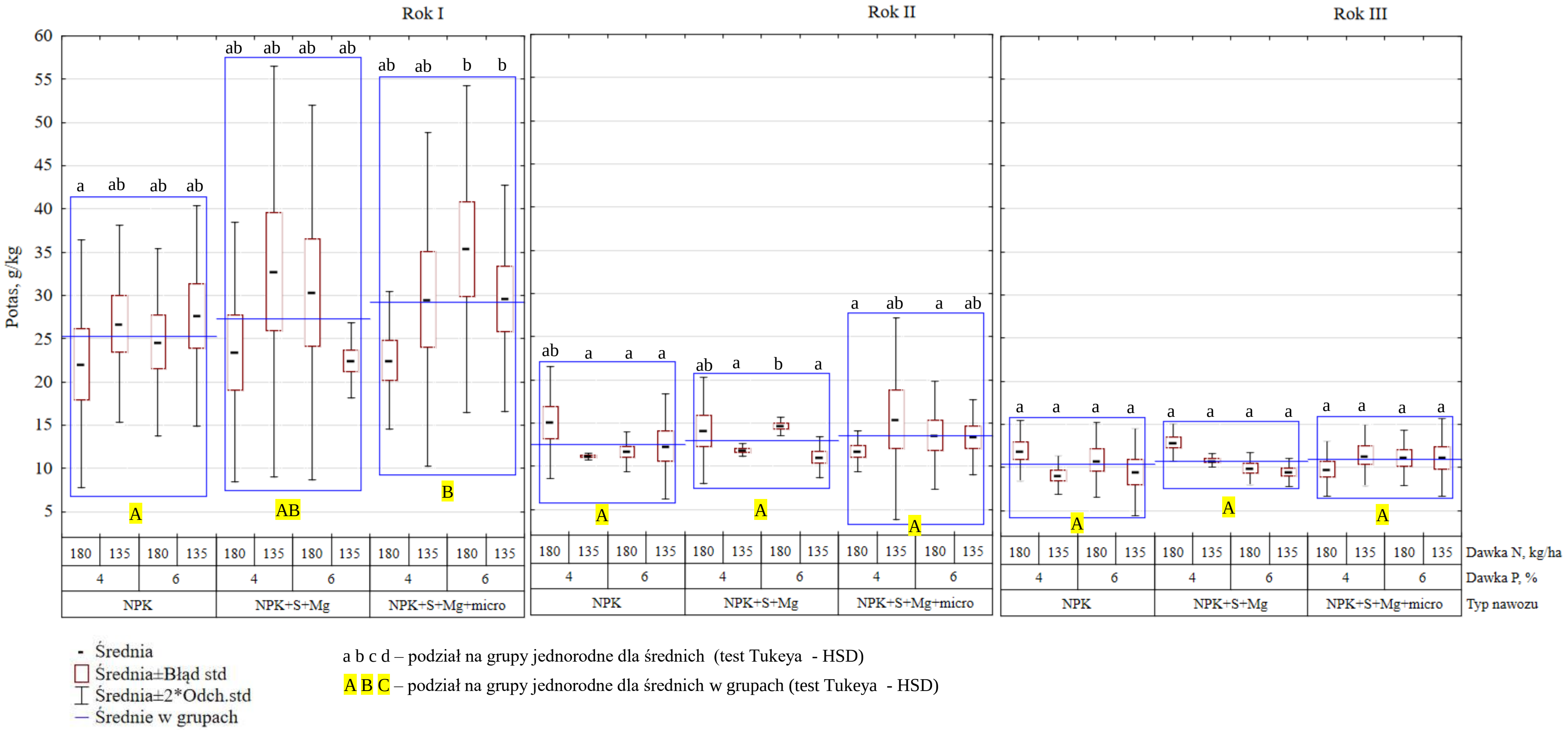
Rodzaj nawozu istotnie różnicował zawartość potasu w kukurydzy tylko w pierwszym roku badań, gdzie istotne różnice odnotowano w przypadku nawożenia roślin nawozami o podstawowym składzie NPK (21,90 g $K \cdot kg^{-1}$ roślina) i nawozami z dodatkiem mikroelementów (24,33 g $K \cdot kg^{-1}$ roślina) bez podziału na zastosowaną dawkę fosforu. Istotne różnice odnotowano w pierwszym roku badań w odniesieniu do zastosowanej dawki fosforu – rośliny nawożone wyższą dawką fosforu charakteryzowały się większą zawartością potasu. Zależności tych nie odnotowano w kolejnych dwóch latach doświadczeń polowych. W przypadku potasu zróżnicowane nawożenie azotem wpłynęło na jego zawartość w roślinach w drugim roku badań polowych, przy poziomie nawożenia fosforem wynoszącym 6%.



a b c d – podział na grupy jednorodne dla średnich (test Tukeya - HSD)

A B C – podział na grupy jednorodne dla średnich w grupach (test Tukeya - HSD)

Rysunek 15. Średnia zawartość potasu w kukurydzy (g · kg^{-1} s.m.) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na rodzaj nawozu zawiesinowego i procentową zawartość fosforu



Rysunek 16. Średnia zawartość potasu w kukurydzy (g · kg^{-1} s.m.) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na rodzaj nawozu zawiesinowego i procentową zawartość fosforu

7.4. Siarka siarczanowa

Niezależnie od źródła fosforu zastosowanego w nawozie, zawartość siarki siarczanowej w roślinie testowej utrzymywała się na podobnym poziomie 0,06–0,2 $g \cdot kg^{-1}$ s.m. rośliny, przy czym mediana wartości wynosiła 0,087 $g \cdot kg^{-1}$ s.m. rośliny. Nie stwierdzono statystycznie istotnych różnic w porównaniu do kukurydzy zebranej z poletek kontrolnych bez nawożenia. Dawki fosforu i azotu nie wpłynęły istotnie na zawartość siarki siarczanowej w roślinach testowych.

Porównując wpływ typu zastosowanego nawozu na zawartość siarki siarczanowej w kukurydzy, istotne różnice stwierdzono w drugim roku badań. W tym roku zawartość siarki siarczanowej była wyższa w kukurydzy z poletek, na których zastosowano wyższą dawkę fosforu (6%). W pozostałych latach badań nie stwierdzono takiej zależności.

7.5. Magnez

Istotne różnice w zawartości magnezu w roślinie testowej obserwowano jedynie w pierwszym roku badań polowych. Istotnie wyższe stężenie magnezu uzyskano w kukurydzy z poletek nawożonych Fosdarem 40.

Zawartość magnezu w roślinach kukurydzy nawożonych nawozami zawiesinowymi mieściła się w zakresie 0,17–1,73 $g \cdot kg^{-1}$ s.m., przy czym mediana wynosiła 0,63 $g \cdot kg^{-1}$ s.m. W przeprowadzonym doświadczeniu rodzaj nawozu i dawka azotu nie wpłynęły istotnie na zawartość tego makroskładnika w kukurydzy.

7.6. Wapń

Surowiec fosforowy nie miał istotnego wpływu na zróżnicowanie zawartości wapnia w roślinach kukurydzy w przeprowadzonym doświadczeniu polowym. W trzecim roku badań średnia zawartość wapnia w badanych roślinach była wyższa w porównaniu z dwoma poprzednimi latami eksperymentu.

Zawartość wapnia w roślinach kukurydzy nawożonych nawozami zawiesinowymi mieściła się w zakresie 1,36–4,26 $g \cdot kg^{-1}$ s.m. W grupie nawozów zawiesinowych o tej samej zawartości fosforu nie odnotowano istotnego wpływu w zależności od rodzaju zastosowanego nawozu na zawartości wapnia w roślinach testowych. W pierwszym roku badań odnotowano istotne różnice w zawartości wapnia w zależności od dawki fosforu, przy czym wyższa dawka fosforu w nawozie skutkowała wyższą zawartością wapnia w kukurydzy. Podobną zależność zaobserwowano również w drugim roku badań. Natomiast w trzecim roku trwania eksperymentu nie odnotowano istotnych różnic, chociaż uzyskane zawartości wapnia w roślinie testowej były wyższe niż w poprzednich latach doświadczenia polowego.

7.7. Sód

W pierwszym roku badań źródło fosforu zastosowane w nawozie istotnie wpłynęło na zawartość sodu w kukurydzy. Stężenie sodu wyższe o 16,7% odnotowano w roślinach z poletek nawożonych nawozami z odpadami z produkcji polioli w porównaniu z nawożeniem Fosdarem 40. W kolejnych latach doświadczenia polowego nie stwierdzono takiej zależności.

Zawartość sodu w roślinach kukurydzy nawożonych nawozami zawiesinowymi mieściła się w zakresie 0,107–0,402 $g \cdot kg^{-1}$ s.m. rośliny, przy czym mediana wynosiła 0,314 $g \cdot kg^{-1}$ s.m..

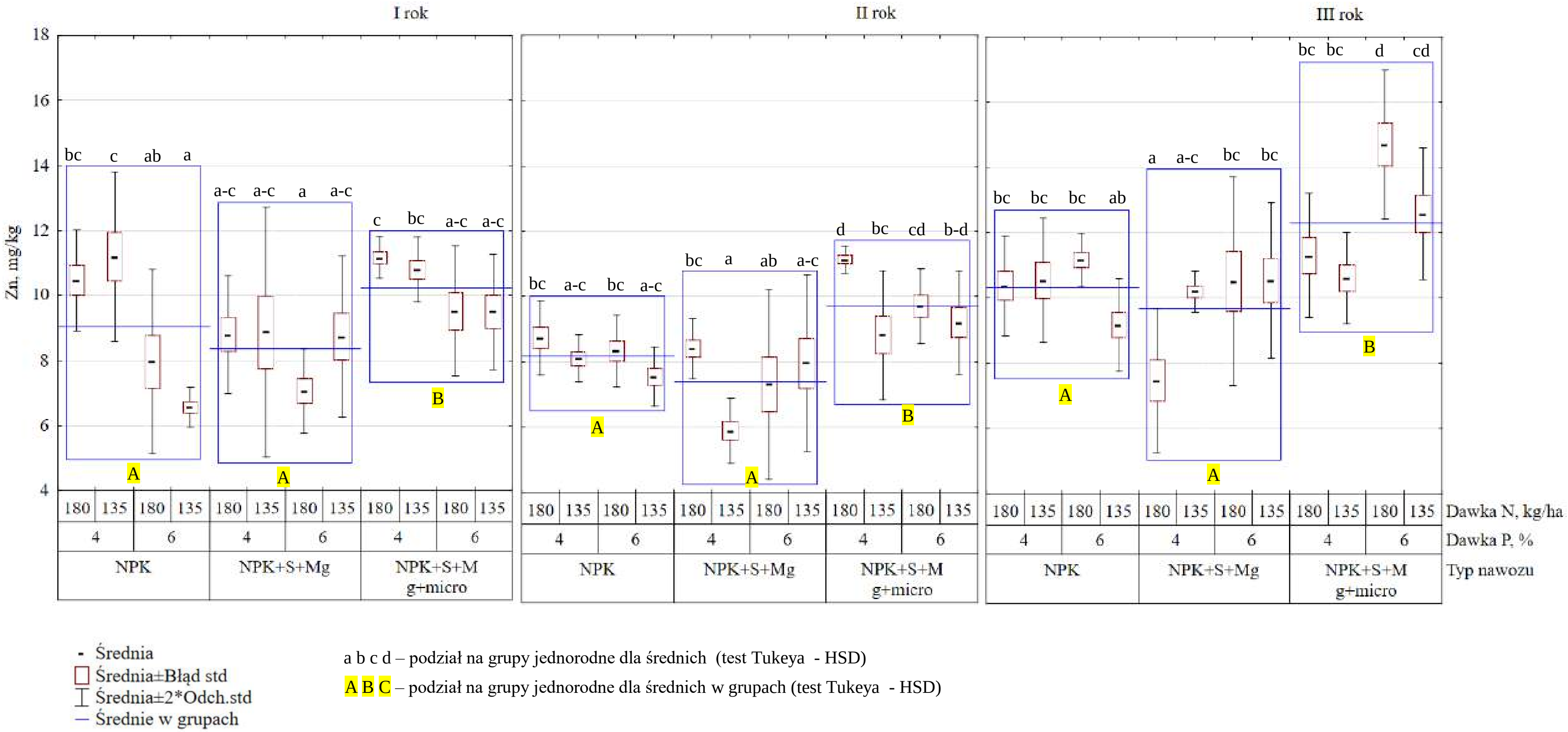
Rodzaj zastosowanego nawozu zawiesinowego istotnie różnicował zawartość sodu w roślinach tylko w drugim roku badań. Nawozy z mikroelementami wpływały na wyższą zawartość sodu w roślinach testowych w porównaniu z pozostałymi nawozami. W pierwszym i drugim roku badań nie stwierdzono istotnych różnic w zawartości sodu w kukurydzy w wyniku stosowania różnych nawozów.

8. Analiza kukurydzy – zawartość mikroelementów (Publikacja nr 6)

8.1. Cynk

Na rysunku 17 przedstawiono średnią zawartość cynku w kukurydzy w zależności od rodzaju wniesionego nawozu zawiesinowego i udziału procentowego fosforu, w podziale na poszczególne lata badań i zastosowaną dawkę azotu.

We wszystkich latach badań wykazano istotnie wyższą zawartość cynku w kukurydzy nawożonej nawozami z dodatkiem mikroelementów. Wpływ dawki azotu i zawartości fosforu w nawozie na koncentrację cynku był zróżnicowany w każdym roku badań i na podstawie przeprowadzonych badań nie można stwierdzić jednoznacznie jego tendencji.



a b c d – podział na grupy jednorodne dla średnich (test Tukeya - HSD)

A B C – podział na grupy jednorodne dla średnich w grupach (test Tukeya - HSD)

Rysunek 17. Średnia zawartość cynku w kukurydzy (g · kg^{-1}) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na typu nawozu zawiesinowego i procentowej zawartość fosforu

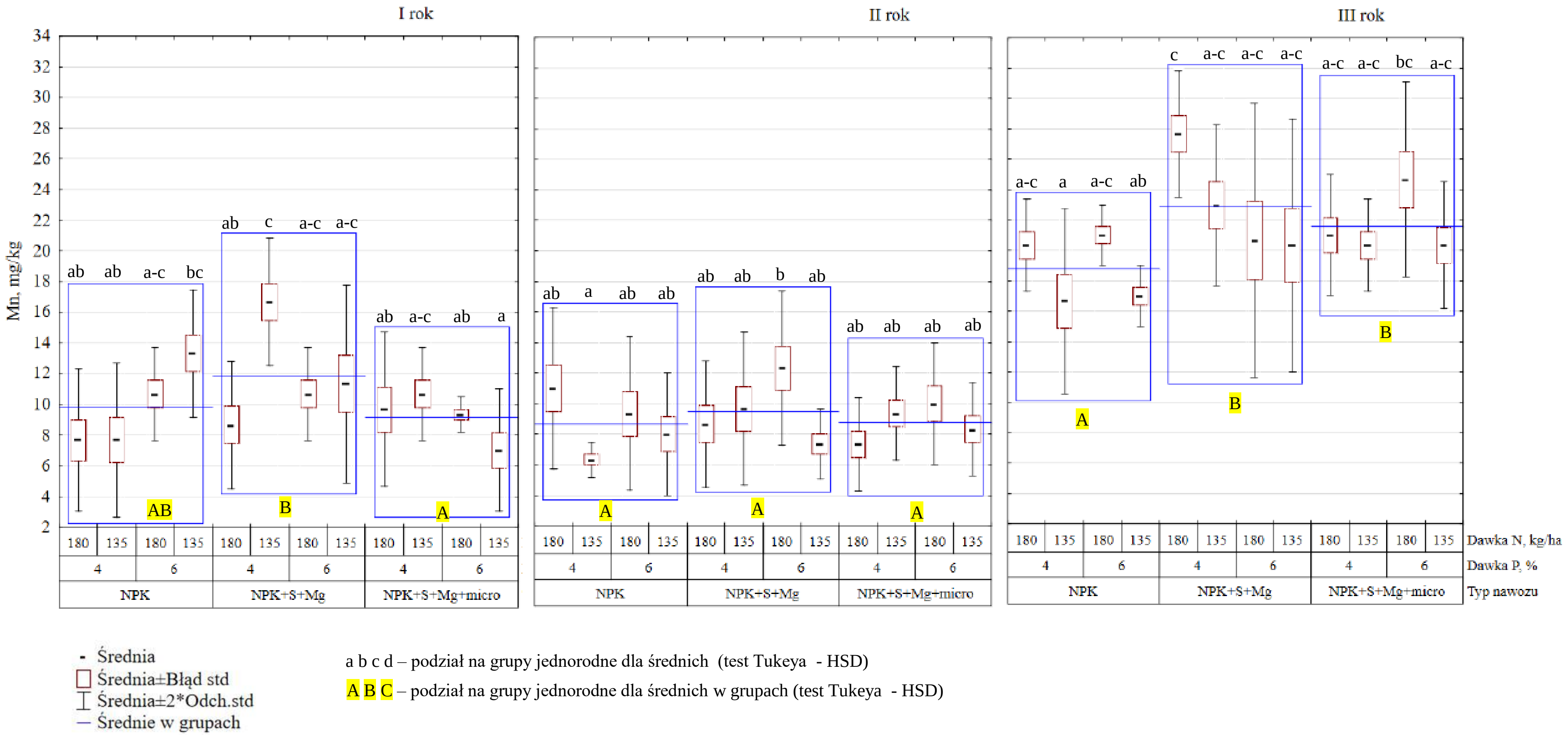
8.2. Mangan

Na rysunku 18 przedstawiono średnią zawartość manganu w kukurydzy w zależności od rodzaju zastosowanego nawozu zawiesinowego i udziału procentowego fosforu, w podziale na poszczególne lata badań i aplikowaną dawkę azotu.

Zawartość manganu w roślinach nawożonych nawozami zawiesinowymi była zróżnicowana w kolejnych latach doświadczenia polowego. Występujące istotne różnice między poszczególnymi typami nawozów nie były powtarzalne. Zawartość fosforu w nawozie nie miała wpływu na różnice w zawartości manganu w roślinie testowej, natomiast zawartość tego składnika była większa przy wyższej dawce azotu w II i III roku badań polowych.

8.3. Miedź

Nie wykazano istotnych statystycznie różnic w zawartość miedzi w kukurydzy w poszczególnych latach badań polowych w efekcie zastosowanych nawozów zawiesinowych. W I roku eksperymentu średnia zawartość tego mikroelementu wynosiła 3,76 mg $\cdot$ kg^{-1} s.m., w drugim roku – 5,58 mg $\cdot$ kg^{-1} s.m. natomiast w trzecim roku – 2,85 mg $\cdot$ kg^{-1} s.m.



a b c d – podział na grupy jednorodne dla średnich (test Tukeya - HSD)

A B C – podział na grupy jednorodne dla średnich w grupach (test Tukeya - HSD)

Rysunek 18. Średnia zawartość manganu w kukurydzy (g · kg^{-1}) i podział na grupy jednorodne za pomocą testu Tukeya (HSD) dla α = 0,05 ze względu na typu nawozu zawiesinowego i procentowej zawartość fosforu

9. Analiza gleby po zbiorze kukurydzy (nieopublikowane)

W tabeli 11 przedstawiono zawartość zanieczyszczeń w glebie po każdym roku doświadczeń polowych z podziałem na poletka, w przypadku których do nawożenia użyto odpadowy fosforan oraz Fosdar 40. Uzyskane wyniki analizy gleby zestawiono z dopuszczalnymi zawartościami według Rozporządzenia Ministra Środowiska z dnia 1 września 2016 r. w sprawie sposobu prowadzenia oceny zanieczyszczenia powierzchni ziemi (66).

Ponieważ analiza statystyczna nie wykazała istotnych różnic między średnimi zawartościami badanych metali ciężkich w glebie względem zastosowanego w nawożeniu źródła fosforu, zawartości fosforu w nawozie i zaaplikowanej dawki azotu, w tabeli przedstawiono średnie zawartości badanych pierwiastków z podziałem na poletka nawożone odpadowym fosforanem i Fosdarem 40

Tabela 11. Zawartość zanieczyszczeń w glebie na poletkach nawożonych odpadowym fosforanem i Fosdarem 40 z uwzględnieniem dopuszczalnych wartości według Rozporządzenia Ministra Środowiska

Substancja	Rok badań	Średnia zawartość w glebie na poletkach gdzie użyto odpadowy fosforan, mg · kg^{-1} gleby	Średnia zawartość w glebie na poletkach gdzie użyto Fosdar 40, mg · kg^{-1} gleby	Dopuszczalna zawartość, mg · kg^{-1} gleby, dla grupy gruntów II-3
Arsen (As)	I	3,94	5,34	50
	II	4,28	3,23	
	III	4,14	4,40	
Chrom (Cr)	I	26.78	27.90	500
	II	26,40	27,15	
	III	27,10	27,64	
Kadm (Cd)	I	< 0,5	< 0,5	5
	II	< 0,5	< 0,5	
	III	< 0,5	< 0,5	
Miedź (Cu)	I	8,33	8,30	300
	II	8,68	8,03	
	III	8,22	8,12	
Nikiel (Ni)	I	10,93	10,58	300
	II	10,03	10,48	
	III	10,36	10,08	
Ołów (Pb)	I	11,23	11,10	500
	II	11,63	11,53	
	III	11.42	11.50	
Rtęć (Hg)	I	0,032	0,035	5
	II	0,038	0,032	
	III	0,032	0,030	

Analiza statystyczna nie wykazała istotnych różnych w zawartości zanieczyszczeń w badanych próbkach gleby w zależności od użytego w nawożeniu źródła fosforu. W żadnym przypadku wyniki analizowanej gleby nie przekroczyły dopuszczalnych wartości według Rozporządzenia Ministra Środowiska z dnia 1 września 2016 r.

Analiza chemiczna odpadu wykazała minimalną ilość zanieczyszczeń, daleką od wartości progowych przewidzianych w przepisach nawozowych. Wyniki badań gleby po zbiorze rośliny testowej potwierdzają nieszkodliwość odpadowego fosforanu z produkcji polioli w przypadku wykorzystania go jako surowca nawozowego.

W tabeli 12 przedstawiono podstawowe parametry gleby po każdym roku doświadczeń polowych z podziałem na poletka, w przypadku których do nawożenia użyto odpadowy fosforan oraz Fosdar 40.

Ponieważ analiza statystyczna nie wykazała istotnych różnic między średnimi zawartościami badanych parametrów gleby względem zastosowanego w nawożeniu źródła fosforu, zawartości fosforu w nawozie i zaaplikowanej dawki azotu, w tabeli przedstawiono średnie zawartości badanych pierwiastków w podzile na poletka nawożone odpadowym fosforanem i Fosdarem 40.

Tabela 12. Podstawowe parametry gleby na poletkach nawożonych odpadowym fosforanem i Fosdarem 40 w poszczególnych latach prowadzenia doświadczenia polowego

Substancja	**Rok badań**	**Średnia zawartość w glebie na poletkach gdzie użyto odpadowy fosforan, mg · 100 g^{-1} gleby**	**Średnia zawartość w glebie na poletkach gdzie użyto Fosdar 40, mg · 100 g^{-1} gleby**
Fosfor (P_2O_5)	I	35,84	32,48
	II	36,83	34,58
	III	43,75	42,96
Potas (K_2O)	I	23,56	21,03
	II	21,03	21,43
	III	30,71	33,92
Magnez (Mg)	I	7,67	7,32
	II	6,33	6,09
	III	7,37	6,74
Siarka (SO_4)	I	< 0,6	< 0,6
	II	0,76	0,88
	III	< 0,6	< 0,6
pH w KCl	I	6,55	6,15
	II	6,72	6,78
	III	6,49	6,41

W przeprowadzonym eksperymencie polowym średnie zawartości przyswajalnego fosforu były wysokie i mieściły się w przedziale od 32,48 do 43,75 mg · 100 g^{-1} gleby.

Najwyższe zawartości analizowanego parametru glebowego, odnotowano po zbiorze kukurydzy w trzecim roku badań polowych, zaś najniższe po pierwszym i drugim roku badań w przypadku zastosowania nawozu Fosdar 40.

Średnia zawartość potasu w glebie po zbiorze kukurydzy byłą wysoka i mieściła się w zakresie 21,03 – 33,92 mg · 100 g^{-1} gleby. Najwyższe wartości tego pierwiastka odnotowano w III roku badań polowych na poetkach, na których zastosowano Fosdar 40.

Średnia zawartość magnezu w glebie w czasie trwania eksperymentu polowego była wysoka i mieściła się w zakresie 6,09 – 7,67 mg · 100 g^{-1} gleby.

Analiza gleby w trakcie trwania eksperymentu polowego wykazała niską zawartość siarki. Jej średnia zawartość w I i III roku badania polowego była poniżej 0,6 mg · 100 g^{-1} gleby. W II roku badań polowych średnia zawartość siarki w glebie była nieco wyższa i dochodziła do 0,88 mg · 100 g-1 gleby.

pH gleby utrzymywało się na podobnym poziomie przez cały okres trwania doświadczenia polowego i jego średnia wartość wynosiła 6,53.

Podsumowanie i wnioski

Przeprowadzone badania wykazały, że odpadowy fosforan sodowo-potasowy może być z powodzeniem wykorzystany do produkcji nawozów zawiesinowych o właściwościach fizykochemicznych spełniających normy przepisów nawozowych. Badania polowe z zastosowaniem tych nawozów potwierdziły ich skuteczność, która jest porównywalna z efektywnością komercyjnego nawozu fosforowego Fosdar 40. Dodatkowo wykorzystanie tego odpadowego źródła fosforu nie wpłynęło negatywnie na jakość roślin oraz na parametry glebowe. Stąd też ze względu na niższy koszt surowca odpadowego, produkcja nawozów z jego wykorzystaniem stanowi konkurencyjną alternatywę dla nawozów opartych na fosforytach.

Produkcja nawozów na bazie polioli ma dodatkowy atut w postaci wykorzystania surowców odpadowych, co czyni ją bardziej ekologiczną i zgodną z ideą zrównoważonego rozwoju. Tego rodzaju podejście doskonale wpisuje się w strategię gospodarki o obiegu zamkniętym, która zakłada minimalizację odpadów i maksymalizację ponownego wykorzystania surowców. Dzięki temu zmniejsza się zależność od pierwotnych źródeł surowców oraz ogranicza negatywny wpływ na środowisko.

Tego rodzaju podejście promuje również rozwój innowacyjnych technologii, które mogą prowadzić do optymalizacji kosztów produkcji. Wykorzystanie odpadów w roli surowców wtórnych nie tylko wspiera zrównoważony rozwój, lecz także pomaga firmom spełniać coraz bardziej restrykcyjne normy środowiskowe, co jest istotnym czynnikiem konkurencyjności na współczesnym rynku.

Wnioski wynikające z analizy odpadu:

- Przeprowadzone badania potwierdzają, że analizowane odpady nie zawierają substancji szkodliwych dla roślin.
- Odpady nie wymagają obróbki ani innych wstępnych procesów przygotowawczych i w niezmienionej postaci mogą być wykorzystywane do produkcji nawozów zawiesinowych. Dzięki temu zawarty w nich fosfor może być w pełni odzyskany i ponownie wykorzystany w nawożeniu.
- Odpadowy fosforan sodowo-potasowy zawiera znaczne ilości fosforu, co czyni go atrakcyjnym surowcem do produkcji nawozów.

- Wykorzystanie odpadu z polioli do celów nawozowych jest zgodne ze strategią gospodarki o obiegu zamkniętym UE i wychodzi naprzeciw wyzwaniom stawianym przez nowe przepisy nawozowe zawarte w rozporządzeniu UE 2019/1009.

Wnioski wynikające z wytwarzania nawozów zawiesinowych:

- Przedstawione badania potwierdzają możliwość wykorzystania fosforanów odpadowych z produkcji polioli jako surowców do produkcji nawozów zawiesinowych.
- W związku z faktem, że odpady z polioli zawierają dużą ilość wody, nawozy zawiesinowe są najbardziej ekonomicznie opłacalną formą produkowanych na ich bazie nawozów.
- Forma zawiesinowa nawozu pozwala na szeroki zakres modyfikacji składu nawozowego. Surowiec odpadowy można rozcieńczyć wodą lub uzupełnić odpowiednimi surowcami zawierającymi w zależności od potrzeb makro- lub mikroelementy. Rozpuszczalność składników nawozowych nie stanowi w tym wypadku żadnego ograniczenia.
- Przy produkcji nawozów zawiesinowych istotną kwestią jest odpowiednia stabilizacja zawiesiny za pomocą środka stabilizującego.
- Przydatność bentonitów do stabilizacji nawozów zawiesinowych należy sprawdzić poprzez wcześniejsze przygotowanie zawiesiny wodnej i ocenę stopnia pęcznienia. Jeżeli bentonit nie tworzy trwałej zawiesiny i ulega rozwarstwieniu, nie nadaje się do przygotowywania na jego bazie nawozów zawiesinowych.
- Dodatek bentonitów do zawiesin nawozowych poprawia ich parametry reologiczne, zwłaszcza stabilność i płynność. W próbkach nawozów z dodatkiem bentonitu płynność poprawia się wraz z upływem czasu.
- Dodatek bentonitu do zawiesin nawozowych zapobiega tworzeniu się dużych kryształów, które mogłyby zatykać dysze podczas aplikacji nawozu.
- Dodatek bentonitu ułatwia przywrócenie właściwych parametrów zawiesin nawozowych po ich ponownym wymieszaniu.
- W próbkach o wysokim stężeniu, podczas przechowywania mogą powstawać grubsze kryształy. Może to powodować zatykanie dysz wylotowych podczas aplikacji nawozu. Może to skutkować nierównomiernym rozprowadzeniem nawozu na polu lub całkowitym zaniechaniem jego aplikacji.

- Wszystkie proponowane testy nawozów z dodatkiem bentonitu, o składzie dostosowanym do wymagań pokarmowych kukurydzy, spełniły kryteria aplikacji nawozów zawiesinowych.

Wnioski wynikające z badań polowych nad wpływem nawozów zawiesinowych na plonowanie i parametry jakościowe roślin kukurydzy:

- W I i II roku badań polowych wykazano nieznacznie wyższy plon suchej masy kukurydzy przy nawożeniu z udziałem nawozu Fosdar 40 w stosunku do roślin nawożonych nawozem na bazie odpadowego fosforanu . W II roku badań parametr ten był na tym samym poziomie niezależnie od zastosowanego w nawożeniu rośliny testowej źródła fosforu. Natomiast we wszystkich latach badań potwierdzono istotnie niższe plony kukurydzy w obiektach kontrolnych bez nawożenia.
- Średnia wysokość roślin kukurydzy w I i II roku badań polowych była nieznacznie wyższa w przypadku nawożenia nawozem Fosdar 40 w porównaniu do roślin nawożonych nawozami na bazie polioli. Natomiast we wszystkich latach eksperymentu polowego parametr ten był istotnie niższy dla kontroli beż nawożenia w odniesieniu do roślin z obiektów nawożonych.
- W każdym roku prowadzenia doświadczenia polowego potwierdzono istotnie wyższą średnią wysokość kukurydzy przy nawożeniu nawozami zawiesinowymi z drugorzędnymi składnikami pokarmowymi i mikroelementami w porównaniu do wysokości roślin z obiektów z nawozami o podstawowym składzie NPK.
- Wpływ nawozów zawiesinowych na bazie odpadowego fosforanu na zawartość azotu ogółem w kukurydzy w I i III roku badań polowych był porównywalny z wpływem nawożenia nawozem komercyjnym Fosdar 40. W II roku badań istotnie wyższe zawartości tego składnika odnotowano dla nawozów zawiesinowych.
- Zawartość fosforu w kukurydzy w I i II roku badań polowych była istotnie wyższa przy nawożeniu odpadowym fosforanem w odniesieniu do kukurydzy nawożonej nawozem Fosdar 40. W każdym roku badań kukurydza na poletkach kontrolnych bez nawożenia charakteryzowała się istotnie niższą zawartością fosforu w porównaniu z poletkami z nawożeniem.
- W przeprowadzonym badaniu polowym nie odnotowano jednoznacznego wpływu stosowanych nawozów na zawartość potasu w kukurydzy.

- W każdym roku przeprowadzonych badań polowych wykazano istotnie wyższą zawartość cynku w kukurydzy nawożonej nawozami zawiesinowymi z dodatkiem mikroelementów.
- Nie wykazano istotnych różnic w zawartości miedzi w roślinie testowej.
- Zawartość manganu w badanej kukurydzy była zróżnicowana, a istotne statystycznie różnice nie miały potwierdzenia w poszczególnych latach prowadzenia doświadczenia polowego.

Wnioski z analizy gleby

- W badanych próbkach gleby nie wykazano różnic w zawartości metali ciężkich w zależności od użytego w nawożeniu źródła fosforu.
- W żadnym przypadku wyniki analizowanej gleby nie przekroczyły dopuszczalnych wartości według Rozporządzenia Ministra Środowiska.

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Oświadczenia współautorów

(Załącznik nr 1)

Lublin, dn. 30.09.2024 r.

dr hab. Marzena S. Brodowska, prof. uczelni
Katedra Chemii i Rolnej i Środowiskowej
Uniwersytet Przyrodnicy w Lublinie
ul. Akademicka 13
20-950 Lublin

Rada Dyscypliny Rolnictwo i Ogrodnictwo
Uniwersytetu Przyrodniczego w Lublinie

Oświadczenie o współautorstwie

Oświadczam, że w publikacji: P. Bogusz, P. Rusek, M. S. Brodowska. **Suspension Fertilizers: How to Reconcile Sustainable Fertilization and Environmental Protection.** Agriculture 2021, 11, 1008; mój udział polegał na udziale w koncepcji pracy.

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Marzena S. Brodowska
....
(podpis współautora)

Puławy, 30.09.2024 r.

dr hab. Piotr Rusek
Grupa Badawcza Nawozy
Sieć Badawcza Łukasiewicz –
Instytut Nowych Syntez Chemicznych
Al. Tysiąclecia Państwa Polskiego 13A
24-110 Puławy

Rada Dyscypliny Rolnictwo i Ogrodnictwo
Uniwersytetu Przyrodniczego w Lublinie

Oświadczenie o współautorstwie

Oświadczam, że w publikacji: P. Bogusz, P. Rusek, M. S. Brodowska. **Suspension Fertilizers: How to Reconcile Sustainable Fertilization and Environmental Protection**. Agriculture 2021, 11, 1008. mój udział polegał na udziale w koncepcji pracy.

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Piotr Rusek
....
(podpis współautora)

Lublin, dn. 30.09.2024 r.

dr Paweł Muszyński
Katedra Chemii
Uniwersytet Przyrodnicy w Lublinie
ul. Akademicka 13
20-950 Lublin

Rada Dyscypliny Rolnictwo i Ogrodnictwo
Uniwersytetu Przyrodniczego w Lublinie

Oświadczenie o współautorstwie

Oświadczam, że w publikacji: P. Bogusz, M. S. Brodowska, P. Muszyński. **The Impact of Suspension Fertilizers Based on Waste Phosphorus Salts from Polyol Production on the Content of Macronutrients in Maize Grown for Green Fodder.** Agronomy 2024, 14(9), 2079; mój udział polegał na wykonaniu analizy chemicznych ASA.

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Muszyński Paweł
....
(podpis współautora)

Publikacje wchodzące w skład pracy doktorskiej

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Review

Suspension Fertilizers: How to Reconcile Sustainable Fertilization and Environmental Protection

Paulina Bogusz [1,*], Piotr Rusek [1] and Marzena S. Brodowska [2]

[1] Fertilizers Research Group, Łukasiewicz Research Network—New Chemical Syntheses Institute, Al. Tysiąclecia Państwa Polskiego 13a, 24-110 Puławy, Poland; piotr.rusek@ins.lukasiewicz.gov.pl

[2] Department of Agricultural and Environmental Chemistry, University of Life Sciences in Lublin, Akademicka 13, 20-950 Lublin, Poland; marzena.brodowska@up.lublin.pl

* Correspondence: paulina.bogusz@ins.lukasiewicz.gov.pl

Abstract: Due to the growing world population, the challenge for the agriculture industry is to produce the right amount of food. This is not possible without the use of fertilizers. Unfortunately, apart from having a positive effect on the yield parameters, they can also adversely affect the natural environment. The use of fertilizers in excess or in a poorly digestible form causes the migration of fertilizer components beyond the reach of the plant root system. In this way, nutrients enter the groundwater, surface water and the atmosphere, contaminating them. The consequence of such actions is further climate warming and the deterioration of water status and air quality. Suspension fertilizers are an interesting proposition that meets the requirements of modern agriculture. They combine the advantages of liquid and solid fertilizers. The liquid form ensures better digestibility of the nutrients, especially in periods of drought, and the concentration of the ingredients is comparable to that of solid fertilizers. At the same time, production costs are lower, which is related to the simplification of the technological process and the possibility of using cheaper raw materials. A valuable advantage of fertilizer suspension is the possibility of using hydrated waste substances in their production.

Keywords: fertilizer; fertilization; recycling; waste management; sustainable agriculture; circular economy

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1. Introduction

The challenge for modern agriculture is to meet the requirements of the constantly growing number of people in the world with efficient food production [1]. Due to the limited possibilities of extending agricultural production via new arable land, fertilization is an essential factor, supporting and intensifying agricultural production [1–3].

Fertile soil is the key to sustainable plant production on an industrial scale but very few agricultural soils have sufficient nutrient content to meet crop requirements [4]. Most of them require the regular use of fertilizers that supplement low-level, or missing, micronutrients and macronutrients in the soil [1,2,4].

Currently, we have reached the point where increasing the fertilizer dose does not bring satisfactory yield-generating effects; on the contrary, it has a negative impact on the natural environment. The excess of nutrients supplied with the fertilizer evaporates into the atmosphere or is washed into the soil profile, creating a network of pollutants [5].

Efficient use of ingredients in the fertilizer sector is the basis for a green economy to produce more food and energy while reducing environmental pollution [6]. Product innovations that meet these requirements include both the chemical composition of fertilizers as well as their physical properties and the method of application [1,5].

Suspension fertilizers are an important tool for agriculture that meets the set environmental and agronomic criteria [6,7]. Their liquid formula and high concentration of fertilizing salts enable the more effective absorption of nutrients by plants [8]. These fertilizers are part of the sustainable management of mineral components, offering the possibility of balancing their distribution and also creating the possibility of utilizing harmful waste [6].

A novel feature of this article is to show the possibility of using hydrated waste, the management of which is often problematic, in the production of liquid suspension fertilizers. Previous works on this subject are very sparse and deal with the subject one-sidedly. A holistic view on this issue, taking into account the characteristics of these types of fertilizers, their impact on the environment, practical aspects of their production and use, and the variety of the waste that can be utilized in their production, allows us to see the opportunities for a wide range of recipients.

The article presents the characteristics of suspension fertilizers, taking into account their advantages and disadvantages, as well as the impact of their use on the natural environment and the economic aspects. The stability of suspension fertilizers is discussed in detail, as the main parameter determining their application. The possibilities of using various types of waste in their production are also discussed.

2. Characteristics of Suspension Fertilizers

When classifying mineral fertilizers (Figure 1), various criteria can be used, the most important of which is the number of nutrients contained in them and their physical form [9]. Solid fertilizers are granules and powders, while liquid fertilizers are fertilizer solutions and suspensions. In terms of composition, fertilizers can be divided into single- and multi-component fertilizers [9].

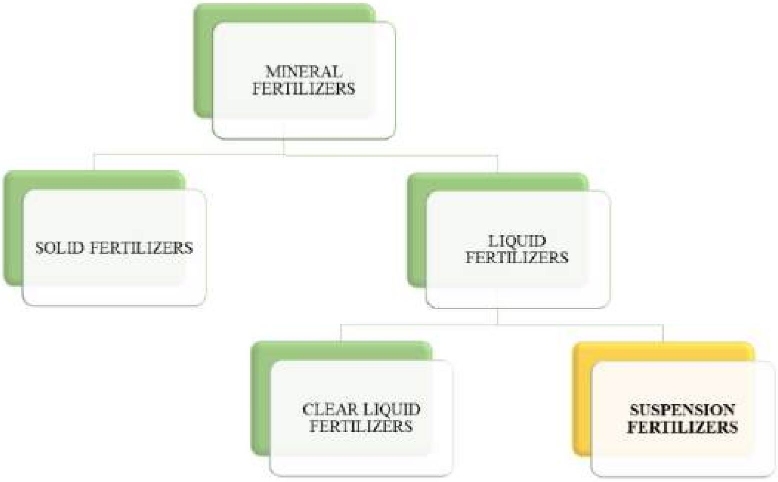

Figure 1. Classification of fertilizers according to their physical form. Due to their physical form, mineral fertilizers can be divided into solid fertilizers and liquid fertilizers. Suspension fertilizers belong in the group of liquid fertilizers.

Potassium salts have limited solubility, which prevents the production of fertilizer solutions with a high concentration of this component. This problem initiated the production of fertilizers in the form of a suspension [10,11].

Suspension fertilizers are defined as liquid fertilizers in which nutrients are present in an amount exceeding their solubility [12]. Apart from the components that are completely dissolved in water, they contain components insoluble in a dispersed form and a stabilizer that is present to maintain the homogeneity of the mixture [12–14]. A saturated aqueous solution of fertilizer salts constitutes the continuous phase, while undissolved salts in the form of fine crystals constitute the dispersed phase, which together forms a dispersed system [15].

The fertilizer salt crystals are kept in solution by a stabilizing agent that swells in the solution to form a viscosity-increasing gel, thereby preventing the sedimentation process of these particles [8].

The use of the suspension form of the fertilizer allows manufacturers to increase the concentration of fertilizing components to almost twice that found in clear liquid fertilizers and allows for competition in this respect with solid fertilizers [8].

3. Benefits and Limitations Resulting from the Production and Use of Suspension Fertilizers

Suspension fertilizers combine the advantages of liquid and solid fertilizers but also have unique features, making them an attractive proposition on the fertilizer market.

The main advantage of these fertilizers is the high concentration of nutrients they offer while maintaining a liquid form. The concentration of fertilizer salts in the suspension is similar to the concentration of solid fertilizers and, therefore, is much higher than that achievable in fertilizers in the form of a solution [8,13,14].

Raw materials used in the production of suspension fertilizers may be of lesser purity, as their complete solubility is not required [13,14,16,17]. It is also possible to use dusty materials and those that are sparingly soluble in water, such as finely ground rock phosphate [18]. A useful feature of the suspension form of fertilizer is the possibility of using waste with a high water content for its production that contains valuable fertilizing ingredients [8]. Waste in the form of suspension from the chemical and agri-food industries is not suitable for the production of other forms of fertilizers due to high humidity and pollution issues [8].

Since the content of nutrients is not limited by their solubility, it is easy to obtain fertilizer suspensions with almost any proportions among the nutrients [8,17]. This creates great flexibility in the selection of fertilizer mixtures [6]. Currently, almost all substitutes of classic solid fertilizers are produced in the form of suspension [11].

Having any combination of components in the fertilizer suspension makes it possible to adjust the fertilizer composition to the specific needs of the cultivated plants [6,8]. At the same time, different variants of the ratio of individual fertilizer components enable their application according to soil fertility [11].

An important advantage of this type of product is the possibility of introducing additional substances improving the condition of plants, together with the nutrients [17]. Microelements in the desired concentrations and forms can be included in the structure of suspension fertilizers without any problems [8,11]. It is also possible to use fertilizer suspension as a carrier of plant protection products, vitamins, nitrification inhibitors, etc., regardless of their physical form [8,17]. Pesticides that are introduced into a suspension fertilizer may dissolve in it or be dispersed as fine, insoluble particles or immiscible liquids [12]. The advantages of the agricultural application of suspension fertilizers are shown in Figure 2.

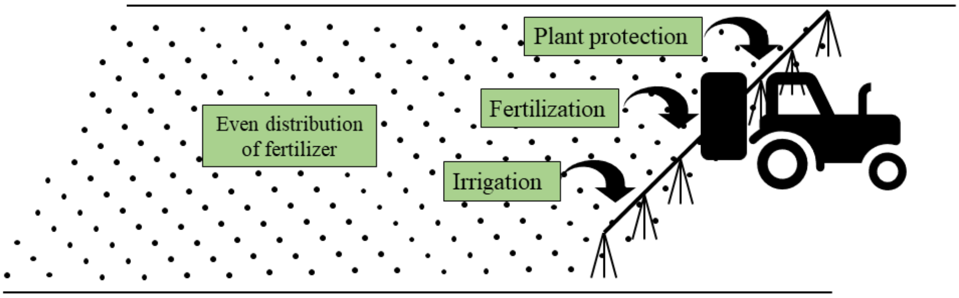

Figure 2. Application of suspension fertilizers. Suspension fertilizers can be applied to the field using typical agricultural equipment, in conjunction with irrigation and plant protection treatment. The effect of such fertilization is an even distribution of the fertilizing ingredients over the surface of the field.

The wide range of possibilities for enriching suspension fertilizers with additional ingredients allows for combining fertilization with other agrotechnical treatments. In addition to combining fertilization and plant protection, a variant including irrigation is also available [8].

A common feature of liquid fertilizers, in both clear and suspension fertilizers, is the high homogeneity of the chemical composition [8]. This results in significant functional benefits related to the even distribution of fertilizer on the field [7,8,18]. There is no separation of components, as is the case with solid fertilization [6,7]. Precise dosing is particularly important in the case of microelements introduced into the fertilizer in small amounts [6,8].

The liquid form ensures the better availability and utilization of nutrients by plants in comparison with the equivalent doses of solid fertilizers [6,7]. Higher yields are also the result of a high, even distribution of nutrients and the adjustment of their composition to the individual needs of the cultivated plants [6]. Moreover, suspension fertilizers give better yield results in those years with lower rainfall [6].

The production of granulated fertilizers at the stage of evaporation and granulation causes the emission of substances harmful to the environment into the atmosphere—mainly ammonia vapors, nitrogen oxides, sulfur oxides and a significant amount of dust from the finished products. In the production of liquid fertilizers, the technological line has been shortened at the most burdensome stages for the environment: granulation, drying, classification and packaging [11]. Additionally, hermetic devices and pumps limit the emission of harmful dust and gases [8]. Figure 3 shows a comparison of the production stages of solid and liquid fertilizers.

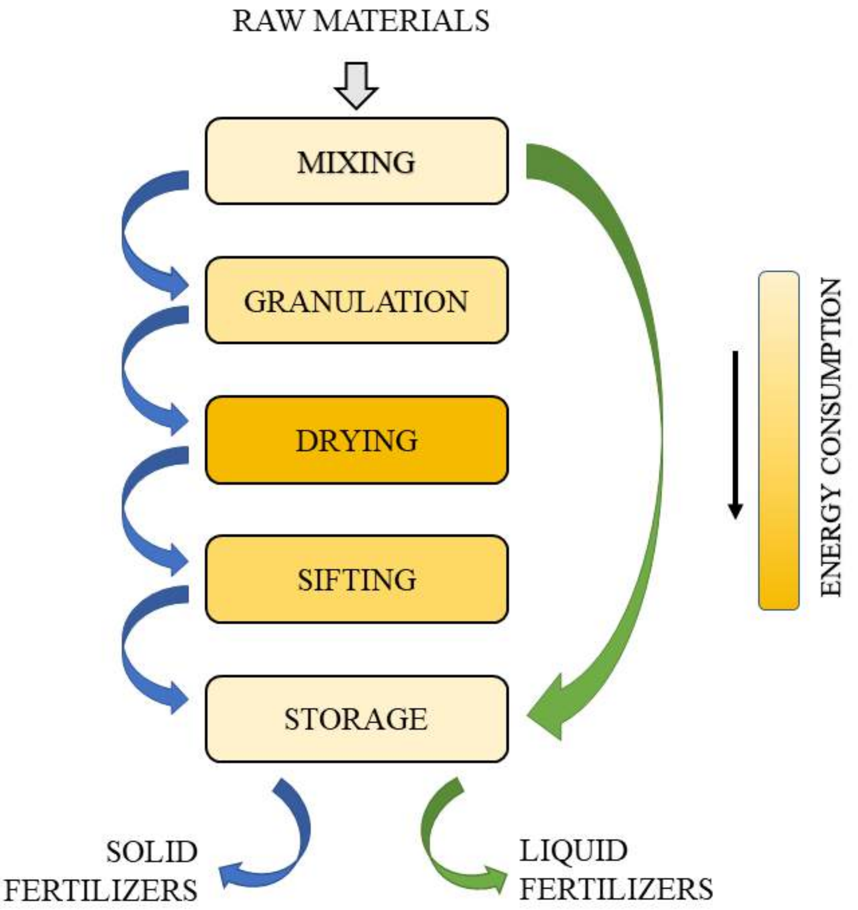

Figure 3. The production of liquid fertilizers consists of two main steps: mixing and storage. Conversely, the production of solid fertilizers consists of the following stages: mixing, granulation, drying, classification and storage. The stages marked with a darker color in the figure require more energy than those marked with a lighter color.

Suspension fertilizers are convenient to use, transport, reload and store [8,18]. Their production and operation are not very laborious because they can be fully mechanized [6,13,14]. As the fertilizer is liquid, it can be pumped through pipes and can be sprayed onto the soil through nozzles. Therefore, the amount of work associated with the application is reduced [19]. These fertilizers do not require packaging, which reduces the consumption of non-biodegradable packaging, and do not contain ballast substances, e.g., anti-caking agents [8].

The use of suspension fertilizers improves the soil structure, thanks to gelling clay substances. Before applying the fertilizer, these substances are designed to disperse the insoluble elements of the suspension system and, when applied to the soil, increase its absorbency [8].

In the case of liquid fertilizers, the difficulties related to segregation and caking, which accompany the storage of solid fertilizers, are eliminated [18]. Due to its liquid form, the explosion hazard associated with the use of solid ammonium nitrate was also excluded [8,19].

Despite numerous advantages, suspension fertilizers also have disadvantages that limit their use. Their main disadvantage is a short storage period, due to their limited stability over time. Therefore, these fertilizers are usually produced for local needs and their storage time is at most a few days [14]. Suspension fertilizer stations must be located close to the fertilized farmland. The use of fertilizer suspensions is most advantageous in the case of large farms with non-dispersed arable land [17]. In addition, suspension fertilizer can have a corrosive effect on storage tanks [20].

4. The Impact of Suspension Fertilizers on the Natural Environment

Over many years, a simple correlation between the amount of fertilizer produced and the production of food has proven itself. It meant that the main goal of the fertilizer industry was to provide agriculture with a sufficiently large quantity of fertilizers. In order to meet these requirements, many new fertilizer factories were launched, and the production capacity was increased [8]. This had a negative impact on the condition of the natural environment, due to the emission of toxic gases, sewage, dust and the produced waste [8,20].

Over-fertilization in the intensive agricultural production system is usually associated with the low efficiency of their use by arable crops. Excess amounts of nutrients, which the soil matrix cannot retain, are released into the atmosphere, e.g., N_2O, NO_x, NH_3, and N_2, and into groundwater and/or surface waters, e.g., NO_3, HPO_4^{2-}, $H_2PO_4^{-}$ [21].

Elements such as nitrogen, phosphorus and potassium are the main factors determining plant production but, at the same time, they can be a potential source of hazards to environmental components such as water, soil, and the air. For this reason, one of the main pillars of sustainable fertilization is the effective use of nutrients [6].

In terms of ecological fertilization, suspension fertilizers demonstrate a wide range of activities. Reducing the nuisance of fertilization for the environment can be achieved by using a liquid form of fertilizer [10,11]. It ensures better utilization of nutrients by plants, limiting the amount of leached nutrients into groundwater. On the other hand, the possibility of fertilization under the soil surface reduces the gaseous losses of nitrogen compounds [6,22].

Greater accuracy in the application of fertilizers in the field with the use of liquid fertilizers significantly improves the efficiency of fertilization [10]. The excessive local concentration of a given nutrient causes its loss because the plant is unable to fully absorb it. Over time, nutrients are leached out of the root system, becoming inaccessible to the plant and accumulating in the environment. Figure 4 shows the environmental benefits of using suspension fertilizers [6,10].

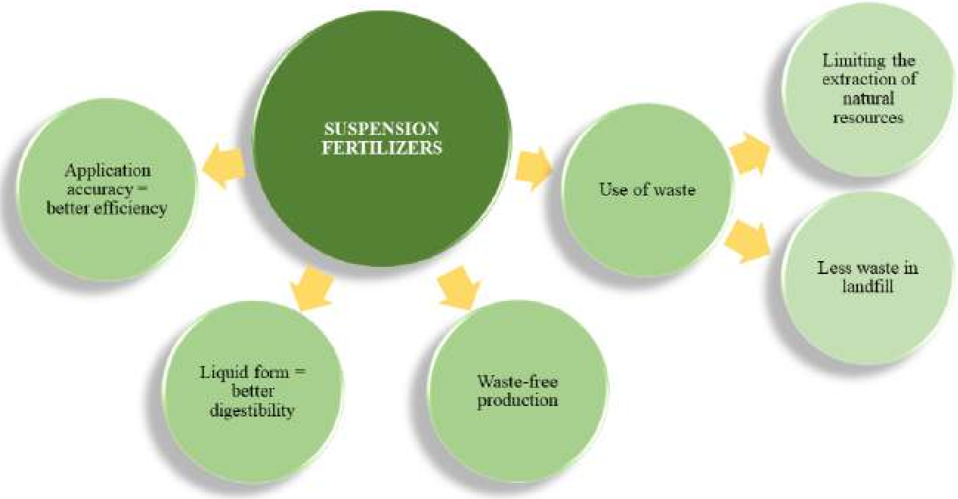

Figure 4. The positive impact of suspension fertilizers on the environment. The use of suspension fertilizers promotes the better use of fertilizing ingredients thanks to the liquid form and even distribution of the fertilizer in the field. The production of fertilizers is waste-free. The use of waste materials in their production results in the lower extraction of natural resources and a smaller amount of landfilled waste.

Using the suspension form of a particular fertilizer is also ecologically beneficial, due to the possibility of utilizing waste substances from other industries in its production [20]. As a result, valuable components can be recovered from the waste stream, and the amount of waste deposited and the extraction of natural resources is reduced [9,20].

The popularization of suspension fertilizers in common use is a response to the current and possible future problems related to the growing amount of waste and the depletion of natural resources. Suspension fertilizers fit into the changing structure of farms, manifested by increased mechanization and the drive toward large-scale, undivided arable land.

5. Economic Effects of Using Suspension Fertilizers

The production and application of suspension fertilizers is justified from the economic point of view, which has a major impact on the demand for this form of fertilizers among farmers. These benefits are a consequence of the physical form of the fertilizer, which is the suspension.

The production of mineral fertilizers is one of the large-tonnage processes, where production costs strongly depend on the raw materials used [23]. In the case of suspension fertilizers, it is possible to use raw materials of lower purity and limited solubility, which are usually cheaper [11,24]. In their production, for example, dusting materials and sparingly soluble salts of micronutrients can be used [8,24].

Agri-food production largely contributes to the exploitation of natural resources. Their scarcity leads to higher production costs in the sectors that use them, including the fertilizer sector [4]. In this aspect, suspension fertilizers create additional opportunities to reduce costs by managing waste substances for their production [8,23].

The technology of the production of suspension fertilizers requires lower operating and investment outlays [8,11]. Compared to the production of solid fertilizers, the construction of granulation and drying nodes is unnecessary, which account for about 60% of fertilizer production costs [6,11]. The liquid form ensures fewer losses related to storage, transport and application [6]. Other benefits of using liquid fertilizer include the elimination of the cost of water evaporation [6,8,19].

Savings are also generated by reducing the number of passes in the field when fertilization is combined with other agrochemical treatments. This is a significant saving, due to rising fuel and labor prices. A high concentration of suspension fertilizer reduces transport costs [7].

Since no waste substances are generated in the production process, the costs of waste disposal or storage are eliminated [9,16].

6. The Required Parameters for Suspension Fertilizers

The primary role of fertilizers is to increase the quality and quantity of the crop. In order to achieve the assumed yield-forming effects, each form of fertilizer has individual requirements resulting from its physical form.

Obtaining the desired parameters of suspension fertilizers requires an appropriate method of their production, the use of appropriate raw materials and semi-finished products, as well as the availability of specialized equipment [8].

Due to the large use of liquid suspension fertilizers in the United States, many procedures are the result of operating experience in this field by the American Tennessee Valley Authority [8].

In the case of suspension fertilizers, it is important to maintain the homogeneity of composition in the entire volume of the fertilizer, from its production to the moment of application [8]. A stable structure during storage determines the possibility of trading these fertilizers [8,13,14]. In suspensions with low gel strength, the suspended particles easily agglomerate into larger particles and sink faster. If the falling particles form a fluffy sludge, they are easily re-dispersed by agitation or recirculation. If, on the other hand, the formed sediment is rubbery, it is impossible to restore the gel structure. To remedy this, it is necessary to use more stabilizing agents, improve the quality of the dispersion, reduce the size of the suspended particles, quickly cool the mixture to produce smaller crystals, or select the appropriate ingredients to create crystals of the appropriate shape. Long storage time influences the growth of crystals that, due to their weight, are more and more difficult to keep suspended in the gel structure. This is the result of slow cooling and cyclic temperature changes. This effect can be minimized by periodic stirring or bubbling. The separation of a clear liquid layer on the surface or in the middle of the suspension, called the supernatant, is an undesirable phenomenon. This is due to shrinkage of the gel structure, called syneresis. It may cause the excessive growth of crystals at the interface, which may result in the formation of deposits capable of cementing the bottom of the reservoir. A blend with such a defect can be easily homogenized by mixing and recirculation. The formation of a supernatant layer indicates improper preparation of the suspension, in which the gel structure is physically unstable until syneresis occurs. In order to improve the parameters of such a suspension, it is necessary to use a larger amount of stabilizing agent at the preparation stage or to better disperse it [12]. Crystals can also be formed as a result of vibrations generated in the transport process. The number of deposited crystals should not exceed 2% of the product volume [8]. For the suspension to be allowed for use, the formed crystals should pass through a 0.246 mm (60 mesh) sieve [8,12]. However, if the crystals present in the suspension can be crushed by recirculation of the suspension or bubbling gas, the fertilizer is still fit for use [25].

For application reasons, an important parameter of suspension fertilizers is the possibility of free, gravity outflow. This value, determined by the pourability index according to American standards, should be 98% at 27 °C [8].

The desired rheological properties are a high apparent viscosity at low shear forces and low apparent viscosity at high shear forces [8,12,25]. Preferred viscosity values are not more than 1000 mPa·s at 27 °C and 1500 mPa·s at 30 °C [8,25]. Suspensions exhibiting this viscosity are stable under pumping and gravity flow, i.e., low shear conditions. On the other hand, low viscosity at high shear rates facilitates the formation of drops during the application of the fertilizer suspension [8,25]. Therefore, this parameter is necessary to determine the technical parameters of equipment intended for the application of suspension fertilizers [13,14]. The permissible range of density for suspension fertilizers should be in the range of 1200–1400 g/cm^3, while the fluidity determined with the use of the outflow cup should be characterized by the outflow time within the range, at 10–15 s [26].

For suspension fertilizers based on monoammonium phosphate, additional criteria were established due to the impurities introduced with it into the fertilizer. For such a fertilizer to be successfully stored for a long time, the quantity of water-insoluble solids, the total amount of cationic impurities (Fe_2O_3, Al_2O_3, CaO and MgO) and the ratio of these cations to fluorine are important. Monoammonium phosphate products with a low cationic to fluorine ratio, low water-insoluble solids and low R_2O_3 (Fe_2O_3 + Al_2O_3) levels result in a higher-quality suspension that is stored longer than products with a higher cation to fluorine ratio and high solids insoluble in water and R_2O_3 [25].

Research by the Tennessee Valley Authority has shown that the addition of fluoride ions can improve the physical properties of monoammonium phosphate fertilizers containing metallic impurities. In granular ammonium phosphate, compounds that form a sludge and gel have been identified, after the use of ammonia in the production of suspension fertilizers. The main cause of the gelation or solidification of suspension products made of monoammonium phosphate, where all phosphorus present is in the form of orthophosphate, are iron, aluminum and ammonium phosphates derived from monoammonium phosphate, which, when converted to suspension fertilizer, forms an iron-aluminum-phosphate-water gel. This gel traps and retains a large volume of water, causing the suspension to become highly viscous or to solidify during production and/or storage [27]. The total amount of cationic impurities, expressed as the percentage by weight of Fe_2O_3, Al_2O_3, CaO and MgO, in granular monoammonium phosphate, in relation to the amount of fluorine, should be at a maximum of 3, and the solids content should be no more than 17% [25,27].

It was confirmed in related studies that the addition of fluorine prevents the precipitation of the metal-phosphate-H_2O compounds contained in ammonium phosphate. Fluoride precipitates magnesium, calcium, and aluminum as fluoride instead of phosphate compounds, which greatly increases the amount of the solution phase, improves the solubility of nitrogen and phosphate in water and prevents the formation of sludge or gels during storage. The maximum amount of fluorine addition, in the form of 23% fluorosilicic acid, is only 0.7% by weight, which is decomposed in suspension into ammonium fluoride, silica gel and ammonium fluorosilicate. When fluorosilicic acid is added after the ammonification step, or in a reaction step where the pH is at least 6, the silica gel hydrates, resulting in an increase in viscosity. Adding it before the ammonification step releases fluorine as NH_4F, and the heat of the reaction dehydrates the silica gel, preventing the slurry from gelling. The addition of fluorine in the form of fluorosilicic acid also significantly reduces the content of P_2O_5, which is insoluble in citrate from monoammonium phosphate [27].

The given recommendations for suspension fertilizers are relatively easy to meet without the use of specialized equipment and with good-quality raw materials.

7. Stability of Fertilizer Suspensions

Stability is the basic factor determining the quality of the suspension. The components of the fertilizer suspension can be kept in a dispersed form only in the presence of a thickener [15]. A high concentration of nutrients in suspension fertilizers is possible, due to the introduction of a substance keeping them in suspension in a regular manner [7]. The main factor ensuring the normative properties of the suspension fertilizer is the dispersion gelling agent [8]. It plays a stabilizing role, giving the liquid the features of a non-Newtonian system where sedimentation is inhibited. The addition of this factor is also accompanied by an increase in the viscosity of the liquid [8,11].

For suspension fertilizers, high gel strength values are highly desirable, affecting the stabilization of suspensions during transport and storage. Moreover, dispersing agents introduced into liquid fertilizers must have an appropriate chemical composition, especially a limited content of heavy metals, and should not interfere with the availability of nutrients for plants [11].

Clay minerals work best in this role [8,13]. They have a large specific surface, which results in excellent sorption properties [28]. Their addition means that, apart from their swelling and ion-exchange action in the fertilizer, after introducing them into the soil they will improve its structure [11,29]. This influences the increase of water sorption in the soil and the accumulation of nutrients, which significantly improves the development of vegetation [14,28].

Clay minerals consist of crystals with a well-defined structure that is mainly layered, with a length of less than 2 µm and a thickness of less than 10 nm [8,28]. The silicate layers are connected by weak interlayer bonds in which the weakly bound cations can be exchanged for other cations and water [8]. The interlayer water loosens the inter-package structure, causing swelling and the formation of crystal agglomerates, forming a needle-like gel network structure [8,11]. Taking into account the crystal structure, clay minerals can be divided into kaolin, with a uniform chemical composition, and smectite, which differ significantly from each other [28].

Minerals from the smectite group are layered silicates with a block structure. There are exchangeable cations between the packages, most often Mg^{2+} and Ca^{2+}, as well as Na^+. The type of dominant cations in exchange positions affects the properties of the clay material [30]. A common property of smectite-rich rocks is the ability to absorb cations and to swell, disperse with water, and form thixotropic suspensions [7,30].

In industry, clay minerals in the amount of 0.5–3% are most often used to stabilize fertilizer suspensions [8]. These are usually minerals from the smectite group, such as attapulgites and bentonites [8,10,13]. For this purpose, organic compounds can also be used, e.g., sorbitol, starch, protein hydrolysates and keratin hydrolysates 1 [7,8,31].

In the United States, attapulgite clay is generally used in the production of fertilizer suspensions [11]. It perfectly meets the requirements for the production and use of fertilizer suspensions; however, it is only available in limited areas in the USA. The main component of this mineral is clusters of hydrated threadlike crystals of magnesium aluminum silicate [11,32]. In the water environment, these agglomerates break down during dispersion, forming a gel with a needle-like mesh. This structure increases the viscosity of the medium and inhibits the sedimentation process of solid fertilizer particles [11,19].

Bentonite is also an aluminosilicate with a layered structure, with the ability to form a gel, especially after activation with Na_2CO_3 solution [11]. Bentonites are formed as a result of the weathering of silicate-aluminum rocks and subsequent sedimentation in the aquatic environment [7].

The effect on gel strength was also noted with the addition of chemical agents, such as tetrasodium diphosphate and fluorosilicate acid. The increase in gel viscosity and strength in suspensions containing polyphosphates is caused by the retraction of condensed phosphates to orthophosphates. Orthophosphates are less soluble compared to polyphosphates, so the number of suspended particles in the suspension increases [12].

To prevent the potential degradation of the gel, the gelling agent is pretreated. As a result, it is possible to crush them to the maximum, activate them with alkali metal salt solutions and introduce them to production directly in the form of a gel structure [8].

Despite the use of the correct gelling agent, there may be disadvantageous consequences changing the properties of the system. In the fertilizer suspension, which is a multicomponent and multiphase system, this may take place under the influence of an agent stabilizing harmful chemical reactions and physical phenomena. Often, freshly prepared suspensions have a greater gel strength than suspensions stored for longer (more than 24 h). This is due to air bubbles that are drawn in at the stage of preparing the suspensions. The strength of the gel decreases as the air bubbles leave the system. Gel strength is also dependent on how the suspension has been handled in earlier steps. The strength of the gel in the suspension immediately after mixing is lower than it is in the same suspension when left for several hours. One very important aspect in the case of agricultural suspensions is the ability to quickly recover gel strength after the breakdown of the gel structure, due to mixing and pumping [8,12].

Temperature may also have a negative impact on suspension stability [10]. Due to temperature changes during storage, large beam-shaped crystals may crystallize out of a saturated solution. Their presence in the suspension makes it difficult to pump the product and also causes the overgrowing of tanks and spray nozzles, disrupting the fertilization process [8,10].

One of the methods of preventing this phenomenon is the addition of small amounts of a substance modifying the shape of the crystals. Such a modifier may, for example, be H_2SiF_6, introduced into the fertilizer in the amount of 0.3–0.5%. It prevents the flocculation process that promotes sedimentation and the syneresis process. Syneresis is a phenomenon caused by the shrinkage of the gel, as a result of which, a layer of clear liquid appears over the gel. The presence of this layer promotes the nucleation and growth of large crystals. In order to eliminate this undesirable effect, fertilizer producers increase the amount of the added gelling agent and have also perfected the method of its activation [8]. A practical dispersing treatment is, for example, the addition of tetrasodium pyrophosphate, which improves the dispersion [12].

However, it is mainly necessary to ensure the correct pH of the solution. In the case of fertilizers based on ammonium phosphate, this results in the precipitation of fine $(NH_4)_2HPO_4$ crystals in place of large $NH_4H_2PO_4$ beam crystals [8].

The production and longer storage of suspension fertilizers may be accompanied by the process of stratification. As a result, layers appear in the product, as shown in Figure 5, in the order below: sedimentation, a cloudy layer of suspension, a layer of clear liquid (supernatant) and a layer of permanent foam. The reason for this may be errors made during the production of fertilizers; it may also be related to the absorption of air bubbles and carbon dioxide, the gradual desorption of air, and the coexistence of the emulsion phase formed during the emulsification of mutually insoluble liquids, which occurs when combining suspension fertilizers and plant protection products [8,12].

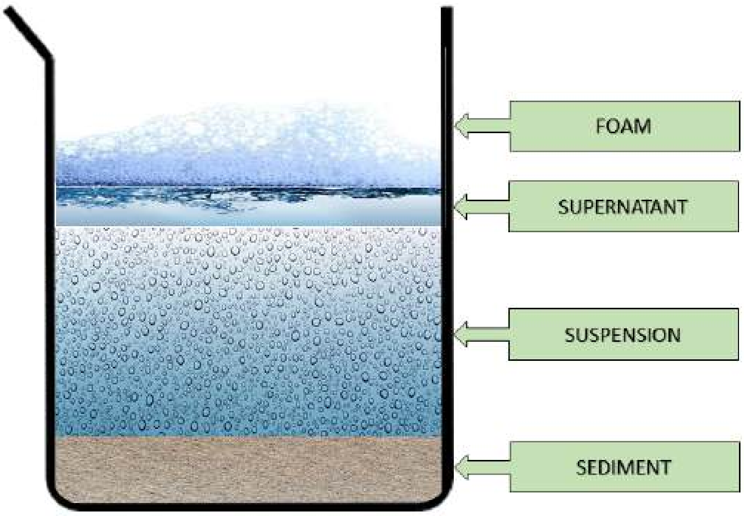

Figure 5. Layers that may appear in the fertilizer during longer storage, in the following order: sedimentation, a cloudy layer of suspension, a layer of clear liquid (supernatant) and a layer of permanent foam.

The stability of the system may be positively influenced by the chemical reactions taking place in it, eliminating the effects of reducing the viscosity of the system, which may be caused by air desorption or the biodegradation of organic components, in the case of mineral-organic fertilizers. Positive effects, in this aspect, are observed by using poly-phosphorus compounds or condensed phosphates in fertilizers as a source of phosphorus. Polyphosphoric anions have the ability to sequestrate Fe^{3+} and Al^{3+} ions and, successively, as the poly-phosphorus chain decays into ortho-phosphorus ions, they release aluminum and iron compounds in colloidal form. Thus, the viscosity of the system increases, inhibiting the sedimentation process [8].

The use of phosphate raw material in the form of post-neutralization sludge also brings a number of benefits because, apart from the very good absorption of phosphorus it offers, it has a stabilizing effect on the fertilizer suspension. Replacing the phosphorus raw material in the fertilizer with at least 50% from post-neutralization sludge eliminates the need to use a stabilizing additive. The high stability of suspensions in systems with post-neutralization sludge is the result of a strong salt effect. This increases the solubility of individual fertilizing components so that the obtained fertilizer solution has a density close to that of the suspension it contains. As a consequence of increasing the density of the solution, the suspended particles are more easily kept in the fertilizer suspension and do not sediment. If the fertilizer is supplied with phosphorus that is 50% from post-neutralization sludge, it is not advisable to use additional stabilizers, as this would increase the viscosity of the fertilizer unnecessarily and make their application difficult. By replacing the phosphate raw material, with at least 20% from post-neutralization sludge, a better-quality product in terms of stability is obtained than in the case of using ammonium phosphate entirely [16].

The stability of the suspensions is a key parameter determining the quality of this type of liquid fertilizer. To ensure it is at the appropriate level, it is necessary to use a stabilizing agent and appropriate techniques for preparing suspensions. Nevertheless, the occurrence of delamination can, in most cases, be readily corrected by remixing.

8. Suspension Fertilizers from Waste Materials

Most production processes are accompanied, as well as the main product, by the generation of significant amounts of waste [23,26]. They are generally irrelevant to the main production but often have valuable components from the point of view of other technologies. Industrial waste is used to a varying degree but still has great economic and pro-environmental potential [9,26].

A new perspective of using the suspension form of fertilizers is the possibility of utilizing environmentally harmful waste in their production cycle [8,20]. Many wastes contain chemical compounds that are valuable from the point of view of fertilization, but some of their properties preclude their economic processing [4,26].

The disadvantages of the waste include low solubility, high moisture content, unstable composition and high fragmentation, resulting in excessive dusting [20,26]. These features make their use in the continuous production of fertilizers difficult, and sometimes impossible [26]. Clear liquid fertilizers have the least possibilities of using cheaper alternatives in the form of waste, due to the requirement of high purity of raw materials. However, in the case of solid granular fertilizers, the need to evaporate a large amount of water makes the process unprofitable. Compounds contained in waste may deteriorate the properties of such fertilizer—critical humidity, compressive strength of granules, and storage time [20].

Nevertheless, these factors are not a problem in the production of suspension fertilizers. In this case, the nutrients do not have to be completely dissolved, and high water content is not an obstacle [20,26]. An additional advantage is batch production, which allows the use of raw materials with a variable composition [26].

From the agronomic point of view, the use of waste for the production of fertilizers is possible when they contain significant amounts of plant nutrients and when their composition contains a limited quantity of substances that are not only toxic to plants but also to those humans and animals consuming the crops. Moreover, the components contained in the waste material should not cause changes resulting in the deterioration of the properties of the fertilizer and negatively affect the production technology [20,23]. In economic terms, the cost of their processing should not reduce the market competitiveness of the fertilizer based on them [23]. However, for safety reasons, their use should not generate toxic gases [20].

Converting waste into valuable fertilizer has positive environmental effects. First of all, the extraction of natural resources is reduced, and the amount of landfilled waste is limited. At the same time, the raw material that is of waste origin is much cheaper, which allows manufacturers to reduce production costs and, as a result, offer cheap and effective suspension fertilizer [9,23].

Recovering valuable components from the waste stream is part of the circular economy strategy. It aims to increase resource efficiency and reduce the dependence on imported raw materials [31]. This is especially true of the phosphorus raw material, the limited deposits of which, in the form of apatite and phosphorites, contain significant amounts of impurities [4,31].

Many effective attempts have been made to manage waste from various industries. One of them is the management of sludge from the production of extinguishing agents formed during the alkaline hydrolysis of keratin, which is rich in phosphorus, potassium and calcium. By supplementing the waste with nitrogen, magnesium and microelements, a multicomponent suspension fertilizer was obtained with the desired agronomic and technological properties. Due to the use of magnesium and micronutrients in the form of an acetate solution and polypeptides, a synergistic protection effect against plant pathogens was obtained. On the other hand, the presence of an organic form of nitrogen, which is less freely available to plants, prolongs the effect of the fertilizer [8].

Work on suspension fertilizers using post-extraction peat sludge produced in the process of alkaline extraction of humus compounds that are used for the production of drugs and peat preparations was also successfully completed. Nitrogen compounds in the form of ammonium sulfate and urea, microelements, and bentonite for stabilization purposes were introduced into the waste to produce a fertilizer suspension. During the production process, nitrogen compounds contained in peat were also activated. As a result, a fertilizer with confirmed agricultural effects and good physical properties was obtained [8].

Livestock waste, such as poultry farm manure, can also be used for fertilization. To reduce the population of pathogenic bacteria and fungi, acidic substances, such as phosphoric and sulfuric acid or urea phosphate, can be added to this type of waste. The specific detoxification of farm waste, increasing the concentration of nutrients and neutralization of the suspension with ammonia water to a pH in the range of 6.5–7, results in a satisfactory fertilizer [8].

The possibility of processing filter sludge from the production of extractive phosphoric acid into suspension fertilizer was also tested. This waste is characterized by not only a high moisture content of nearly 50% but also a high P_2O_5 content of approx. 20%. In order to transform the waste into fertilizer, the content of nutrients was supplemented by adding ground phosphate rock, potassium salt, urea-ammonium nitrate solution, ammonium sulfate, urea and bentonite stabilizing the whole, in amounts depending on the desired composition of the final fertilizer. Additionally, in this case, many positively assessed fertilizer combinations were identified [26].

The production of magnesium sulfate, consisting of the decomposition of burned magnesite with sulfuric acid, is accompanied by the release of a precipitate, the so-called post-magnesium mud. It is a valuable source of calcium, magnesium and sulfur, which can be successfully reused in the production of suspension fertilizers [9].

The effective use of sodium sulfate solutions, generating by-products via the production of trimethyl-propylene, in the production of suspension fertilizers was also confirmed. The use of this waste does not reduce the total concentration of nutrients. The only condition for suitability here is adequate purity [14].

An interesting proposal is the use of waste potassium sulfate from the production of biofuels. The suspension fertilizers produced using it as a basis have favorable rheological properties and a high content of nutrients. There is no need to apply an additional substance stabilizing the suspension and there is a great possibility of configuration with other raw materials [26].

Industrial processes generate a great deal of waste, the hydrated form of which makes it difficult to process economically. On the other hand, the disposal of waste in the production cycle of suspension fertilizers is relatively simple and does not require expensive modernization of the installation. In this matter, it is important to coordinate the activities of fertilizer producers and industrial plants.

9. Conclusions

The article is a compendium of knowledge on suspension fertilizers in relation to modern agriculture and environmental requirements. It presents their characteristics, taking into account their advantages and disadvantages, offers a comparison with other forms of fertilizers, and establishes the required parameters—in particular regarding stability, environmental impact, and economic analysis of their production and use. The possibility of using hydrated waste, the management of which is often problematic, in the production of liquid suspension fertilizers was also presented.

A recent revision of the EU regulation on the placing of fertilizers on the market includes the possibility of using waste for the production of fertilizers and soil conditioners. These changes may contribute to the increased interest in suspension fertilizers, thanks to which it is easy to manage waste with high water content. This prospect is also supported by the high prices of pure fertilizer raw materials and their limited resources, especially phosphorus.

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Article

The Possibility of Using Waste Phosphates from the Production of Polyols for Fertilizing Purposes

Paulina Bogusz [1,2]

[1] Fertilizers Research Group, Łukasiewicz Research Network–New Chemical Syntheses Institute, Al. Tysiąclecia Państwa Polskiego 13a, 24-110 Puławy, Poland; paulina.bogusz@ins.lukasiewicz.gov.pl
[2] Department of Agricultural and Environmental Chemistry, University of Life Sciences in Lublin, Akademicka 13, 20-950 Lublin, Poland

Abstract: The limited resources of phosphorus raw materials, which are located outside of Europe, make it necessary to obtain phosphorus from the waste stream. This is reflected in the new EU Regulation 2019/1009, which concerns making fertilizing products available on the market. Its main goal is to harmonize the standards for fertilizers obtained from organic or secondary raw materials in the EU and to create new opportunities for their production and sale. The fertilizer sector uses almost 90% of the phosphorus raw material, for which there is no substitute, and the demand for fertilizers is constantly growing, stimulated by the growing number of people. A substitute for expensive imported raw materials can be waste sodium–potassium phosphate from the production of polyols. This study analyzes the composition and form of waste from PCC Rokita S. A. from Brzeg Dolny in Poland, in terms of the possibility of using it in the production of fertilizers according to the new EU regulations. Research shows that it contains nearly 19% phosphorus, as well as potassium and sodium. Low-level impurities and low organic matter content classify it as a raw material for the production of inorganic fertilizers. Due to the high water content, the most advantageous form of its use is the production of fertilizers in the form of a suspension. A certain difficulty in the production of this type of fertilizer may be the layers of crystals of different sizes precipitating in the waste.

Keywords: phosphorus; critical raw materials; circular economy; fertilizers; waste management; liquid waste

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1. Introduction

The population is growing very fast and in order to meet its requirements, plant growth intensification measures are necessary. Phosphorus, along with nitrogen and potassium, plays a key role here. As a building block of living organisms, it is one of the most important elements for plants and animals [1–4]. It is necessary to supplement its deficiencies in the soil [2,5].

Phosphorus deficiency in soil is often the main factor limiting plant growth. Its insufficient amount, especially in the early stages of the development of one-year-old plants, may result in a reduction in the yield. Later adjustment of its dose will not restore normal plant growth [6].

The world's profitable reserves of phosphate are gradually declining [2]. It is estimated that their production capacity is in the range of 165–195 million tons per year. Specialists determine the duration of use of such resources differently, but they agree on one thing: they are a non-renewable source and sooner or later they will be exhausted [7,8]. Another problematic issue is the uneven distribution of phosphate mines of economic importance in the world [4,7]. More than two-thirds of the raw material they extract comes from Morocco, China, and the United States. Europe is almost entirely dependent on its imports [2,4,7,8].

The importance of this raw material for agricultural production is evidenced by the fact that over 80% of its resources are used for fertilization, where it is the basis for the production of almost all phosphorus fertilizers [7]. There is no way to compensate for its shortcomings in this sector by shifting resources from other industries [4,8].

This is particularly important due to the growing demand for fertilizers, stimulated by the continuous growth of the population [9]. The risk of deficits in the fertilizer market determines the threat to food production [10,11].

Rational phosphorus management is particularly important for European countries, where economically profitable resources of this raw material are small. As a result, Europe's dependence on the import of this raw material reaches 90% [4,10,12]. In order to minimize the impact of external markets, European Union countries turned to the search for alternative sources of phosphorus, including those from waste materials. This corresponds to the goals of the circular economy, which assumes the minimization and recycling of waste and the extension of the life cycle of economic products [4,13–15].

Losses of phosphorus concern not only the waste of natural resources, but also water, energy, and other resources used in its processing cycle. Thus, the production of fertilizers powered by waste materials brings both ecological and economic benefits. Taking this course of action in the long term will enable the closure of the phosphorus cycle [4,16].

The distribution and availability of phosphate ores are not the only problems for the fertilizer industry and its beneficiary, the agricultural sector. The pollution associated with phosphate deposits is of great concern. Cadmium is particularly dangerous, as it is mainly contaminated with phosphate minerals of sedimentary origin. This applies to deposits located in North and East Africa and the Middle East. Less pollution is observed in minerals of volcanic origin (deposits in Finland, Russia, and South Africa). When it enters the soil through fertilizers, it easily migrates and accumulates in plants [4,10]. Some crops, such as tobacco, rapeseed, and sunflower, tend to take up cadmium in particularly large amounts [4]. In turn, consumption of contaminated crops is the main route of exposure for humans [10].

The bad news is that there is no substitute for phosphorus, which is a non-renewable resource; the good news is that phosphorus does not disappear after use. The basic scenario assumes its uptake from ore and dispersion in the environment as a result of fertilization. The key to maintaining the continuity of its flow is sustainable management and its effective recovery from the waste stream. This is the way to guarantee phosphorus resources for future generations [4,9].

Additionally, in order to emphasize high economic importance and high supply risk, phosphorus and phosphate rock were included in the list of critical natural resources [10].

Limited resources of phosphorus raw materials, the political situation in the areas of their extraction, poor quality of exploited deposits, and increasing requirements for fertilizer products based on these conditions necessitate the development of new technologies for the processing of waste phosphorus raw materials [2,4]

In the EU, there is a great potential for recovering phosphorus raw materials from waste materials, including: municipal and industrial wastewater, sewage sludge, ashes from sewage sludge incineration, meat and bone meal, slurry, biomass, and industrial waste. Intensive work is still underway to allow for the economic processing of this waste, mainly for fertilization purposes, where the demand for this element is the highest [17].

Many effective attempts to manage waste from various industries in the production of suspension fertilizers have been made. One of them is the development of sludge from the production of firefighting agents formed during alkaline hydrolysis of keratin, which is rich in phosphorus, potassium, and calcium [18]. Peat slime from the alkaline extraction process of humus compounds used to produce drugs and peat preparations is also successfully used [18]. For fertilizer purposes, breeding waste, such as slurry from poultry farms, can also be used [18]. The possibility of processing this into fertilizer in the form of a suspension of filtration slime from the production of extraction phosphoric acid was also tested [19,20]. The production of magnesium sulfate, consisting of the decay of roasted magnesite with sulfuric acid, is accompanied by the formation of sediment. It is a valuable source of calcium, magnesium, and sulfur, which can be successfully used in the production of suspension fertilizers [21]. Effective use of sodium sulfate solution, emerging as a by-product in the production of trimethylpropane, has also been confirmed [22]. An interesting proposition is the use of potassium waste sulfate from biofuels. There is no need for the application of an additional substance stabilizing the suspension, and there is a large possibility of configuring with other raw materials [23].

Recently, an interesting option, using waste from the production of polyols in the form of an aqueous suspension of sodium and potassium phosphates, has emerged. Due to the high water content of these wastes, the possibilities of their economic processing are limited and so far, they have not been used. The greater emphasis on the recovery of the raw material from the waste stream contained in the new EU fertilizer regulations has contributed to the review of the possibility of its use and is undergoing research with its use in the production of suspension fertilizers [18,19].

In Poland, the largest producer of polyols is PCC Rokita in Brzeg Dolny, which generates approximately 1500 tons/year of waste phosphate salts in the form of a liquid suspension. It cannot be returned to the process and reused.

The aim of the research is to assess the possibility of using waste phosphates from the production of polyols from PCC Rokita S. A. for fertilization purposes based on the physico-chemical analysis of the waste.

2. Results and Discussion

2.1. Organic Carbon Content Analysis Results

The waste was left for the time needed to stabilize it, and then six samples were taken from the surface layer and subjected to TOC analysis to determine whether an organic layer was separating on the surface. The obtained results were then compared with the results obtained for the mean sample. Since the waste is in the form of an unstable suspension (part of the solid phase falls to the bottom during storage), three samples were taken for the analysis of the averaged sample during intensive mixing with a stream of compressed air. The results of the TOC measurements are summarized in Table 1 for the surface layer and Table 2 for a homogeneous sample.

Table 1. TOC analysis results for waste samples collected on the surface.

Sample	TOC [ppm]	Average
1	137 137 178	151
2	246 239 344	276
3	457 460 467	461
4	383 372 394	383
5	445 436 377	419
6	318 344 402	355
Average	341	

Table 2. TOC analysis results for mixed waste samples.

Sample	TOC [ppm]	Average
1	555 628 572	574
2	592 616 557	581
3	555 628 572	585
Average	586	

The samples taken from the surface layer showed a large variety of the obtained results. The results of the averaged samples were more stable. The average value of the organic carbon content in the surface layer (341 ppm) is lower than the average TOC value obtained for the homogenized sample (586 ppm). On this basis, it can be concluded that no organic layer is separated on the surface of the waste after settling. The mean TOC value of 586 ppm (0.0586%) in a sample homogenized by mixing with compressed air is low. Therefore, for a fertilizer produced by mixing this waste with other mineral raw materials, the organic carbon content will be even lower. According to the EU Regulation 2019/1009, a fertilizer with an organic carbon content below 3% (m/m) is classified as an inorganic fertilizer. The content of organic carbon at a level lower than 1% (m/m) additionally eliminates the need to test the content of pathogens in the fertilizer (*Salmonella spp. and Escherichia coli or Enterococcaceae*) [24].

2.2. The Results of the Chemical Analysis of the Waste

Waste phosphate from the production of polyols contains a large amount of water; therefore, it will be most economical to use it for the production of suspension fertilizers [25]. Therefore, Table 3 summarizes the results of the chemical analysis of waste along with the requirements for this type of fertilizer provided for in the new Regulation of the European Parliament and of the Council (EU) 2019/1009 of 5 June 2019: PFC 1 (C)(I)(b)(ii): multi-component liquid inorganic macronutrient fertilizer [24].

The high content of phosphorus in the waste, at the level of almost 19%, makes it an attractive raw material for fertilizing and confirms the economics of its use in the production of fertilizers. The content of pollutants in the waste is well below the threshold value established by the European Commission in the new regulations. This makes the tested waste a competitive raw material in relation to phosphate rock, often contaminated with cadmium [10,24].

2.3. The Results of the Sediment Composition Analysis in the Waste

During the storage of waste phosphate, three clearly separated layers are formed at its bottom (Figure 1). They differ in the composition and size of the crystals. The size of the crystals formed in the sediment is important when applying fertilizer based on waste phosphate from the production of polyols. The fine crystals that settle to the bottom can be successfully mixed again. On the other hand, large crystals will clog the spray nozzles in application/dispensing devices [25].

In the sample with sediment 1, there are two crystalline phases of $Na_2HPO_4 \cdot 2H_2O$ (ICSD 01-074-6210) with characteristic reflections for the angle 2θ: 10.5°; 16.8°; 19.1°; 27.3°; 31.1°; 32.6°, and KH_2PO_4 phase (LPF 04-007-5247) with reflections for 2θ angles: 23.9°; 30.7°; 33.9°; 46.5°. No other crystalline phases have been found, and if they are present, they are of small content in relation to those found. The $Na_2HPO_4 \cdot 2H_2O$ phase is approximately

62%, and KH_2PO_4 is approximately 38% of the crystal phases assigned to the performed diffraction pattern (Figure 2).

Table 3. The results of the chemical analysis of the waste.

Tested Feature	**Unit**	**Result y ± U [1]**	**Requirements for Suspension Fertilizers According to EU Regulation No. 2019/1009**
Phosphorus soluble in mineral acids expressed as P_2O_5	%	23.46 ± 0.3	min. 1.5% by mass of total phosphorus pentoxide (P_2O_5)
Potassium as K_2O	%	9.89 ± 0.16	min. 1.5% by mass of total potassium oxide (K_2O)
Sodium (Na)	%	7.60	min. 0.5%-max. 20% by mass of total sodium oxide (Na_2O)
Copper (Cu)	mg/kg	less than 1.0	6002
Iron (Fe)	mg/kg	46.0	-
Zinc (Zn)	mg/kg	less than 1.0	15002
Cadmium (Cd)	mg/kg	less than 1.0	60
Lead (Pb)	mg/kg	less than 8.0	120
Nickel (Ni)	mg/kg	less than 1.0	100
Aluminum (Al)	mg/kg	74.7	-
Arsen (As)	mg/kg	less than 4.0	40
Mercury (Hg)	mg/kg	less than 0.002	1
Chrome (VI)	mg/kg	less than 0.3	2

[1] The reported expanded uncertainty (U) is based on the standard uncertainty multiplied by a coverage factor k = 2 providing a confidence level of 95%. The uncertainty of sampling was not taken into account in the calculations (U). These limit values do not apply where an ingredient has been intentionally added to correct deficiencies in soil.

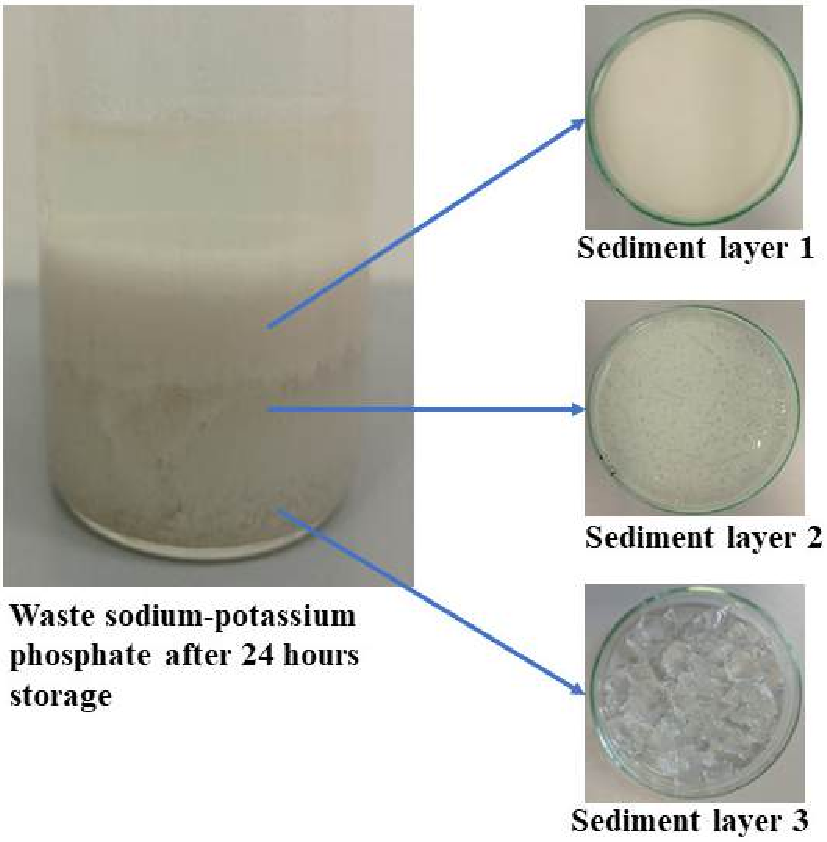

Figure 1. Sludge layers in waste phosphate with different crystal sizes.

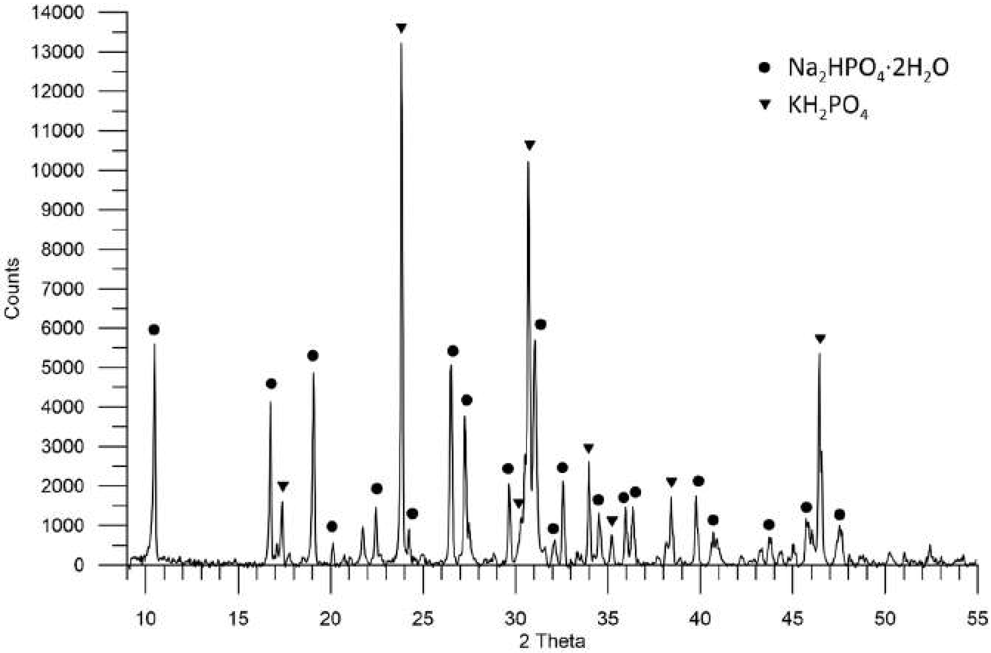

Figure 2. A diffractogram showing the composition of sediment 1 in the sample of waste phosphate from polyol production.

In the sample with sediment 2, there are two crystalline phases of $Na_2HPO_4 \cdot 2H_2O$ (ICSD 01-074-6210) with characteristic reflections for the angle 2θ: 10.5°; 16.8°; 19.1°; 27.3°; 31.1°; 32.6° and KH_2PO_4 phase (LPF 04-007-5247) with reflections for 2θ angles: 23.9°; 30.7°; 33.9°; 46.5°. No other crystalline phases have been found, and if they are present, they are of small content in relation to those found. The $Na_2HPO_4 \cdot 2H_2O$ phase is estimated to be 92%, and KH_2PO_4 to be approx. 8% of the crystal phases assigned to the performed diffraction pattern (Figure 3).

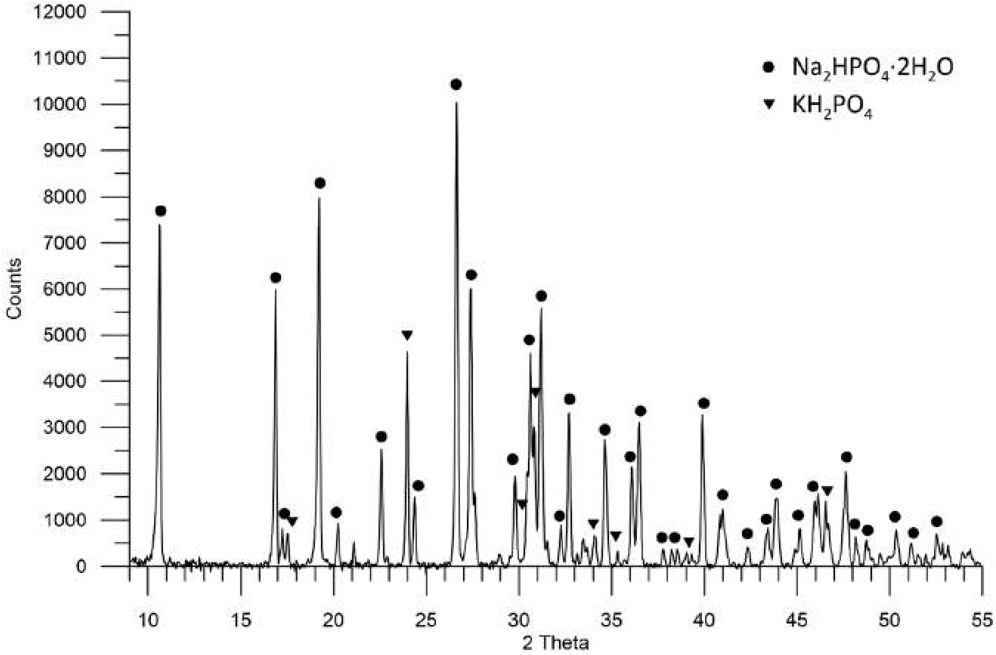

Figure 3. A diffractogram showing the composition of sediment 2 in the sample of waste phosphate from polyol production.

In the sample with sediment 3, the crystalline phase of $Na_2HPO_4 \cdot 7H_2O$ (ICDD: 00-010-0191) with characteristic reflections at the angle of 2θ: 16.2° can be distinguished: 20.9°; 29.5°; 31.2°; 31.7°. The second crystalline phase is $Na_2HPO_4 \cdot 12H_2O$ (ICDD 00-011-0657) with characteristic reflections at the angle of 2θ: 14.6°; 16.2°; 17.1°; 20.5°; 22.2°; 22.7°; 29.8°; 31.4°; 36.3°. These are the main crystallographic phases recorded on the diffraction pattern. Due to the lack of relevant information in the database for this sample, it is not possible to estimate the content of the phases present in it (Figure 4).

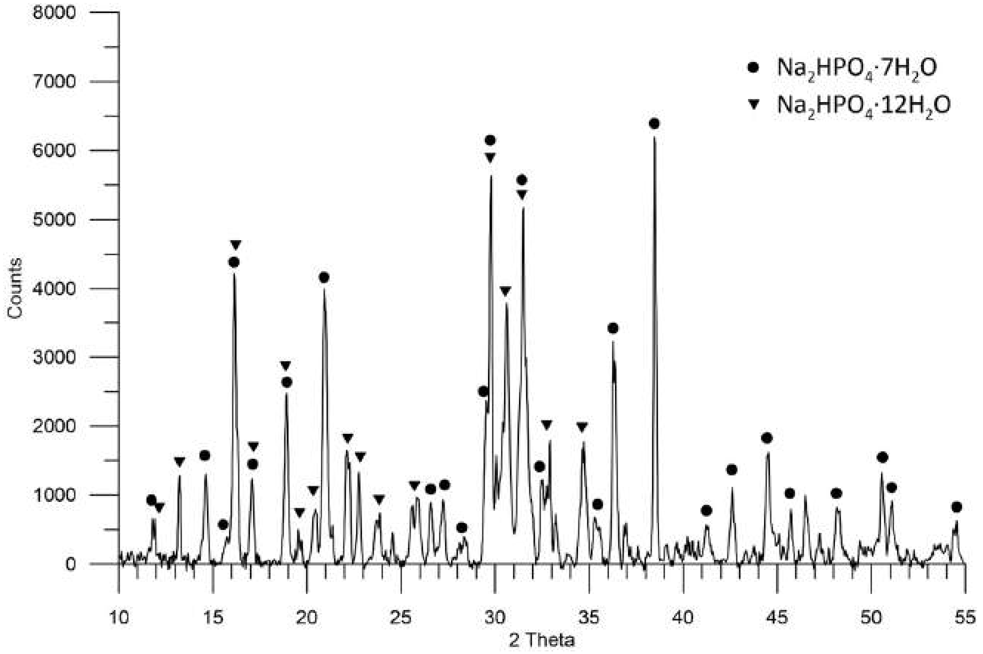

Figure 4. A diffractogram showing the composition of sediment 3 in the sample of waste phosphate from polyol production.

Sediment 1, which is the finest crystal, consists of two phases: hydrated secondary alkali metal phosphate—$Na_2HPO_4 \cdot 2H_2O$ (~62%) and primary alkali metal phosphate—KH_2PO_4 (~38%). On the other hand, sediment 2, whose crystals are larger, mainly consists of $Na_2HPO_4 \cdot 2\ H_2O$ (~92%). The largest crystals are formed by hydrated secondary phosphates: $Na_2HPO_4 \cdot 7H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ in sediment 3. They pose the greatest threat during fertilizer application. The conditions for the formation of individual layers in the waste phosphate sludge require further studies.

3. Materials and Methods

The research material is waste sodium–potassium phosphate from PCC Rokita S.A. in Brzeg-Dolny, Poland. There, waste phosphates are formed in the polyol production plant in the phase separation stage, where the organic phase (product), the aqueous phosphate phase, and the interphase containing the filter aid are separated. Phosphates are formed as a result of the neutralization of sodium and potassium ions (from the polymerization catalyst) with acidic disodium pyrophosphate.

Waste phosphates are in the form of an aqueous suspension with a water content of 49%. At PCC Rokita, it is not possible to reuse them in the polyol production process. However, the phosphorus salts contained in them are well-absorbed by plants and can be successfully used as a fertilizer component. The high water content of the waste, which is peeled after the production of polyols, significantly limits the possibilities of its economic processing. Evaporating such an amount of water would be very energy-consuming, which is associated with high costs. The best solution is to use unchanged waste phosphorus salts for the production of liquid suspension fertilizers.

3.1. Methods for the Analysis of Organic Carbon Content

In order to determine the feasibility of producing a given type of fertilizer, it is necessary to know the content of carbon in its organic form. According to the new EU regulation 2019/1009 of 5 June 2019, the organic carbon content classifies the fertilizer into the appropriate category (organic, organo-mineral, or mineral fertilizer). Belonging to particular categories of fertilizers determines further quantitative and qualitative requirements [24].

The organic carbon content was analyzed using the InnovOx series TOC analyzer using the supercritical water oxidation technology. CO_2 determination is performed using NDIR spectrometry. First, the total inorganic carbon (TIC) in the sample is determined by acidification (lowering the pH turns carbonates and bicarbonates into CO_2). This carbon dioxide is blown from the sample and then directed either to the atmosphere (NPOC measurement) or to an NDIR detector (TOC measurement), which calculates the carbon dioxide content based on specific wavelength absorption. After detection, the device calculates the TIC and reports as parts per million (ppm) of the TIC. The NDIR detector allows one to determine the amount of carbon regardless of changes in sample pH or temperature and prevents the potential influence of other gases such as chlorides, chlorine dioxide, sulfur dioxide, etc., on the result. The analyzer measures total organic carbon (TOC) by measuring carbon dioxide obtained from chemical oxidation of organic carbon in the sample. After removing TIC from the sample, the analyzer doses sodium persulfate ($Na_2S_2O_8$), which, as a strong oxidant, quickly reacts with organic carbon in the sample (at approx. 100 °C) to form carbon dioxide. After the oxidation process is complete, carbon dioxide is blown from the sample and determined on the NDIR detector. When the detector calculates the TOC content of the sample, it generates a result in ppm TOC.

3.2. Methods of Chemical Analysis of Waste

The key issue determining the suitability of waste for fertilization purposes is the content of plant nutrients and the level of impurities. Therefore, the content of the expected nutrients in the waste was determined: phosphorus (P), potassium (K), sodium (Na) and impurities in the form of: cadmium (Cd), chromium (Cr VI), mercury (Hg), nickel (Ni), lead (Pb), arsenic (As), copper (Cu), zinc (Zn), iron (Fe), and aluminum (Al.). The standard methods and procedures listed in Table 4 were used for the tests.

Table 4. Research methods used for waste analysis.

Tested Feature	Test Method	Procedure
Phosphorus soluble in mineral acids expressed as P_2O_5	weight method	PN-EN 15956:2011 PN-EN 15959:2011
Potassium expressed as K_2O	weight method	PN-EN 15477:2009
Sodium (Na) Copper (Cu) Iron (Fe) Zinc (Zn) Cadmium (Cd) Lead (Pb) Nickel (Ni) Aluminum (Al)	inductively coupled plasma atomic emission spectrometry (ICP-OES)	PB 35 ed. III of 02/03/2020 PN-EN 16319 + A1: 2016-02 with the exception of point 8.2
Arsen (As)	inductively coupled plasma atomic emission spectrometry (ICP-OES)	PB 35 ed. II of 02/03/2020 PN-EN 16317 + A1: 2017-04 with the exception of point 8.2
Mercury (Hg)	atomic absorption spectrometry with the amalgamation technique	RMG annex 3, p. 4 *
Chrome (VI)	ion chromatography	PN-EN 16318+A1:2016-03

* RMG—Ordinance of the Minister of Economy of 8 September 2010 on the method of packaging mineral fertilizers, placing information on fertilizer ingredients on these packages, methods of testing mineral fertilizers and types of fertilizer lime. (Journal of Laws No. 183 item 1229).

3.3. Methods of Sludge-in-Waste Analysis

Waste sodium–potassium phosphate is a white suspension that easily delaminates during storage (Figure 5).

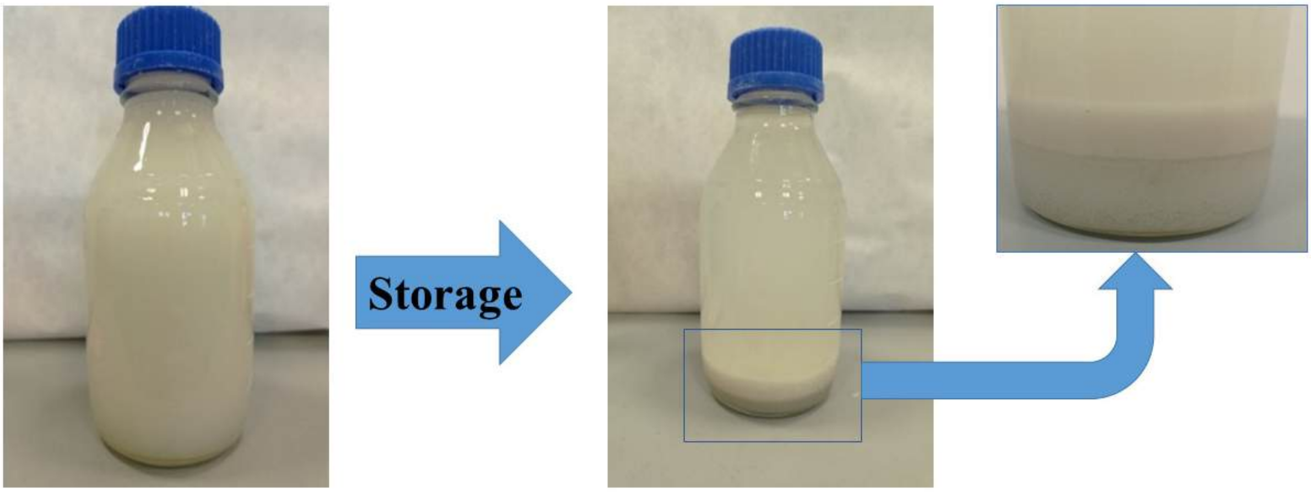

Figure 5. Waste phosphate immediately after mixing with compressed air (**left**) and after one day of storage (**right**).

There are three sediment layers with different crystal sizes. The sediments from individual layers were in a semi-liquid form and were separated by decantation. In order to avoid mixing the crystals from the individual layers, the sediment at the junction of the layers was poured separately and not used for further studies. The individual layers of the sediment were then dried and subjected to X-ray fluorescence analysis (XRF) to determine their composition. XRD measurements were carried out on a PANalytical Empyrean powder diffractometer operating in the Bragg–Brentano geometry. The standard equipment includes a Cu X-ray tube, a rotating transmission-reflection table and a fast linear PIXcel3D detector. The intensity and voltage of the X-ray tube were respectively: I = 40 mA and U = 40 kV. PreFix system configuration (pre-aligned fast interchangeable X-ray modules) made it possible to carry out measurements with the following optical beam settings:

Optical path parameters for the XRD incident beam:

- 0.04 rad soller gap;
- mask: 5 mm;
- slit for beam divergence adjustment: $1/2^0$;
- anti-scatter gap: 1^0.

Optical path parameters for the XRD diffracted beam:

- 0.04 rad soller gap;
- anti-scatter gap: 8 mm PIXel 3D;
- elliptical mirror.

XRD Scan Parameters:

- initial angle [$^0 2\theta$]: 5;
- end angle [$^0 2\theta$]: 75;
- scan step [$^0 2\theta$]: 0.0394;
- exposure time [s]: 68.6;
- sample rotation: yes, disc rotation with a period of 4 s.

The material was ground in a mortar (including the obtained crystals) and placed on a table enabling work in a reflection system with the possibility of sample rotation. All measurements were made on the same program with the use of the same incident beam and diffracted beam optics for the entire series. The diffractogram analysis was performed in the HighScorePlus program. The quantitative analysis of the crystallographic phases was performed automatically with the Rietveld method with manual refinement of the results to obtain the best matching parameters. Rietveld's analysis consists of refining the parameters of the crystal structure by applying the least squares method, fitting the theoretical curve to experimental data. However, the application of this method is usually limited to well-characterized phases in which the number of structural defects is limited. The quantitative determination of the phase content using the Rietveld method can be problematic, and the numerically calculated (using a crystal model with ideal parameters) X-ray diffraction signal can significantly differ from the recorded signal. The problem may also be the uptake by the grain of chemical compounds included in the samples of privileged orientation, which disturbs the quantitative ratios of the crystalline phases read from the diffractogram. In the case of tested samples, the quantitative analysis can only be used as a guide.

4. Conclusions

The conducted research confirms that the analyzed waste does not contain substances harmful to plants. However, it contains significant amounts of phosphorus, which makes it an attractive raw material for the production of fertilizers. The waste does not require treatment or other preliminary preparation processes and, unchanged, can be used in the production of suspension fertilizers. As a result, the phosphorus it contains can be fully recovered and reused in fertilization. Its use is in line with the EU's circular economy strategy and meets the challenges posed by the new fertilizer regulations contained in the EU Regulation 2019/1009.

Further research should be aimed at checking the possibility of enriching waste phosphates with additional nutrients: macro- and micronutrients. In addition, the research should cover methods of stabilizing the produced fertilizer suspensions and the conditions of their storage, preventing the formation of sediment with large crystals.

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Sample Availability: Samples of the compounds are not available from the authors.

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Suspension Fertilizers Based on Waste Phosphates from the Production of Polyols

Paulina Bogusz [1,2,*], Piotr Rusek [1] and Marzena Sylwia Brodowska [2]

[1] Fertilizers Research Group, Łukasiewicz Research Network–New Chemical Syntheses Institute,
Al. Tysiąclecia Państwa Polskiego 13a, 24-110 Pulawy, Poland
[2] Department of Agricultural and Environmental Chemistry, University of Life Sciences in Lublin,
Akademicka 13, 20-950 Lublin, Poland
* Correspondence: paulina.bogusz@ins.lukasiewicz.gov.pl

Abstract: Phosphorus raw materials are non-renewable, and their resources are shrinking faster and faster as a result of increased fertilizer production. This is due to the increasing population and the need to produce more food. Phosphorus, on the other hand, is one of the main nutrients of plants, without which it is impossible to conduct intensive agricultural production. There are no economically significant phosphate resources in Europe, so they must be imported. That is why it is so important to reduce losses and recover this element from waste streams, which was reflected in the new EU Regulation 2019/1009. A prospective option is to use waste phosphates from the production of polyether polyols. Previous studies show that they contain about 20% phosphorus. Due to their high water content, the most advantageous form of their application is the production of fertilizers in the form of a suspension. The aim of the study is to assess the possibility of using waste phosphates from the production of polyols as raw materials for the production of suspension fertilizers.

Keywords: phosphorus; critical raw materials; circular economy; waste management; liquid waste

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1. Introduction

Suspension fertilizers on an industrial scale were introduced in the United States in the late 1960s [1]. Although they are an American specialty, they have many followers in Canada, developed countries, Europe, and Asia [2,3]. The economics of production and the efficiency of using this form of fertilizer have contributed to a steady increase in their agricultural use starting from the 1970s [3].

In the United States, where these fertilizers are the most popular, their production takes place at satellite liquid fertilizer stations and base suspensions at fertilizer factories. The share of suspension fertilizers there accounts for about 1/3 of the entire liquid fertilizer market [4]. About 70% of suspension fertilizer mixtures are made of base suspensions and nitrogen solutions, while the remainder is produced on the basis of solid fertilizers [1].

The first fertilizer suspensions were developed by the Tennessee Valley Authority (TVA), which, in the late 1960s, improved the manufacture, handling, and use of stable suspensions [4]. Further research in the 1970s on optional raw materials, suspending agents, and processing techniques resulted in a spectacular improvement in product quality and versatility, thus ensuring commercial success, not only in the United States, but also beyond [5].

In the early 1980s, fluid fertilizer foundation was established to sponsor field work to determine the optimal use of liquid fertilizer systems in plant production [6]. Currently, liquid products, including suspensions, are gaining more and more popularity in the most developed markets. In terms of the global nitrogen market, liquid fertilizers currently account for around 12% of the total market [5,7].

Suspension fertilizer manufacturers offer a diverse range of products based on various techniques. The proposed production procedures are aimed at ensuring better stability of the suspensions, increasing the concentration of fertilizing components, and improving the bioavailability of the components.

A common practice in the production of suspension fertilizers is the production of base fertilizers that can be stored for a longer period, provided that they are periodically mixed. Depending on the demand, the base suspensions are enriched with appropriate raw materials to obtain a multi-component fertilizer with the desired composition, which requires application within several hours from the end of production [8,9].

Clear solutions of urea ammonium nitrate can be prepared for a nitrogen concentration of about 32% at normal use temperatures. The concentration of liquid suspension type fertilizers may exceed this limit, and processes for this have been developed in the United States. The hot 87% urea solution and the hot 88% ammonium nitrate solution are mixed and then cooled to 55 °C before being transferred to the gelling tank. An urea-to-ammonium nitrate ratio is used, which provides 70% of total urea nitrogen. Resultingly, it is the urea that crystallizes on subsequent cooling. Dry attapulgite clay is added to the solution in an amount constituting 1.5% of the product. The clay gelation tank is a baffled vessel that provides good mixing, equipped with recirculation by a centrifugal pump to assist the gelation. A corrosion inhibitor is added, if necessary. After this step, the mixture must be cooled rapidly below 45 °C in order to induce intense nucleation of small urea crystals. They are easy to hang and provide a large surface area for further crystal growth that may occur during storage. It is important to avoid the slow growth of large crystals that could block the operation of the equipment. Rapid cooling is achieved by passing the mixture through a forced draft spray tower. The partially cooled slurry is recirculated from the pond at the base of the tower. Crystal size can be controlled by varying the recycle rate (which is typically 15:1 from the product removal rate). The suspension prepared in this way and cooled is transferred to the warehouse [5,10].

The Luxen method for the production of suspension fertilizers is based on the use of ground raw materials with particles above 20 mesh, appropriate mixing speeds (1280 rpm for the clear solution mixing stage and 2620 rpm for the suspension mixing stage), maintaining the temperature in the range of 30–40 °C, and using xanthan gum as a stabilizing factor in the amount of 2.5% [11].

This method was used for the production of NPK suspension fertilizer with a composition of 25-7-7. The process consists in introducing a part (about 85%) of the ground urea, water, and the stabilizing agent—xanthan gum in the stage of mixing at a lower speed. The remainder of the urea, water, KCl, and MAP are added in a second mixing step with increased agitator speed and are mixed until homogenization is achieved. The urea added in the first mixing step dissolves completely to give a saturated solution with a three-dimensional network of xanthan gum. In the second stage of mixing, the remaining raw materials are introduced. The undissolved ingredients are kept in suspension in dispersion by the xanthan gum by Van der Wals forces, and the saturated solution gradually becomes supersaturated. The dispersed phase of the slurry consisted of urea crystals 1 added in the first mixing step, urea particles 2 added in the second mixing step, and KCl and MAP added in the third mixing step. The environment of the urea 1 particles by the xanthan gum particles prevented the formation of clusters, which limited the formation of large crystals during the cooling of the suspension [11].

The method of producing a MAP-based suspension fertilizer with the addition of fluoride ions developed by TVA consists in adding appropriate amounts of MAP, water, H_2SiF_6, and ammonia to the reactor in an amount ensuring a pH of about 6.5. Then, attapulgite clay was added in an amount of 0.75–1.5%. The total mixing time of all ingredients was 20 min. At the stage of ammonization, the temperature of the suspension was in the range of 65–93 °C and it was higher with the addition of fluorine [12].

The use of a nucleating agent in the suspension causes the excess fertilizer salts to crystallize in the form of fine crystals, which remain suspended in a saturated solution of the same salts [13,14]. Without the use of a nucleating agent, the crystals expand, settle to the bottom, and form a hard mass that makes the resulting product unusable [13].

According to the invention in US Patent 3,113,858, the beneficial effect of the nucleating agent can be improved by the unique combination of appropriate size selection of the solids and the cooling of the hot fertilizer solution prior to the addition of the solids. Essential requirements are that the hot fertilizer solution is cooled prior to the introduction of the fine particle solids. Pre-cooling minimizes the dissolution of the solids and, thus, reduces the subsequent recrystallization in the form of large crystals. The fine size promotes the dispersion of undissolved solid particles. The combination of these effects with the beneficial effects of the nucleating agent results in a fertilizer suspension with improved properties [13].

The order in which the materials are added is not critical as long as the necessary sequence of cooling the produced fertilizer solution and adding solids is followed. It may be desirable to cool the fertilising solution prior to adding the remaining liquid materials in order to obtain a more efficient use of the coolant used, but this is not necessarily the case [13].

It is essential that the temperature of the slurry quickly reaches ambient levels after the addition of solids. The inevitable partial dissolution of the solids gives some cooling, as does the addition of any make-up liquids. Therefore, it is necessary to cool the solution to at least such an extent that the further cooling by additional fluids and by dissolving the solid brings the temperature down to ambient temperature [13].

The initial comminution of the solids is important since the particle size of the solids in the final suspension depends in this case more on the initial size than on the degree of growth during recrystallization [13].

According to US patent 3,109,729, the best suspension is obtained when the amount of water is limited to the extent that at least 1/3 of the total nutrients are in the dispersed phase [14].

The nucleating agent is best added at a time when the salts start to crystallize out of solution. Then, it can fully cause rapid nucleation of crystallizing salts, resulting in the production of a large amount of very small easily suspended crystals and not a small amount of large crystals. However, the nucleating agent will have a beneficial effect, even if added after excess salt has crystallized out. When the ambient temperature changes, the salts alternately dissolve and recrystallize. The presence of a nucleating agent then prevents the formation of hard masses by recrystallizing salts, which would cause deposition and segregation of nutrients and interfere with the application [14].

When the slurry is prepared by the ammonification of phosphoric acid to obtain ammonium phosphate, it is desirable that all the salts in the solution be introduced at one stage of the process so that the nucleating agent can exert its full effect. This is most easily accomplished by adding salt prior to the ammonification of the acid so that the heat of the neutralization reaction raises the temperature of the mixture high enough to dissolve the salts. However, salts can also be added during or even after acid neutralization, if added immediately before cooling the solution. Adding salt prior to neutralization has the advantage that more of the heat of reaction goes to providing the heat to dissolve the salt rather than evaporating the water. If these steps are not implemented in production, excess salt may crystallize as a heavy mass, settling on the bottom of or clinging to the walls of the container, rendering the product unusable [14].

The nucleating agent can be one of several fine inert materials. Examples are clay, dolomite, and other naturally occurring materials [14].

A popular option is the slow-acting urea-formaldehyde suspension fertilizers produced by the polymerization of urea and formaldehyde. According to US patent 4,526,606, a good quality urea-formaldehyde suspension fertilizer can be obtained, which additionally, leaves no color. For some commercial applications, such as fertilizing lawns, the trait of color is quite important. Coloring refers to the tendency of dried fertilizer suspension particles to remain on a substrate for extended periods, e.g., grass blades, driveways, sidewalks, etc. The dried suspension appears as a white unsightly deposit. Coloring is inversely proportional to particle size, e.g., smaller particles color more than larger particles.

Therefore, particle size considerations for a stable fertilizer suspension run counter to the non-staining needs [15].

The addition of a low-foaming surfactant promotes the dispersion of the fertilizer after application, helping to re-wet the dried water-insoluble fertilizer material. In other words, the surfactant helps to reduce the tendency to stain from fertilizer suspensions [15].

US patent 3,155,489 discloses a fertilizer slurry preparation method that uses nitrogen oxides to acidify the slurry of calcium compounds, thereby obtaining nitrogen without the need for nitric acid. The process according to the invention combines the steps of oxidation, absorption, and acidification and allows the use of low-grade phosphates and a cheap source of nitrogen [16].

Usually, nitric acid is used to acidify phosphate rocks. However, it is expensive and produces a by-product, calcium nitrate. Since calcium nitrate is a very hygroscopic substance, it creates problems in the production of solid fertilizers. In order to overcome these difficulties, the invention uses nitrogen oxides and produces the end product in the form of a liquid slurry. The cost advantage of the invention is largely due to the direct absorption of nitrogen oxides by aqueous suspensions of calcium compounds to form a fertilizer suspension of solid particles in a liquid medium [16].

US patent 4,133,670 describes a method for the production of a monoammonium phosphate (MAP) suspension fertilizer with improved storage parameters [17].

A troublesome problem with ammonium phosphate suspension fertilizers is the formation of relatively large crystals (20 mesh or more). These crystals reduce storage time and clog the spray nozzles and other critical points in the spray device. This, in turn, means that frequent stoppages and cleaning work are necessary during use [17].

The process of the invention comprises initially mixing a portion of the amount of monoammonium phosphate (MAP) with water and adding ammonia thereto to induce an immediate ammonia reaction. The remainder of the MAP is then added to make the final fertilizer composition. This division of the MAP additive (preferably 70–30%) serves to minimize the formation of large ammonium phosphate crystals in the fertilizer, thanks to the improved storage properties, and the fertilizer can be sprayed without fear of frequent clogging of the spray equipment [17].

Patent US 3,677,736 describes a method of obtaining a suspension fertilizer containing large amounts of urea, the solubility of which is quite low, which excludes the formation of highly concentrated solutions on its basis [18].

The urea formaldehyde liquid suspension has the advantage that one application will provide a dose of rapidly available nutrients along with a slowly available nitrogen reserve. Moreover, the suspended particles of urea, when applied to soil or lawn, leave a visible bloom, which can serve as an indicator of which parts of the area have been sprayed with the liquid fertilizer mixture and which still require fertilizer application [18].

The pH of the starting material should be higher than 7 to prevent premature formation of urea formaldehyde or other products resulting from side reactions. When the pH drops below 5, the rate of the reaction between urea and formaldehyde to form urea formaldehyde is increased. However, when the pH drops below 1, the acid destroys the urea before combining it with the formaldehyde. The urea-formaldehyde compounds obtained in this case are, moreover, highly insoluble and undesirable [18].

The starting material is preferably heated for 15 min at 40–70 °C. The reaction speed is very slow at temperatures below 30 °C. At temperatures close to 80 °C, highly insoluble compounds were formed [18].

It is important to mix, during the reaction, to obtain a finely divided urea formaldehyde product. If the mixing is insufficient, highly insoluble nitrogen compounds are formed. High shear mixing using a baffled turbine mixer is preferred when the reaction of urea formaldehyde is carried out at a reaction temperature below 60 °C. On the other hand, mixing with a pump or impeller type agitator gives satisfactory results when the reaction is carried out at a temperature above approx. 60 °C [18].

At the end of the reaction time, an alkaline material is added to the mixture to raise the pH above 5 and thereby complete the urea formation reaction. The pH of the product should not exceed 8, as it may cause the suspension to react with the container and introduce impurities into the mixture. In addition, the increase in alkalinity attacks the urea in the product suspension. Typically, supplemental plant nutrients are added after the urea-formaldehyde acid reaction to form the urea formaldehyde suspension due to better control of pH conditions [18].

Detailed characteristics of suspension fertilizers are presented in the review article: Suspension Fertilizers: How to Reconcile Sustainable Fertilization and Environmental Protection [19].

The paper presents the results of tests on the production of suspension fertilizers based on waste phosphate from the production of polyols. The composition of the tested fertilizers was selected for maize grown for silage, with the intention of checking their effectiveness in field experiments for this plant. The six proposed fertilizers differ in their phosphorus content and the addition of secondary fertilizing components and microelements.

In the stabilization of samples of suspension fertilizers, the performance of four different bentonites was compared. In the first step, their swelling capacity was tested, producing a 12% aqueous solution. Bentonites showing a high swelling factor were tested in the stabilization of the proposed tests of suspension fertilizers by examining their basic operational parameters: stability, density, viscosity, and fluidity.

2. Materials and Methods

2.1. Fertilizer Raw Materials

Fertilizers based on waste phosphates presented in the paper are to be a replacement for fertilizers based on monoammonium phosphate (MAP). Therefore, the tests used typical fertilizer raw materials most often used in the production of suspension fertilizers, with the exception of the raw material, which is a source of phosphorus.

In the research, waste phosphates from the production of polyols were used as the phosphorus raw material, the detailed characteristics of which are presented in this paper: The Possibility of Using Waste Phosphates from the Production of Polyols for Fertilizing Purposes [20].

Tables 1–6 show the parameters of the remaining fertilizer raw materials used in the presented trials of suspension fertilizers.

Table 1. Urea ammonium nitrate solution (RSM).

Parameter	Unit	Value
Total N content	% wt.	2
Content NH_4NO_3	% wt.	44.3
Urea content	% wt.	35.4
Specific density	$kg \cdot m^{-3}$	1320
Crystallization temperature	°C	0

Table 2. Potassium salt—technical potassium chloride.

Parameter	Unit	Value
Content K_2O	% wt.	60
Particle content less than 0.6 mm	% wt.	min. 80
Angle of repose	degree	35
Bulk density	$kg \cdot m^{-3}$	1110

Table 3. Magnesium sulfate 7 hydrate.

Parameter	Unit	Value
Content MgO	%	16
Content SO_3	%	32

Table 4. Boric acid.

Parameter	Unit	Value
Type		p.a.
Content	%	min. 99.5%

Table 5. Zinc Sulphate 7 hydrate.

Parameter	Unit	Value
Type		p.a.
Content	%	min. 99.5%
pH (5%, H_2O)		4.4–5.6

Table 6. Manganu (II) siracha 1 hydrate.

Parameter	Unit	Value
Type		p.a.
Content	%	min. 99.5%

2.2. Stabilizing Agent

For the stabilization of fertilizer suspensions, bentonites are the most frequently used raw material due to their price and availability. Four bentonites from Zakłady Górniczo-Metalowe "ZĘBIEC" in Zębcu S.A. were tested in the research.

These are the bentonites selected for research:

Bentonite GM—due to the high content of montmorillonite, it has a high viscosity and perfectly binds materials. It is characterized by high water absorption—bentonite swells quickly.

Bentonite Special—a bentonite enriched with sodium cation (i.e., activated), which significantly improves its functional properties. It increases the swelling ratio, i.e., bentonite hydration.

Bentonite Special 45—high-quality bentonite with a high montmorillonite content is used for its production. The suspensions made of Special 45 bentonite have excellent rheological and thixotropic properties, which translates into very good stabilization. Thanks to the high thixotropy, they keep the soil grains suspended.

Bentonite SN—is universally applicable and works well in many industries. It is used as an additive to animal feed, in the production of concrete, plasters, paints and varnishes, in the food and pharmacological industries, and in the sewage industry for wastewater treatment.

GM, Special and Special 45 bentonites with 75% montmorillonite content were activated with sodium cations. And SN bentonite is only ground and dried calcium bentonite that is not subject to the activation process.

2.3. Composition of Fertilizers

Two series of fertilizers were prepared. In the first series, three fertilizers were proposed with the percentage of the main NPK nutrients: 9.5-4-11 (4 × 2.4: 1: 2.8). Fertilizer 1 contains only the main nutrients (N, P, K), fertilizer 2 is additionally enriched with secondary nutrients (Mg, S), and fertilizer 3 is enriched with microelements (Table 7).

Table 7. Composition of fertilizers of the 1st series with the main composition of NPK: 9.5–4-11.

Sample	Type of Fertilizer	The Content of Fertilizing Ingredients, %							
		N	**P_2O_5**	**K_2O**	**MgO**	**S**	**Zn**	**Mn**	**B**
1	NPK	9.5	**4**	11	-	-	-	-	-
2	NPK + MgO + S	9.5	**4**	11	3	6	-	-	-
3	NPK + MgO + S + microelements	9.5	**4**	11	3	6	0.01	0.1	0.01

In the second series, the phosphorus dose was increased by 2% with the same content of nitrogen, potassium, secondary nutrients, and microelements as in the fertilizers in the first series. The composition of series II fertilizers (fertilizer 4, 5 and 6) is presented in Table 8.

Table 8. Composition of fertilizers of the 1st series with the main composition of NPK: 9.5–6-11.

Sample	Type of Fertilizer	The Content of Fertilizing Ingredients, %							
		N	**P_2O_5**	**K_2O**	**MgO**	**S**	**Zn**	**Mn**	**B**
4	NPK	9.5	**6**	11	-	-	-	-	-
5	NPK + MgO + S	9.5	**6**	11	3	6	-	-	-
6	NPK + MgO + S + microelements	9.5	**6**	11	3	6	0.01	0.1	0.01

The proposals of six suspension fertilizers were selected so as to easily compare the yield-generating efficiency of maize in relation to the amount of phosphorus component and depending on the addition of secondary nutrients and microelements.

2.4. Research Methodology

2.4.1. Production of Suspension Fertilizers

Suspension fertilizers were produced using a high-speed DISPERMAT mixer with a dissolver type mixer. Appropriate amounts of liquid raw materials were metered into the reactor and mixed at the speed of 800 rpm for about 5 min. Then, solid raw materials were gradually dosed, increasing the stirrer speed to 1500 rpm. After the dosing of all raw materials was completed, the suspension was mixed for about 15 min.

2.4.2. Stability Study

The basic study determining the durability of the prepared suspensions is a sedimentation test conducted for 48 h in order to observe all the phenomena occurring in the suspension from its production to application or complete degradation. 48 h is considered a satisfactory time to keep the suspension in a stable form. This is the minimum time that allows the suspension to be transported and applied. In order to measure the stability, the tested suspensions were placed immediately after production in measuring cylinders with a stopper of a capacity of 100 mL and a diameter of 30 mm, and the changes taking place were observed by measuring the height of delamination.

2.4.3. Castability Testing

The pourability test was performed at the temperature of 20 °C with the use of a 100 mL Ford cup with a 4 mm diameter discharge nozzle. After the cup was fully filled with the tested suspension, the time of free flow of all the liquid through the nozzle at the bottom of the container was measured. The pourability measurements were performed immediately after preparing the suspensions and 48 h after previous mixing.

2.4.4. Density Test

Density was measured at 20 °C using an aerometer. The suspension fertilizer was poured into the measuring cylinder immediately after its production, and the aerometer was placed in it in such a way that it would not touch the cylinder walls. After the aerometer level in the slurry had stabilized, the measurement result was read and recorded.

3. Results and Discussion

3.1. Selection of the Composition of Fertilizers

The suspension fertilizers presented in the study were dedicated to the cultivation of maize for silage due to its great importance in the production of food and feed. In later studies, it is planned to evaluate their effectiveness in field experiments with this plant.

The composition of the fertilizers was developed on the basis of recommendations for the cultivation of maize for green matter developed by the Institute of Soil Science and Plant Cultivation—National Research Institute in Puławy (IUNG) [21]. Maize extracts large amounts of nutrients and water from the soil. With a yield of 10 tons of forage, it consumes, on average: 38 kg of nitrogen (N), 16 kg of phosphorus (P_2O_5), 45 kg of potassium (K_2O), 20 kg of calcium (CaO), 12 kg of magnesium (MgO), 5 kg of sulfur (S) or converted to SO_3—12.5 kg and 17 g of boron (B), 13 g of copper (Cu), 150 g of manganese (Mn), 1.5 g of molybdenum (Mo), and 150 g of zinc (Zn). It shows high sensitivity to zinc deficiency and average sensitivity to boron, manganese, and copper deficiency. On this basis, the ratio of the main nutrients N, P, and K was established: 38:16:45 = 2.4:1:2.8.

For fertilizers with the addition of micronutrients, three micronutrients of key importance in maize cultivation were selected: boron, manganese, and zinc. The amount of these ingredients in suspension fertilizers was selected as the minimum amount that can be declared in a fertilizer containing primary and/or secondary nutrients with the addition of microelements for soil application in field crops according to the Regulation of the Minister of Economy on 8 September 2010 concerning the method of packaging mineral fertilizers, placing information about fertilizing ingredients on these packages. The method of testing mineral fertilizers and types of fertilizing lime amounts to: Zn—0.01% (m/m), Mn—0.1% (m/m), and B—0.01% (m/m). According to the new Regulation (EU) 2019/1009 of the European Parliament and of the Council [22], repealing Regulation (EC) No 2003/2003, which applies from 16 July 2022, manganese and zinc in liquid inorganic fertilizers can be declared with lower contents: Mn—0.01% (m/m) and Zn—0.002% (m/m). The new EU regulations do not pose a threat to the necessity to change in the adopted compositions for suspension fertilizers.

3.2. Assessment of the Suitability of Bentonites for the Stabilization of Fertilizer Suspensions

In order to determine the suitability of certain types of bentonites for the stabilization of fertilizer suspensions, their 12% aqueous solutions were prepared. After approximately 30 min, their swelling was assessed visually.

The greatest swelling was observed in the solutions of Specjal and Specjal 45 bentonites. They took the form of a jelly-like substance that did not change position even when the container was turned upside down (Figure 1b,c). The GM bentonite formed a stable and fluid slurry (Figure 1a). However, the SN bentonite solution did not swell at all. After 30 min, it delaminated into a water layer at the top and a bentonite sediment at the bottom (Figure 1d). Therefore, it was not used in further studies aimed at stabilizing suspension fertilizers.

3.3. Assessment of Physical Parameters of Suspension Fertilizer Trials

3.3.1. Assessment of the Density and Fluidity of Suspension Fertilizers

The proposed tests of suspension fertilizers without the addition of bentonite were prepared: tests 1.0–6.0 and with the addition of 3% of selected types of bentonites in the form of a 12% solution; with GM bentonite, tests 1.1–6.1; with Special 45 bentonite, tests 1.2–6.1; and with bentonite, Special tests 1.3–6.3. Table 9 shows the results of the density and fluidity tests for the given fertilizer samples. The test was carried out immediately after production and 48 h after mixing the bottle with the fertilizer by shaking it.

(**a**) (**b**) (**c**) (**d**)

Figure 1. 12% water solution of bentonite: (**a**) GM, (**b**) Special, (**c**) Special 45, and (**d**) SN 30 min after production.

Table 9. Physical parameters of the produced samples of suspension fertilizers.

		Density, g/cm^3		**Castability, s**	
	Recommended Range	**1200–1400**		**10–15**	
Bentonite	**Sample**	**After 0 h**	**After 48 h**	**After 0 h**	**After 48 h**
-	1.0	1.251	1.260	10.35	9.70
	2.0	1.378	1.372	11.24	10.54
	3.0	1.378	1.373	11.91	*
	4.0	1.292	1.285	10.22	9.76
	5.0	1.435	1.406	13.46	10.87
	6.0	1.546	1.414	18.71	*
GM	1.1	1.262	1.262	10.23	9.74
	2.1	1.251	1.350	16.64	10.82
	3.1	1.250	1.344	15.60	10.92
	4.1	1.287	1.282	10.53	9.76
	5.1	1.454	1.381	34.09	11.71
	6.1	1.482	1.390	22.92	10.76
Specjal 45	1.2	1.267	1.272	9.98	10.01
	2.2	1.235	1.343	16.15	10.72
	3.2	1.297	1.337	17.83	10.63
	4.2	1.285	1.286	10.43	9.87
	5.2	1.368	1.375	20.36	10.72
	6.2	1.565	1.364	38.24	11.20
Specjal	1.3	1.263	1.270	9.72	9.78
	2.3	1.227	1.269	20.72	11.75
	3.3	1.260	1.281	21.16	12.38
	4.3	1.275	1.291	10.11	10.44
	5.3	1.447	1.346	30.58	12.88
	6.3	1.710	1.367	39.43	11.64

* clogging of the nozzle by large, rapidly falling crystals.

The density in fertilizers without the addition of bentonite did not change significantly after 48 h. Moreover, in fertilizers without bentonite with a higher concentration (tests 3.0 and 6.0), thicker crystals were formed, which clogged the outlet nozzle of the Ford cup.

In fertilizers with the addition of bentonite, compared to fertilizers without their addition, the fluidity of the fertilizers improved after 48 h. In these tests, the washout time from the Ford cup was shortened, which was outside the recommended range immediately after being produced in the tests with the higher concentration. This is related to the structure produced by bentonite over time, which separates the grains of the dispersed phase. For this reason, the addition of bentonite facilitates the re-mixing of the fertilizer. The samples without the addition of bentonite required a longer shaking time in order to agitate the sediment collected at the bottom.

3.3.2. Stability of Suspension Fertilizers

The graphs show the stability of the produced suspension fertilizer tests, as measured by the amount of clear liquid layer at the top in relation to the elapse of time.

In each case, the tests with the addition of bentonites had better stability than the tests without their addition. The best stability parameters are demonstrated by tests with Special bentonite, in which the smallest amount of clear liquid was produced (Figure 2 samples: 1.3–6.3). The greatest delamination was observed in the samples without bentonite, especially at those with a lower concentration (Figure 2 (1), (2) samples: 1.0–6.0). Moreover, the samples containing magnesium sulphate showed lower delamination: less than 60% for the samples 2 and 3 (Figure 2 (2), (3)) and less than 40% for the samples 5 and 6 (Figure 2 (5), (6), compared to the samples containing only the main nutrients (samples 1 and 4). The samples with the addition of bentonites were easily mixed (2–3 times by shaking the cilnder) and regained their initial stability.

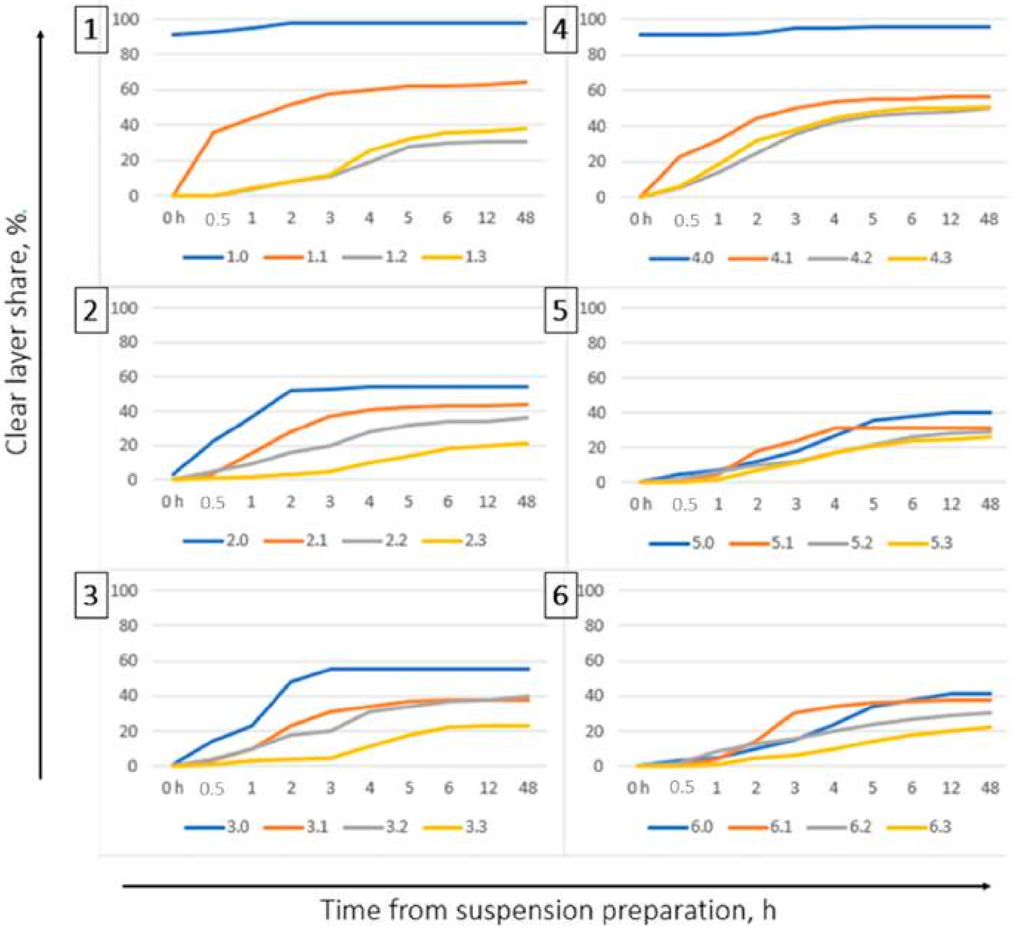

Figure 2. Graphs showing the stability of suspension fertilizer samples depending on the time that has elapsed since their production. Each graph concerns one type of fertilizer (1–6) in the variants of the addition of various bentonites.

3.3.3. Viscosity of Suspension Fertilizers

Viscosity influences the suspension's stability and its pourability. When the viscosity of the dispersion medium increases, the sink rate decreases, and the dispersed phase sinks slower and stays dispersed longer, resulting in a more stable suspension. However, as the viscosity of the system increases, the potential for leakage decreases, and a dosing problem arises. Highly viscous slurries consume energy excessively during the manufacturing process, so low viscosity is more cost-effective.

The viscosity of all samples of suspension fertilizers increases with the increasing speed of rotation of the measuring spindle (Figure 3). This may be the result of solid particles falling to the bottom of the measuring container where the measuring spindle tip is located. This causes the suspension to thicken in this region and a greater resistance to the measuring spindle to occur. Overall, it was found that the tests with GM bentonite (1.1–6.1) had a higher viscosity than the other tests. On the other hand, the value of the viscosity of the samples without the addition of bentonite (1.0–6.0) is at the lowest level.

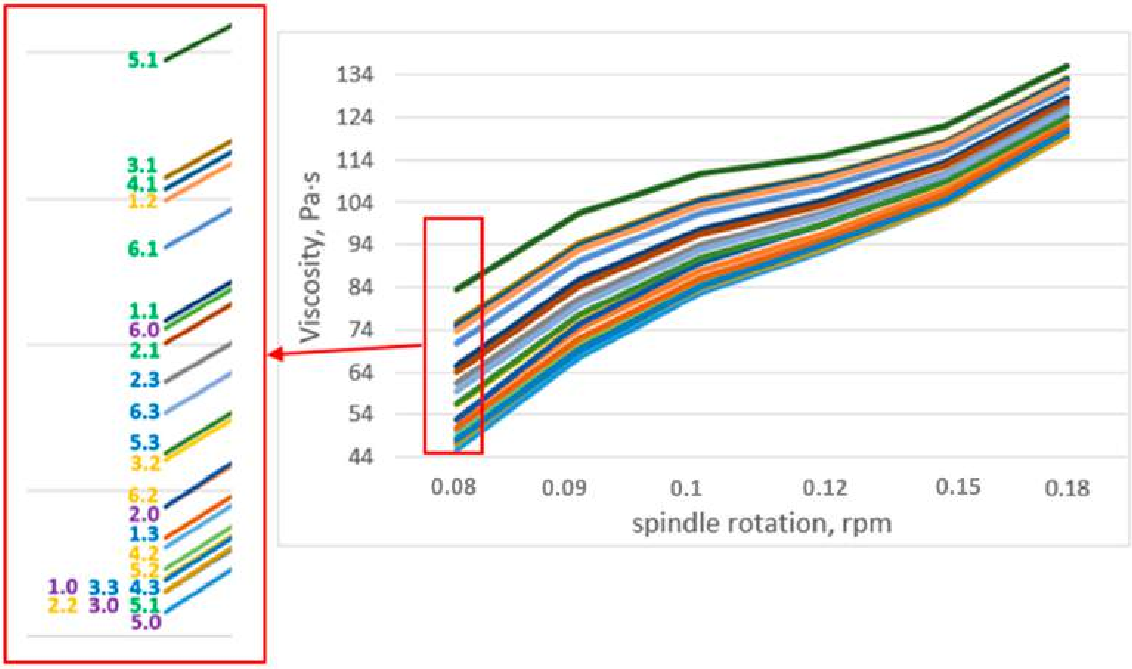

Figure 3. Dependence of the viscosity of fertilizer suspensions on the rotational speed of the measuring spindle.

4. Conclusions

The presented research confirms the possibility of using waste phosphates from the production of polyols as raw materials for the production of fertilizers. Since this waste contains a large amount of water, suspension fertilizers are the most economically viable form of fertilizers produced. This form of fertilizer allows for a wide range of modification of the fertilizer composition. The waste raw material can be diluted with water or supplemented with appropriate raw materials that provide macro or micronutrient nutrients, depending on the needs. The solubility of the ingredients is not a limitation here. An important issue is the proper stabilization of the suspension with a stabilizing agent.

The suitability of bentonites for the stabilization of suspension fertilizers should be checked by prior preparation of the aqueous suspension and assessment of the degree of swelling. If bentonite does not form a stable suspension and delaminates, it is not suitable for preparation of suspension fertilizers on its basis. Addition of bentonites to fertilizer suspensions improves their rheological parameters, especially stability and fluidity. In the samples of fertilizers with the addition of bentonite, the fluidity improves with the passage of time.

The addition of bentonites to fertilizer suspensions prevents the formation of large crystals that could clog the nozzles during fertilizer application.

The addition of bentonite facilitates the restoration of the proper parameters of fertilizer suspensions after their remixing. All the proposed tests of fertilizers with the addition of bentonites, with a composition adapted to the nutritional requirements of maize, met the application criteria for suspension fertilizers.

In samples of high concentration, thicker crystals may develop during storage. This can cause clogging of the outlet nozzles during fertilizer application. This can result in an uneven distribution of the fertilizer in the field or a complete avoidance of its application.

In order to verify the agricultural efficiency, the proposed fertilizers are currently being tested in field experiments with maize intended for silage.

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The Impact of Suspension Fertilizers Based on Waste Phosphorus Salts from Polyol Production on the Yield of Maize Intended for Green Fodder

Paulina Bogusz [1,2,*], Marzena Sylwia Brodowska [2] and Piotr Rusek [1]

[1] Fertilizers Research Group, Łukasiewicz Research Network–New Chemical Syntheses Institute, Al. Tysiąclecia Państwa Polskiego 13a, 24-110 Puławy, Poland; piotr.rusek@ins.lukasiewicz.gov.pl
[2] Department of Agricultural and Environmental Chemistry, University of Life Sciences in Lublin, Akademicka 13, 20-950 Lublin, Poland; marzena.brodowska@up.lublin.pl
* Correspondence: paulina.bogusz@ins.lukasiewicz.gov.pl

Abstract: The need to import phosphorus raw materials for fertilizer purposes in Europe as well as the need to manage increasing amounts of waste contributed to the search for alternative sources of phosphorus. One of these is waste sodium–potassium phosphate from the production of polyols. Additionally, a current problem is providing an adequate amount of food, where fertilizers play the main role. Due to the increase in meat consumption, the attractiveness of growing corn for feed is increasing due to its high yield potential and rich composition. The article presents the impact of suspension fertilizers based on waste from the production of polyols on the yield of corn intended for green fodder. In a 3-year field study, the effects of a waste phosphorus source were compared with a commercial granulated phosphorus fertilizer—fosdar. In addition, the suspension fertilizers were assessed according to their composition by testing fertilizers containing only basic nutrients (NPK) and ones enriched with secondary ingredients (S and Mg) and microelements (Zn, Mn and B). The research confirmed the effectiveness of the tested suspension fertilizers. Although the yield obtained was lower than in the case of fosdar fertilization, it still remained at a high level of over 70 t·ha^{-1} of fresh yield.

Keywords: maize; green fodder; suspension fertilizer; waste phosphorus

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1. Introduction

Corn (*Zea mays* L.) comes from Central America, where it was domesticated about 7000 years ago, and since European settlement, it has spread rapidly around the world. Since then, it has played an increasingly larger and more diversified role in the agri-food system [1–5].

In response to the growing world population, increasing crop production has become one of the main goals to ensure enough food. Within this framework, cereals play a key role [6]. The world's three staple grains—wheat, rice and corn—are key components of the human diet, accounting for approximately 42% of global calorie intake and 37% of protein intake [1,3,6,7]. In Sub-Saharan Africa, Latin America and some Asian countries, corn plays an important role in human food, providing over 20% of calories consumed [1,8].

The advantage of corn over other cereals is its high yield potential for both grain and fodder [6]. Moreover, it can be grown in a wide range of climatic and soil conditions. It provides more nutrients compared to other cereals and legumes [5,9,10]. Corn contains approximately 72% starch, 10% protein and 4% fat, providing an energy density of 365 Kcal·100 g^{-1}, but has a lower protein content compared to rice and wheat [7].

Corn is a very versatile grain that has many prospective applications [9,11,12]. It can be used as a plant for food, animal feed, industrial raw material and in energy production [9,11,12]. In the food field, corn is used in the production of a variety of products, such as corn starch, dextrose, corn syrup and corn flakes [1,9,11].

In developed economies, the consumption of more animal products leads to the increased use of corn in the production of feed for farm animals [1]. It is one of the most valuable and efficient fodder plants cultivated on a global scale [13–15]. It is used to produce roughage, used mainly in winter, but increasingly also throughout the year to feed ruminant animals. The most popular form is silage made from whole corn plants [14].

The development of green fodder production is due to its potential for high yields, its high digestibility and its greater resistance to lodging compared to small-grain cereals such as barley and oats [13]. In cultivation, it ensures stable yields in various environmental and agronomic conditions. It is characterized by high energy values and excellent properties for pickling [10].

Corn creates an opportunity to increase meat and milk production without the need to expand the use of agricultural land [16]. In the diet of dairy cows, it increases feed intake, milk yield and protein content [9]. On farms, feed silage is typically cheaper than dry concentrates and can be produced with lower energy inputs, such as energy needed for drying and transportation [17,18].

Over the last few decades, corn production around the world has increased rapidly. This is the result of the growing demand for this plant raw material, as well as the synergy between technological progress, higher yields and expansion of cultivation areas. Corn cultivation extends to more than 170 countries around the world, including both emerging and developed economies. The area of its cultivation is mainly concentrated in both Americas and Asia, with the largest share in North America (mainly in the USA) and East Asia (especially in China). These regions provide more than half of the world's corn production [1,4]. The main corn-exporting countries are the United States, Brazil, Argentina and Ukraine. In 2020–2021, cumulative maize exports from these four countries accounted for 88.12% of global exports. This means that while China is a major corn producer, it is not a major corn exporter. The US and China are the two largest consumers of corn [5].

The paper presents the results of 3-year field tests with corn intended for green fodder in which the effect of suspension fertilizers based on waste sodium–potassium phosphate from the production of polyols was tested.

2. Materials and Methods

2.1. Field Research Methodology

In a field experiment, the effects of 6 suspension fertilizers, in which the source of phosphorus was waste sodium–potassium phosphate from the production of polyols, were tested. Polyols are raw materials for the production of polyurethanes, which are widely used in such areas of life and economy as transport, construction, the furniture industry and mining.

The waste used came from PCC Rokita S. A. in Brzeg Dolny, Poland. Research shows that it contains nearly 19% phosphorus and about 8% potassium. The content of impurities is well below the threshold value set by the European Commission in new regulations. This makes the tested waste a competitive raw material in relation to phosphate rocks, which are often contaminated with cadmium. Due to its high water content, the most advantageous form of its use is the production of fertilizers based on it in the form of suspensions [19].

The compositions of the fertilizers were developed based on recommendations for growing green maize. In the first series, three fertilizers were proposed with the main nutrients, NPK, in the following percentages: 9.5–4-11. Fertilizer 1 contained only the main nutrients (N, P and K); fertilizer 2 was additionally enriched with secondary nutrients: magnesium (3% MgO) and sulfur (6% S); and fertilizer 3 was enriched with microelements of key importance in corn cultivation: boron (0.01%), manganese (0.1%) and zinc (0.01%). In the second series, the dose of phosphorus was increased by 2% with the same content of nitrogen, potassium, secondary nutrients and microelements as the fertilizers in the first series. The proposals for the 6 suspension fertilizers were selected in such a way as to easily compare the yield-forming efficiency of corn in relation to the amount of the phosphorus component and depending on the addition of secondary nutrients and microelements [20].

The detailed characteristics of the waste used are presented in the article "The Possibility of Using Waste Phosphates from the Production of Polyols for Fertilizing Purposes" [19], while the article "Suspension Fertilizers Based on Waste Phosphates from the Production of Polyols" [20] describes the method of producing the used waste suspension fertilizers.

Table 1 shows the division of fertilizers used in the field experiment according to their composition and the nitrogen dose applied.

Table 1. Division of fertilizers used in the field experiment according to their composition and the nitrogen dose applied (a—180 kg·ha^{-1}; b—135 kg·ha^{-1}).

Basic Composition NPK	9.5-4-11				9.5-6-11				0
P, %	4				6				0
P source	Waste			Fosdar	Waste			Fosdar	0
Type of fertilizer	NPK	NPK S Mg	NPK S Mg micro	NPK	NPK	NPK S Mg	NPK S Mg micro	NPK	0
Fertilizer	1	2	3	K2	4	5	6	K3	K1
N dose	a b	a b	a b	a b	a b	a b	a b	a b	0

The field experiment consisted of a total of 17 objects. The fertilizers marked nos. 1–6 were multi-component suspension fertilizers in which the source of phosphorus was liquid sodium–potassium phosphate from the production of polyols. All suspension fertilizers had the same N and K composition—9.5 and 11%, respectively. Suspension fertilizers 1–3 contained 4% P, and fertilizers 4–6 contained 6% P. Suspension fertilizers 1 and 4 contained only the main nutrients—NPK. Fertilizers 2 and 5, in addition to the main nutrients, contained secondary components—S and Mg. Fertilizers 3 and 6, in addition to the main and secondary nutrients, also contained microelements. The research included 3 controls: K1 (without fertilization), K2 (NPK composition the same as for suspension fertilizers 1–3) and K3 (NPK composition the same as for suspension fertilizers 4–6). Each fertilizer was applied to the field in an amount corresponding to two doses of nitrogen: a—180 kg·ha^{-1}; b—135 kg·ha^{-1}. The sources of N and K for all fertilizers (suspension and control) were potassium salt and ammonium urea solution. The source of P in the suspension fertilizers was liquid sodium–potassium phosphate from the production of polyols, while in the control samples (K2 and K3) it was granulated commercial fosdar fertilizer.

Field tests were carried out at the Experimental Farm of the University of Life Sciences in Lublin in Czesławice (51°18′24″ N, 22°16′04″ E) in the growing seasons of 2021, 2022 and 2023. The experimental plant was a new variety of corn grown for silage by the company Pioneer P8244. It is a medium-early variety with FAO: K240, single S.C. hybrid, grain type—dent. The field experiment was carried out using the randomized block method in three repetitions, giving a total of 51 experimental plots (3 × 17). The plots had an area of 25 m^2 and consisted of 8 rows spaced 75 cm apart (due to the spacing of the seeder nozzles).

The soil in the area designated for the field experiments was characterized by a very high content of phosphorus (350 mg·kg^{-1} of soil P_2O_5), potassium (291 mg·kg^{-1} of soil K_2O)

and magnesium (92 mg·kg^{-1} of soil) and an average content of sulfur (10.4 mg·kg^{-1} of soil SO_3) and nitrogen (30.3 kg·ha^{-1}). Microelements important for corn cultivation, such as zinc and manganese, were at an average level (10.6 mg·kg^{-1} of soil Zn, 260 mg·kg^{-1} of soil Mn), while the boron content was low (0.99 mg·kg^{-1} of soil). The soil reaction was slightly acidic (pH 6.3 in 1 mol KCl · dm^{-3}).

Sowing was carried out on the optimal dates for maize, i.e., 12 May 2021, 15 June 2022 and 9 May 2023. The maize sowing date in the second year of the study was later than in the remaining years due to the damage caused by wild boars and the need to repeat sowing. The sowing density was 80,000 grains·ha^{-1}. During the growth period, the plants were protected against weeds by spraying with Lumax 537.5SE insecticide. Fertilizers were applied before sowing in an amount corresponding to 70% of the total fertilizer dose with the remaining part as top dressing in the 5–6 leaf phase.

Corn was harvested at the milky–waxy ripeness stage, when the dry matter content was 30–35%. Yield parameters were determined based on a 2 m^2 harvest taken from the two central rows of each experimental plot. Above-ground plant parts were collected by manually cutting the plants 10 cm above the soil surface.

The yield of the above-ground part was weighed as the sum of the grain yield and the vegetative part, and the weight of the cobs was measured separately. From each experimental plot, 8 plants were randomly selected, their height was measured, and the number of cobs and the number of rows of grains in the cob were counted. Then, test plants from each plot were cut into pieces in a forage harvester, from which, after mechanical mixing, 500 g samples were taken. After weighing, the samples were placed in an air circulation oven set at 70 °C until the plant biomass reached a constant weight in order to estimate the dry weight value. The dried samples were ground and some were mineralized to prepare them for further research.

2.2. Statistical Analysis

The statistical results were prepared using the Statistica 13 program. For this purpose, ANOVA (analysis of variance) for factorial designs was used, and the significance of differences was determined using the Tukey test at a significance level of $\alpha = 0.05$ for each year of research separately. Assumptions for the ANOVA test were tested using the Levene test (homogeneity of variances) and the Shapiro–Wilk test (normality of distribution).

For each parameter in individual years, the impact of individual factors (marked with the letters A, B and C) and the impact of their interaction effects (A × B, A × C, B × C and A × B × C) are presented. The measure of this influence was determined by calculating the coefficient—partial eta squared (η^2_P)—which determines which factor explains to a greater extent the variability in the measured parameter.

The statistical analysis of the results was divided into two parts:

Part I—The effects of fertilizers were compared depending on the source of phosphorus (superior factor, 2 levels: polyol waste or phosphorus fertilizer). The secondary factors in this analysis were the phosphorus dose (2 levels: 4% or 6%) and the nitrogen dose (2 levels: 135 or 180 kg N·ha^{-1}). The obtained results were compared after a control test without fertilization. Using the Tukey test, homogeneous groups were determined for individual results (marked with lowercase letters: a or b) and homogeneous groups for mean values regardless of the nitrogen dose (vertical) and mean values regardless of the phosphorus dose (horizontal), marked with capital letters: G, H, I or J.

Part II—The effects of the produced suspension fertilizers were compared in terms of the dose of phosphorus (4% or 6%), the type of fertilizer (NPK, NKP + Mg + S or NPK + Mg + S + micro) and the dose of nitrogen (135 or 180 kg N·ha^{-1}). Using the Tukey test, homogeneous groups were distinguished for individual results (marked with lowercase letters: a or b) and homogeneous groups for average values regardless of the nitrogen dose (vertical) and average values regardless of the type of fertilizer (horizontal), which were marked with uppercase letters: G, H, I or J.

3. Results

3.1. Meteorological Conditions during the Field Experiment

Meteorological conditions during the field experiment varied in individual years of the study (Tables 2 and 3).

Table 2. Average monthly air temperatures (°C) throughout the field experiment.

Years	Months						Avg.
	IV	V	VI	VII	VIII	IX	
I	6.4	12.6	19.7	22.3	17.3	12.8	15.2
II	5.9	12.8	19.4	19.4	20.5	10.8	13.1
III	8.2	12.9	17.4	20.0	21.0	17.6	16.1
Avg.	6.8	12.8	18.8	20.6	19.6	13.7	
Avg. 2011–2020	9.5	14.4	18.5	20.1	19.7	14.7	

Table 3. Monthly totals of rainfall (mm) throughout the field experiment.

Years	Months						Avg.
	IV	V	VI	VII	VIII	IX	
I	49.1	55.7	43.2	43.0	231.7	62.1	80.7
II	53.2	36.3	38.7	111.8	52.3	112.3	67.4
III	57.9	66.0	60.0	84.7	46.4	28.5	57.3
Avg.	53.4	52.7	47.3	79.8	110.1	67.6	
Avg. 2011–2020	40.8	80.3	64.3	91.3	54.9	60.2	

The highest average temperature during the growing season was recorded in the third year of field research (16.1 °C), and the lowest was recorded in the second year (13.1 °C). However, the highest average rainfall was recorded in the first year of research (80.7 mm) and the lowest in the third year (57.3).

The third year of field research was the most favorable during the plant emergence period—it was characterized by the highest temperature and rainfall in April and May.

In order to more fully characterize the meteorological conditions that occurred during the field experiment, the Sielianinow hydrothermal index (k) was calculated [21]:

$$k = \frac{P}{0.1 \cdot \Sigma t}$$

where:

P—monthly sum of atmospheric precipitation (mm);
Σt—monthly sum of air temperatures > 0 °C.

The Sielianinow coefficient indicates the water supply of plants during the growing season and is divided into classes presented in Table 4.

Table 4. Division of the Sielianinow coefficient into classes.

Color Coding	k-Factor Range	Description
🟥	$k \leqslant 0.4$	Extremely dry conditions
🟧	$0.4 < k \leq 0.7$	Very dry conditions
🟨	$0.7 < k \leq 1.0$	Dry conditions
🟨	$1.0 < k \leq 1.3$	Quite dry conditions
🟩	$1.3 < k \leq 1.6$	Optimal conditions
🟦	$1.6 < k \leq 2.0$	Quite humid conditions
🟦	$2.0 < k \leq 2.5$	Humid conditions

🟦	2.5 < $k \leq 3.0$	Very humid conditions
🟦	k > 3.0	Extremely humid conditions

Using the Sielianinow coefficient (Table 5), it can be stated that in each year of field research, corn sowing was preceded by a month with favorable moisture conditions (*k*: 2.35–3.01). The best sowing conditions occurred in May in the first year of research (*k*: 1.43) and the worst in June in the second year of research (*k*: 0.66). The subsequent stages of corn development were accompanied by different conditions in individual years. The harvest stage in September varied greatly each year. The most optimal conditions were recorded in the first year of research (*k*: 1.62), in the second year the conditions were extremely humid (*k*: 3.47), and in the third year they were very dry (*k*: 0.54).

Table 5. Sielininov's coefficient values throughout the field research period.

Years	**Months**					
	IV	**V**	**VI**	**VII**	**VIII**	**IX**
I	2.56	1.43	0.73	0.62	4.32	1.62
II	3.01	0.91	0.66	1.86	0.82	3.47
III	2.35	1.65	1.15	1.37	0.71	0.54

3.2. Results of Field Tests

Figure 1 shows a top view of experimental plots with corn made in the third year of field research. The marked plots with a clearly lighter shade of green represent objects without fertilization.

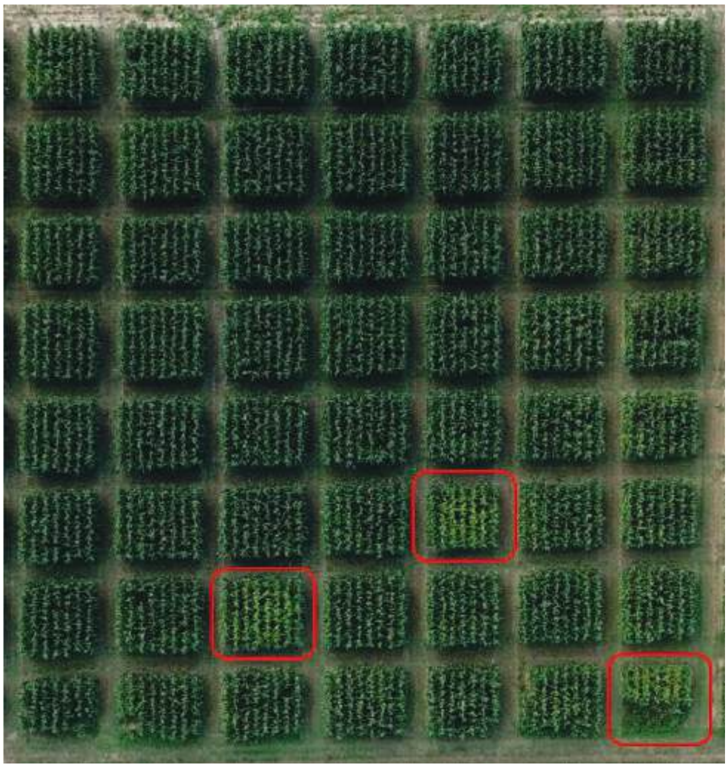

Figure 1. Drone photo of experimental plots in the third year of research—marked plots show objects without fertilization.

3.2.1. Dry Matter Content

The date of corn harvest was determined based on the dry matter content so that its value was in the range of 30–35%. In the first year of the study, the average dry matter content was 33.49%, in the second year it was 32.49%, and in the third year of the study it was 33.06%.

Table 6 lists the average yield of dry matter of corn plants depending on the type of phosphorus source in the fertilizer and its percentage, separated into individual years of research and the nitrogen dose applied.

Table 6. Average amount of dry matter (t·ha^{-1}) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the source of phosphorus and its percentage in the fertilizer.

Year	**N dose, kg N/ha (C)**	**Source of Phosphorus in Fertilizer (A)**						**Control without Fertilization**
		Polyol Waste			**Fosdar (Control)**			
		Percentage of P (B)						
		4%	**6%**	**Avg.**	**4%**	**6%**	**Avg.**	
I	**180**	24.74 ab	24.86 ab	24.80 GH	25.90 b	26.13 b	26.02 H	19.27 c
	135	22.87 a	24.98 ab	23.93 H	25.53 b	25.72 b	25.63 H	
	Avg.	23.81 G	24.92 GH		25.71 H	25.93 H		
	Avg.	24.36 G			25.82 H			
	A–η^2_P = 51.57% B–s.i.		C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	
II	**180**	23.41 ab	23.48 ab	23.45 G	23.11 ab	24.55 b	23.83 G	18.52 c
	135	22.45 a	24.32 ab	23.39 G	22.99 ab	23.99 ab	23.49 G	
	Avg.	22.93 G	23.90 GH		23.05 G	24.27 H		
	Avg.	23.42 G			23.66 G			
	A–s.i. B–η^2_P = 45.80%		C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	
III	**180**	23.98 a	24.43 a	24.21 G	24.80 a	24.91 a	24.85 G	19.31 b
	135	23.05 a	24.22 a	23.64 G	24.84 a	25.08 a	24.96 G	
	Avg.	23.52 G	24.33 GH		24.82 GH	24.99 H		
	Avg.	23.92 G			24.91 H			
	A–η^2_P = 32.52% B–s.i.		C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	

In the first and third years of the study, the source of phosphorus used in fertilizers had a significant impact on the amount of fresh matter obtained, explaining 51.57% of the variability in the first year and 32.52% in the second year. In each case, a higher yield of green matter was obtained on plots where fosdar was the source of phosphorus. However, regardless of the type of phosphorus source in the fertilizer, the average dry matter yield exceeded 22 t·ha^{-1}, while the yield of plots without fertilization was around 19 t/ha. In the second year of the study, the cause of significant variability in the amount of biomass obtained was the phosphorus content in the fertilizer. For fertilizers containing 6% P, a higher average dry matter yield was obtained (24.09 t·ha^{-1}) than for fertilizers containing 4% P (22.99 t·ha^{-1}). The nitrogen dose applied did not have a significant impact on this parameter.

Table 7 lists the average yield of dry matter of corn plants depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of research and the nitrogen dose applied.

Table 7. Average amount of dry matter (t·ha^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the type of suspension fertilizer and the percentage of phosphorus.

Year	**N Dose, kg N/ha (C)**	**Percentage of P (A)**							
		4%				**6%**			
		Type of Fertilizer (B)							
		NPK	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**	**NPK**	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**
I	**180**	24.74 ab	25.71 a	25.22 ab	25.22 G	24.86 ab	25.14 ab	25.71 a	25.24 G
	135	22.87 b	24.92 ab	24.97 ab	24.25 G	24.98 ab	24.67 ab	25.55 ab	25.07 G
	Avg.	23.81 G	25.31 GH	25.10 GH		24.92 GH	24.91 GH	25.63 H	
	Avg.	24.74 G				25.15 G			
	A–s.i. B–η^2_P = 26.72%			C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	
II	**180**	23.41 a	24.81 a	24.08 a	24.10 G	23.48 a	24.21 a	24.76 a	24.15 G
	135	22.45 a	23.44 a	24.10 a	23.33 G	24.32 a	24.13 a	24.44 a	24.30 G
	Avg.	22.93 G	24.12 GH	24.09 GH		23.90 GH	24.17 GH	24.60 H	
	Avg.	23.71 G				24.22 G			
	A–s.i. B–η^2_P = 26.93%			C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	
III	**180**	23.98 a	23.90 a	24.53 a	24.14 GH	24.43 a	24.64 a	25.59 a	24.89 H
	135	23.05 a	24.06 a	23.30 a	23.47 G	24.22 a	24.51 a	25.10 a	24.61 GH
	Avg.	23.52 G	23.98 GH	23.91 GH		24.33 GH	24.57 GH	25.35 H	
	Avg.	23.80 G				24.75 H			
	A–η^2_P = 27.45% B–s.i.			C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	

The type of suspension fertilizer significantly differentiated the average dry matter yield in the first and second years of field tests, accounting for approximately 26% of the variability. In both years, significant differences were noted between NPK fertilizers and NPK S Mg micro fertilizers, for which the dry matter yield was significantly higher. In the third year of research, the cause of variability in the average dry matter yield turned out to be the phosphorus content in the fertilizer (η^2_P = 27.45%). In this case, fertilizers with a higher phosphorus content gave an average dry matter yield significantly higher by 0.95 t·ha^{-1}. In the experiment, the nitrogen dose had no significant effect on the yield.

Figure 2 shows the distribution of dry matter measurement results for all objects tested in the field test over 3 years. It is clearly visible that the dry matter yield for plots without fertilization is much lower than for plots where fertilization was applied. However, there are no such significant differences between fertilized plots. It can be noticed that the median value of dry matter for plots where a reduced dose of nitrogen was applied (b—135 kg/ha) is lower compared to plots where the nitrogen dose was 180 kg/ha (a). This difference is most clearly visible in suspension fertilizers with a basic NPK composition and a lower dose of phosphorus (1a and 1b). The presented graph also indicates higher dry matter yields for plots fertilized with suspension fertilizers with a phosphorus content of 6% (fertilizers 4–6) compared to suspension fertilizers with a 4% phosphorus content (fertilizers 1–3). For the control plots (K2 and K3), where the source of phosphorus was granulated fosdar fertilizer, a large scatter of results was observed. In these cases, however, the obtained media values were higher compared to the values obtained in plots where the source of phosphate was polyol waste (fertilizers 1–6).

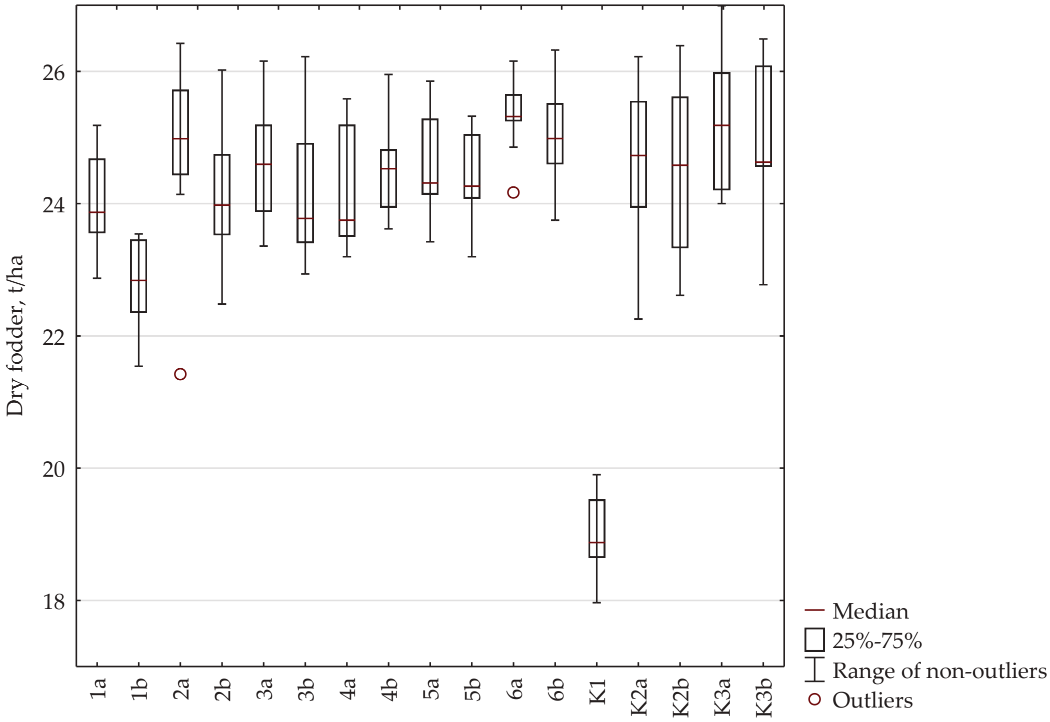

Figure 2. Box-plot showing the distribution of the amount of dry matter for individual objects in the field experiment, taking into account the median value, the range between 25 and 75% of the results, the range of non-outlier results and outliers.

3.2.2. Maize Plant Height

Table 8 lists the average height of corn plants depending on the type of phosphorus source in the fertilizer and its percentage, divided into individual years of research and the nitrogen dose applied.

Table 8. Average height of plants (cm) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the source of phosphorus and its percentage in the fertilizer.

Year	**N Dose, kg N/ha (C)**	**Source of Phosphorus in Fertilizer (A)**						**Control without Fertilization**
		Polyol Waste			**Fosdar (Control)**			
		Percentage of P (B)						
		4%	6%	Avg.	4%	6%	Avg.	
I	**180**	283.71 b	280.67 ab	282.19 GH	287.42 b	285.71 b	286.56 H	
	135	272.29 a	285.29 b	278.79 G	285.38 b	282.54 ab	283.96 GH	256.75 c
	Avg.	278.00 G	282.98 GH		286.40 H	284.13 GH		
	Avg.	280.49 G			285.26 H			
	A–η^2_p = 4.02% B–s.i.*		C - s.i.		A × B - η^2_p = 2.36% A × C–s.i.		B × C - η^2_p = 2.49% A × B × C - η^2_p = 3.28%	
II	**180**	274.04 ab	279.88 abc	276.96 GH	284.38 bc	281.67 abc	283.02 G	
	135	273.04 a	273.38 ab	273.21 H	281.38 abc	286.13 c	283.75 G	254.38 d
	Avg.	273.45 G	276.63 GH		282.88 HI	283.90 I		
	Avg.	275.08 G			283.39 H			
	A–η^2_p = 9.13% B–s.i.		C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	
III	**180**	272.21 a	274.08 a	273.15 G	274.38 a	278.17 a	276.27 G	
	135	273.57 a	275.29 a	274.48 G	276.83 a	278.50 a	277.67 G	243.08 b
	Avg.	272.94 G	274.69 G		275.60 G	278.33 G		
	Avg.	273.81 G			276.97 G			
	A–s.i. B–s.i.		C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	

* Statistically insignificant.

In the first and second years of the study, there were slightly significant differences in the height of corn plants depending on the source of phosphorus used in fertilization. The highest average height of plants in both years was recorded for plants fertilized with fertilizers containing fosdar ($x_{\mathrm{I\ fosdar}}$ = 285.26 cm, $x_{\mathrm{II\ fosdar}}$ = 283.39 cm). The height of plants fertilized with suspension fertilizers based on polyol waste was lower by an average of 4.77 cm and 8.31 cm in the first and second years of the study, respectively. In each year, the lowest values of average plant height were obtained for plants on plots without fertilization. The percentage of phosphorus in the fertilizer did not significantly differentiate the height of plants, nor did the dose of nitrogen.

Table 9 lists the average height of corn plants depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of research and the nitrogen dose applied.

Table 9. Average plant heights (cm) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the type of suspension fertilizer and the percentage of phosphorus.

Year	N Dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg Micro	Avg.	NPK	NPK S Mg	NPK S Mg Micro	Avg.
I	180	283.71 a	285.88 a	287.92 a	285.83 H	280.67 ab	283.87 a	287.88 a	284.14 GH
	135	272.29 b	283.88 a	287.75 a	281.31 H	285.29 a	284.58 a	286.50 a	285.46 GH
	Avg.	278.00 G	284.88 H	287.83 H		282.98 GH	284.23 H	287.19 H	
	Avg.		283.57 G				284.80 G		
	A–s.i. B–$\eta^2_p = 7.68\%$		C–s.i.		A × B–s.i. A × C–$\eta^2_p = 2.10\%$		B × C–s.i. A × B × C–$\eta^2_p = 3.31\%$		
II	180	274.00 ac	280.71 abcd	285.29 abd	280.55 G	279.88 abcd	284.71 abd	285.79 bd	283.46 G
	135	273.04 c	276.25 abc	275.67 abc	274.99 H	273.38 c	287.21 d	284.71 abd	281.76 G
	Avg.	273.54 G	278.48 GH	280.48 HI		276.63 GH	285.96 I	285.25 I	
	Avg.		277.50 G				282.61 H		
	A–$\eta^2_p = 4.87\%$ B–$\eta^2_p = 8.87\%$		C–$\eta^2_p = 2.16\%$		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.		
III	180	272.21 a	283.04 abc	280.67 abc	278.64 G	274.08 ab	286.13 abc	288.83 c	283.01 G
	135	273.67 ab	275.67 abc	282.50 abc	277.28 G	275.29 abc	282.63 abc	287.17 bc	281.69 G
	Avg.	278.94 G	279.35 GHI	281.58 HIJ		274.69 GH	284.38 IJ	288.00 J	
	Avg.		277.96 G				282.35 H		
	A–$\eta^2_p = 2.26\%$ B–$\eta^2_p = 9.34\%$		C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.		

The analysis of variance showed a significant impact of the type of suspended fertilizer used on the average height of plants in each year of the study. Regardless of the percentage of P, fertilizers with a basic NPK composition significantly influenced the lower height of plants compared to fertilizers with the addition of secondary and micronutrients. In the second and third years of field tests, a significant impact of the percentage of P on this parameter was also noted, in favor of fertilizers with a higher P content.

Figure 3 shows the distribution of the obtained results of plant height measurement for all objects examined in the field test over 3 years. The graph clearly shows that the lowest plant heights were recorded in plots without fertilization.

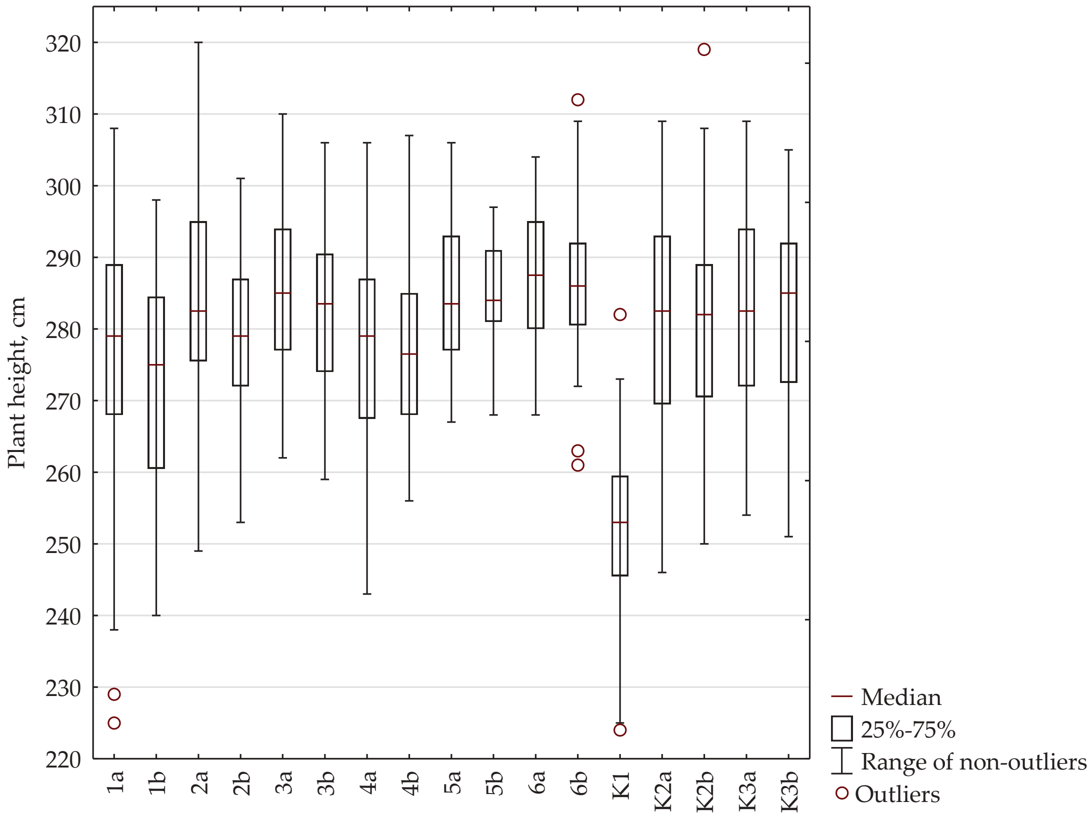

Figure 3. Box-plot showing the distribution of plant heights for individual objects in the field experiment, taking into account the median value, the range between 25 and 75% of the results, the range of non-outlier results and outlier values.

3.2.3. The Ratio of the Weight of the Cob to the Weight of the Green Fodder

Table 10 lists the average share of corn cobs in biomass depending on the type of phosphorus source in the fertilizer and its percentage, divided into individual years of research and the nitrogen dose applied.

Table 10. The ratio of the mass of cobs to the total green fodder (%) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the source of phosphorus and its percentage content in the fertilizer.

Year	N Dose, kg N/ha (C)	Source of Phosphorus in Fertilizer (A)						Control without Fertilization
		Polyol Waste			Fosdar (Control)			
		Percentage of P (B)						
		4%	6%	Avg.	4%	6%	Avg.	
I	180	45.37 a	45.68 a	45.52 G	44.97 a	45.02 a	44.99 G	38.21 b
	135	45.60 a	45.07 a	45.34 G	45.04 a	45.81 a	45.43 G	
	Avg.	45.48 G	45.38 G		45.39 G	45.03 G		
	A–s.i. B–s.i.		C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	
II	180	45.75 ab	45.67 ab	45.71 G	47.91 b	46.59 b	47.25 G	38.58 a
	135	45.99 ab	46.23 ab	46.11 G	46.83 b	44.95 ab	45.89 G	

	Avg.	45.87 G	45.95 G		47.37 G	45.77 G		
	A–s.i. B–s.i.		C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	
III	**180**	45.43 a	44.86 a	45.15 AG	45.47 a	46.16 a	45.81 G	36.97 b
	135	45.36 a	47.44 a	46.40 G	47.22 a	45.45	46.34 G	
	Avg.	45.39 G	46.15 G		46.35 G	45.80 G		
	A–s.i. B–s.i.		C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	

The average percentage of cobs in the total biomass was significantly different only compared to the treatment without fertilization. For fertilized plots, it was in the range of 44–47%, and for plots without fertilization it was 36–38%.

Table 11 lists the average share of corn cobs in biomass depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of research and the nitrogen dose applied.

Table 11. The ratio of the mass of cobs to the total green fodder (%) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the type of suspension fertilizer and the percentage of phosphorus.

Year	**N Dose, kg N/ha (C)**	**Percentage of P (A)**							
		4%				**6%**			
		Type of Fertilizer (B)							
		NPK	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**	**NPK**	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**
I	**180**	45.37 a	46.21 a	45.74 a	45.77 G	45.68 a	46.05 a	45.11 a	45.61 G
	135	45.60 a	45.34 a	45.40 a	45.45 G	45.07 a	46.20 a	45.19 a	45.49 G
	Avg.	45.48 G	45.77 G	45.57 G		45.38 G	46.13 G	45.15 G	
	A–s.i. B–s.i.			C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	
II	**180**	45.75 a	45.20 a	48.59 a	46.51 G	45.67 a	46.83 a	48.27 a	46.92 G
	135	45.99 a	45.38 a	45.19 a	45.52 G	46.23 a	45.38 a	46.10 a	45.90 G
	Avg.	45.87 G	45.29 G	46.89 G		45.95 G	46.10 G	47.18 G	
	A–s.i. B–s.i.			C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	
III	**180**	45.43 a	46.76 a	44.79 a	45.66 G	44.86 a	44.80 a	46.20 a	45.29 G
	135	45.36 a	46.18 a	45.75 a	45.76 G	47.44 a	45.30 a	46.67 a	46.47 G
	Avg.	45.39 G	46.47 G	45.27 G		46.15 G	45.05 G	46.43 G	
	A–s.i. B–s.i.			C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	

The type of suspension fertilizer applied in the field study did not have a significant impact on the share of cobs in biomass.

3.2.4. Cobs on the Plant

Table 12 lists the average number of cobs on a single plant depending on the type of phosphorus source in the fertilizer and its percentage, broken down into individual years of research and the nitrogen dose used.

Table 12. Average number of cobs per plant (pcs) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the source of phosphorus and its percentage in the fertilizer.

Year	**N Dose, kg N/ha (C)**	**Source of Phosphorus in Fertilizer (A)**						**Control without Fertilization**
		Polyol Waste			**Fosdar (Control)**			
		Percentage of P (B)						
		4%	**6%**	**Avg.**	**4%**	**6%**	**Avg.**	
I	**180**	1.63 a	1.83 a	1.73 G	1.79 a	1.67 a	1.73 G	
	135	1.67 a	1.83 a	1.75 G	1.75 a	1.88 a	1.81 G	1.71 a
	Avg.	1.65 G	1.83 G		1.77 G	1.77 G		
	Avg.	1.74 G			1.77 H			
	A–s.i. B–s.i.		C - s.i.		A × B–s.i. A × C–s.i.		B × C - s.i A × B × C–s.i.	
II	**180**	1.50 a	1.54 a	1.52 G	1.75 a	1.79 a	1.77 GH	
	135	1.83 a	1.83 a	1.83 H	1.67 a	1.63 a	1.65 GH	1.58 a
	Avg.	1.67 G	1.69 G		1.71 G	1.71 G		
	Avg.	1.68 G			1.71 G			
	A–s.i. B–s.i.		C–s.i.		A × B–s.i. A × C–η^{2}_{p} = 4.97%		B × C–s.i. A × B × C–s.i.	
III	**180**	1.58 a	1.33 a	1.46 G	1.46 a	1.50 a	1.48 G	
	135	1.33 a	1.25 a	1.29 G	1.67 a	1.33 a	1.50 G	1.25 a
	Avg.	1.46 GH	1.29 G		1.56 H	1.42 GH		
	Avg.	1.38 G			1.49 G			
	A–s.i. B–η^{2}_{p} = 2.58%		C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.	

In the field study, no significant differences were found in the number of cobs per plant due to the source of phosphorus in the fertilizers used. The number of cobs on individual plants usually ranged between one and two pieces; occasionally, there were plants with three cobs. In the third year of the study, the content of phosphorus in fertilizers had a slightly significant impact, differentiating the number of cobs in plots fertilized with fertilizers containing 6% P and those in plots without fertilization. In the latter there was a greater share of plants with one cob.

Table 13 shows the average number of cobs on a single plant depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of research and the nitrogen dose applied.

Table 13. Average number of cobs per plant (pcs) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the type of suspension fertilizer and the percentage of phosphorus.

Year	N Dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**	**NPK**	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**
I	**180**	1.63 a	1.67 a	1.71 a	1.67 G	1.83 a	1.88 a	1.88 a	1.86 G
	135	1.67 a	1.79 a	1.75 a	1.74 G	1.83 a	1.67 a	1.71 a	1.74 G
	Avg.	1.65 G	1.73 G	1.73 G		1.83 G	1.77 G	1.79 G	
	Avg.	1.70 G				1.80 G			
		A–s.i. B–s.i.		C–s.i.	A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.		
II	**180**	1.50 a	1.67 a	1.71 a	1.62 G	1.54 a	1.67 a	1.83 a	1.68 G
	135	1.83 a	1.46 a	1.58 a	1.63 G	1.83 a	1.63 a	1.88 a	1.78 G
	Avg.	1.67 GH	1.56 G	1.65 GH		1.69 GH	1.65 GH	1.85 H	
	Avg.	1.63 G				1.73 G			
		A–s.i. B–s.i.		C–η^2_P = 2.16%	A × B–s.i. A × C–s.i.		B × C–η^2_P = 3.69% A × B × C–s.i.		
III	**180**	1.58 ab	1.38 ab	1.78 b	1.56 H	1.33 ab	1.17 a	1.21 a	1.24 H
	135	1.33 ab	1.50 ab	1.75 b	1.53 H	1.25 a	1.50 ab	1.33 ab	1.36 GH
	Avg.	1.46 GH	1.44 G	1.73 H		1.29 G	1.33 G	1.27 G	
	Avg.	1.30 G				1.54 H			
		A–η^2_P = 6.55% B–s.i.		C–s.i.	A × B–η^2_P = 2.75% A × C–s.i.		B × C–η^2_P = 3.07% A × B × C–s.i.		

When differentiating the suspension fertilizers used in the experiment due to their composition, no significant differences were noted in the number of cobs on individual plants. In the third year of research, a significant relationship was noted between the number of cobs and the phosphorus content in fertilizers, where a lower amount of P in the fertilizer resulted in a larger number of plants with fewer cobs. The nitrogen dose applied did not significantly affect the number of cobs on the plants.

3.2.5. Number of Rows of Grains in the Cob

Table 14 lists the average number of rows of grains in a cob depending on the type of phosphorus source in the fertilizer and its percentage, divided into individual years of research and the nitrogen dose applied.

Table 14. Average number of rows of grains in a cob (pieces) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the source of phosphorus and its percentage in the fertilizer.

Year	N Dose, kg N/ha (C)	Source of Phosphorus in Fertilizer (A)						Control without Fertilization
		Polyol Waste			Fosdar (Control)			
		Percentage of P (B)						
		4%	6%	Avg.	4%	6%	Avg.	
I	180	14.33 ab	13.83 ab	14.08 G	13.88 ab	14.79 b	14.33 G	
	135	14.38 ab	13.96 ab	14.17 G	14.13 ab	13.33 a	13.73 G	13.71 ab
	Avg.	14.35 G	13.90 G		14.00 G	14.06 G		
	Avg.	14.13 G			14.03 G			
	A–s.i. B–s.i.			C - s.i.	A × B–s.i. A × C–s.i.		B × C - η^2_p = 1.91% A × B × C–η^2_p = 2.31%	
II	180	14.13 a	14.88 ab	14.50 G	14.83 ab	15.33 ab	15.08 G	
	135	14.58 ab	15.00 ab	14.79 G	15.71 b	14.83 ab	15.27 G	15.08 ab
	Avg.	14.35 G	14.94 GH		15.27 H	15.08 GH		
	Avg.	14.65 G			15.18 H			
	A–η^2_p = 2.58% B–s.i.			C–s.i.	A × B–s.i. A × C–s.i.		B × C–η^2_p = 2.14% A × B × C–s.i.	
III	180	13.96 ab	14.29 abc	14.13 G	15.13 c	14.67 abc	14.90 H	14.63 abc
	135	14.92 bc	13.67 a	14.29 GH	14.46 abc	14.54 abc	14.50 GH	
	Avg.	14.44 GH	13.98 G		14.79 H	14.60 GH		
	Avg.	14.21 G			14.70 H			
	A–η^2_p = 3.36% B–s.i.			C–s.i.	A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–η^2_p = 3.94%	

In the second and third years of the study, significant differences were noted in the number of grain rows in the cob due to the phosphorus source used in fertilization. In both years, corn fertilized with fosdar had cobs with a larger number of rows of grains. Table 15 lists the average number of grain rows in a cob depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of research and the nitrogen dose applied.

Table 15. Average number of grain rows in a cob (pieces) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the type of suspension fertilizer and the percentage of phosphorus.

Year	N Dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg Micro	Avg.	NPK	NPK S Mg	NPK S Mg Micro	Avg.
I	180	14.33 ab	14.50 ab	13.96 ab	14.26 G	13.83 a	14.63 ab	15.21 b	14.56 G
	135	14.38 ab	14.29 ab	14.38 ab	14.35 G	13.96 ab	14.54 ab	14.54 ab	14.35 G
	Avg.	14.35 GH	14.40 GH	14.17 GH		13.90 G	14.58 GH	14.87 H	
	Avg.		14.31 G				14.45 G		
	A–s.i. B–s.i.		C–s.i.		A × B–η^2_p = 3.17% A × C–s.i.		B × C–s.i. A × B × C–s.i.		
II	180	14.13 a	15.00 a	14.92 a	14.68 G	14.88 a	14.58 a	14.08 a	14.51 G
	135	14.58 a	14.75 a	14.92 a	14.75 G	15.00 a	14.75 a	14.33 a	14.69 G
	Avg.	14.35 G	14.88 G	14.92 G		14.94 G	14.67 G	14.21 G	
	Avg.		14.72 G				14.60 G		
	A–s.i. B–s.i.		C–s.i.		A × B–η^2_p = 3.83% A × C–s.i.		B × C–s.i. A × B × C–s.i.		
III	180	13.96 a	14.08 a	14.38 a	14.14 G	14.29 a	14.46 a	13.92 a	14.22 G
	135	14.92 a	14.38 a	14.67 a	14.65 G	13.67 a	14.46 a	14.38 a	14.17 G
	Avg.	14.44 G	14.23 G	14.52 G		13.98 G	14.46 G	14.15 G	
	Avg.		14.40 G				14.19 G		
	A–s.i. B–s.i.		C–s.i.		A × B–s.i. A × C–s.i.		B × C–s.i. A × B × C–s.i.		

In the first and second years of field research, the only significant influence on the number of grain rows in the cob was the interaction effect between the type of fertilizer and the phosphorus content. In both cases, it accounted for only 3–4% of the variability.

4. Discussion

- Choice of variety

The appropriate selection of varieties is a key factor in growing corn for silage from whole plants because it determines the success of this process in almost 30% of cases [14,22]. A new "stay-green" corn variety intended for green fodder from Pioneer-P8244- was selected for field tests. It is a medium-early variety with FAO 240 and dent-type grain.

Hybrids intended for the production of whole-plant silage should be so early that the grain reaches at least the waxy maturity phase during the growing season [14]. The introduction of new varieties contributed to qualitative and quantitative progress in maize breeding. Hybrids with a shorter vegetation period were created, which enabled cultivation in regions that were less favorable in terms of thermal conditions and a shorter vegetation period. This had a direct impact on the growth of crops [12,16].

High-yielding modern corn hybrids accumulate more biomass and respond better to fertilizers. This, combined with increased photosynthetic efficiency, results in greater yield and nitrogen use efficiency, which reduces fertilizer doses, lowering costs [9]. Modern corn varieties have greater yield potential than those developed a few or a dozen years ago. In addition to higher productivity, they are also characterized by greater resistance to stress factors and have other important agronomic and utility features [23].

"Stay-green" varieties work very well in crops for fodder purposes. This genetically modified feature affects the prolonged accumulation of nutrients in plants and leaves during the ripening period. Therefore, these varieties are characterized by a large share of green plant parts when the grain reaches late-wax maturity. This allows for the production of good-quality raw material containing properly developed grain with preserved green leaves and stems. Such raw material is beneficial for the proper ensiling process [23].

The "stay-green" effect is particularly beneficial when growing on soils with weaker water retention and when droughts occur frequently. Such varieties are less susceptible to premature drying of plants. Their higher drought tolerance is due to their developed root system, which ensures better use of available moisture [23].

Long-term preservation of green and healthy leaves also acts as a natural barrier hindering the development of fungal diseases in plants. Corn varieties with the "stay-green" feature show higher resistance to fusarium diseases, which particularly attack corn under stressful conditions, such as drought [23].

- Selection of the earliness of the variety

The earliness of the variety is decisive when choosing the direction of cultivation—grain or silage [23]. When selecting it, the climatic conditions of the region where the cultivation is planned should also be taken into account [22,23].

Early varieties are characterized by a shorter vegetation period. As a result, they have lower yields but have a large share of cobs in both green and dry matter. They are also characterized by lower humidity of 25–30% [22].

Medium-early ripening hybrids take 10–12 days longer to fully mature but produce a 5–10% higher seed yield. Nevertheless, the share of cobs in the mass intended for ensiling is lower compared to early varieties [22]. Medium-late ripening varieties reach harvest maturity 23–26 days after early varieties. The grain yield is up to 15% higher, but they have the lowest share of cobs in silage [22].

- Influence of climatic conditions

Environmental parameters such as temperature, precipitation and sun exposure significantly modify physiological processes and plant growth on a large spatial scale, which can have a significant impact on yield and quality [24].

Corn, a C4-type plant, is characterized by high efficiency of photosynthesis and the ability to adapt to various environmental conditions. It can grow both in the tropics and in temperate and sub-tropical zones [1,25]. However, drought and heat, common environmental factors, have a significant impact on green fodder yield and quality [26].

Corn is a plant with high thermal requirements resulting from its natural origin [22]. The rate of subsequent development stages of corn is determined by the sum of physiologically effective temperatures (SPET). The base temperature is assumed to be approximately 8 °C. It is assumed that half of the heat needs to fall in the vegetative growth period (until flowering) and the other half in the generative period (kernel development). SPETs vary depending on the corn variety. The higher the FAO number, the higher the SPET value and the longer the growing season. For example, for medium-earliness varieties, regardless of the biomass purpose, the sum of effective temperatures ranges from 1310 °C to 1370 °C, while for late varieties it most often ranges from 1420 °C to 1480 °C [22].

The growth of corn intended for silage can be favorably stimulated by relatively high temperatures, provided that it is supplied with an appropriate amount of water. As a result, plants reach the SPET more quickly and the growth period may be shorter compared to crops in regions with lower temperatures and rainfall. However, corn, being a short-day plant, may delay the flowering phase in case of longer hours of sunlight. This leads to delayed maturity and an extended growth period. The quality of the feed then gradually deteriorates as a result of the increasing stem-to-leaf ratio. This leads to a decrease in dry matter digestibility due to an increase in cellulose and lignin content [16,24].

Heat stress, in addition to affecting the pollination process, may limit the development of the seed after pollination. This development is divided into a phase of stagnation and a phase of linear growth, during which a significant accumulation of dry matter occurs. The stagnation phase begins immediately after pollination and lasts from 10 to 12 days. Despite the small growth of the seed during this period, it plays a key role in development. The division of endosperm cells in this phase affects its ability to accumulate starch in the grain. High temperatures after the silking period limit this process. Grains subjected to heat stress accumulate from 18% to 75% less dry matter, which is associated with reduced starch synthesis in the endosperm at temperatures above 35 °C [26].

Low temperature causes leaves to narrow, cell walls to thicken and fiber content to increase [24]. However, thanks to the introduction of short-season hybrids, green fodder production has also become possible in colder regions [16]. There, corn grown for feed may also outweigh corn for grain [1]. Therefore, silage maize varieties that have a short growth period and are resistant to low temperatures should be grown in high-latitude areas [24].

A plant’s water supply is determined by various factors, including the amount and distribution of rainfall, evapotranspiration, and the water retention capacity of the soil. The interaction of these factors can have a significant impact on the yield and nutritional composition of maize intended for silage production [26].

Despite the farmer’s limited influence on water conditions in the soil, it is possible to modify the soil profile to better prepare plants for abiotic stress. This often requires adjusting the agrochemical characteristics of the soil, such as pH and mineral content [22].

Corn is characterized by intensive growth and extensive above-ground biomass, which translates into a high demand for water, despite a relatively low transpiration coefficient [22].

Corn is water efficient, using less per unit weight than wheat and alfalfa. To produce 1 kg of dry matter, corn uses about 360 L of water, while wheat needs approximately 500 L and alfalfa as much as 860 L [1,25,27]. Despite this, growing corn per 1 ha requires significant amounts of water, even several or several million liters [23]. Corn also has a favorable water footprint per energy unit of 0.41 L of water per kilocalorie but still contributes 6% to the global water footprint [1,25].

Corn reacts strongly to periodic water shortages, especially before flowering [22]. Appropriate soil hydration is crucial for efficient germination and emergence. Reducing irrigation in the silking phase leads to a reduction in grain yield, but the number of grains in the ear does not change. Drought stress during the growing season may threaten dry matter yields but does not necessarily affect grain development and the potential nutritional composition of silage [26].

Drought stress and heat stress often occur simultaneously. High ambient temperatures increase evapotranspiration, which worsens the effects of drought, especially when accompanied by low relative humidity [26].

- Optimal date for sowing corn

Selecting the appropriate sowing date allows for optimal use of climatic conditions, such as temperature, humidity and day length, and allows for synchronizing the flowering time with the appropriate temperature [6,28].

Corn is characterized by a strong photoperiodic response and responds very strongly to day length [23]. Therefore, the selection of the appropriate date for sowing corn is crucial for the proper course of its development phases, yielding and shaping the proportions between various components of the yield [15].

When severe frosts occur in early spring, all emerging plants die, regardless of their developmental stage. Temporary frosts damage the first leaves, but the plant can quickly regenerate from the underground part of the stem, where the growth cone is located, when thermal conditions become favorable. Corn plants are susceptible to damage at temperatures of 0–5 °C. If they are exposed to such cooling for a long time, it may lead to their death [22].

Timely and correctly performed sowing ensures optimal conditions for germination and emergence, adequate time for growth and development, greater resistance to pests and diseases, and greater competitiveness with weeds [22].

There are greater benefits from accelerating sowing than delaying it [23]. Early and intermediate sowing dates usually allow the best use of solar energy for grain production [13,29]. However, too early sowing results in prolonged germination and emergence due to too low soil temperature, and the seeds are susceptible to damage by diseases and pests [22].

When corn sowing is delayed, the initial development of plants occurs during the lengthening of the day. In such a situation, the corn accumulates a larger vegetative mass and moves to the phase of generative development and maturation with a delay [15]. A delayed sowing date has a beneficial effect on quick and uniform emergence, but in the case of growing maize for silage, it leads to a reduction in the share of cobs in the total yield, which in turn reduces the feed value of the silage [22].

Research has shown that delaying the sowing date leads to a reduction in the thousand-seed weight, the number of seeds per corn cob, the length of the cob, the seed yield, and the protein, ash and oil content in the seeds. These effects result from shortening the vegetation period and limiting the seed filling process [6,29,30]. The reduction in yield in the case of late sowing of corn is the result of the fact that the grain filling phase coincides with the arrival of cold weather in autumn, as well as the lack of adequate heat supply during the growing season [6]. Early varieties are more tolerant of delayed sowing [23].

The optimal sowing date varies depending on the region, due to the length of the growing season and the level of average temperatures [22].

- Proper sowing depth of corn seeds

The seed sowing depth depends on the type of soil and the sowing date. In the case of more compact and moist soil and earlier sowing, it is recommended to sow at a depth of 4–5 cm. However, on lighter and more permeable soils, and when sowing later, the optimal depth is 5–8 cm [22].

The use of deeper sowings has a beneficial effect on the availability of moisture, but in this case the soil temperature around the seeds is lower, which leads to a slower process of nutrient uptake. However, in a situation where the top layer of soil is significantly dry and there are no forecasts of upcoming rainfall, the decision to sow seeds deeper is justified [23].

- Sowing density and its impact on yield

Corn is one of the plants that is particularly susceptible to fluctuations in planting density [31]. Due to its photophilous origin, it reacts very strongly to any shading. Therefore, accuracy and precision during sowing are of great importance in corn cultivation technology [23].

Adjusting sowing density is one of the key crop management tools that allows the use of environmental factors, nutrients and especially light to optimize the structure of corn plantations and maximize yields [6,32].

The optimal density of plants aims to minimize competition between them while ensuring the largest possible number of well-seeded cobs per unit area. Any errors in this area have a strong impact on the yield, and repairing them during the growing season is impossible [22,23].

The selection of plant stock should take into account the variety, its earliness, soil fertility and the recommendations of specialists from breeding and seed companies [22,23].

Higher plant density has a positive effect on dry matter production [10].

In the 1930s in the United States, the average planting density of grain corn was approximately 3 plants·m^{-2} or less [14]. Currently, in intensively cultivated areas in the USA, the average planting density is about 8 plants·m^{-2} [14,31]. However, in European Union countries, where soil and climatic conditions are more diverse, this value may vary from 6 to 8 plants·m^{-2} [23,31,33]. In both of these regions, a common row spacing at current planting densities is around 0.70–0.75 m [31,33].

When growing maize for silage and on less fertile soils, as well as when using earlier varieties, a higher planting density is recommended. In this case, the sowing density is 9–10 plants·m^{-2} [22,23] and may even reach 12–16 plants·m^{-2} [12].

In areas where there are repeated periods of drought, especially in fields with light soils, a lower planting density is recommended. In the case of better soils, a larger number of plants per unit area is favorable for development and yield [22,23].

The optimal plant density is not only a matter of the number of plants per unit area but also their even distribution [22,23]. Minimizing local crowding caused by uneven sowing reduces competition between plants for key growth factors. The most important of these factors is light, followed by nutrients and water. Even planting increases the productivity of individual plants and allows them to achieve their full yield potential [31,34,35].

The main goal of increasing the planting density of corn plants is to achieve higher grain or biomass yields, which contributes to greater efficiency and competitiveness of the cultivation system per unit area. In the absence of biotic and abiotic stresses, yield is directly related to the amount of sunlight the crop is able to capture [31].

Modern hybrids show higher tolerance to higher plant densities and are more resistant to stressful conditions of intraspecific competition. This leads to fewer barren plants and less stem lodging [31]. These hybrids are characterized by more vertical growth and shorter leaves and also have greater synchronization between female and male inflorescences, which reduces infertility [16,31].

Reducing the distance between adjacent rows of plants brings a number of benefits. Close row spacing accelerates corn growth at the beginning of the season, which leads to more efficient use of radiation and higher yields. Optimal light capture by closing the canopy earlier limits light penetration, reducing competition from weeds, especially those that are shade-intolerant. Faster shading ensures better water management by limiting the evaporation of water from the soil. In addition, it contributes to better soil protection, reduces water runoff and prevents erosion [35].

Increasing the plant density above the critical density increases competition between neighboring plants [6,35]. Too high a density of plants in a field impairs the supply of light and access to water and nutrients [15]. This has a negative impact on the quantity and quality of the obtained crop. In extreme cases, it prolongs the intervals between flowering and silking, which leads to failure to set the cobs, poorer graining and delayed ripening [6,15,35,36]. Moreover, in such an environment, more plants are infertile. Plants are weakened and more susceptible to lodging, and with increased humidity in the canopy, they are more susceptible to the development of diseases [22,36]. Increased corn planting densities may exacerbate the negative effects of drought, thereby reducing biomass yields [36]. Such effects are observed both in the case of excessive density of corn plants and heavy weed infestation [23]. Too sparse sowing, however, reduces the yield and deteriorates its quality due to the increased risk of weed infestation [22].

Increasing planting density increases the yield of silage corn but does not increase its nutritional value [24,36]. Competition between plants causes a decrease in nitrogen uptake by plants, which reduces the quality of feed, especially the protein content [24,37]. Whole green fodder under such conditions has a higher fiber content and lower energy concentration due to limited grain development and a lower grain-to-biomass ratio [36]. The fiber content also increases, which adversely affects the digestibility of the produced silage [15,24,37]. Appropriate planting density is therefore essential to obtain silage maize yield and quality balance [24,37]

5. Conclusions

The conducted 3-year field tests confirm the positive impact of the applied suspension fertilizers on the yield of green maize. There were significant differences in dry matter yield and plant height compared to the control, where no fertilization was used, in favor of suspension fertilizers. However, compared to the control where phosphorus was applied, they had a less beneficial effect on corn yield. However, the advantage of using suspension fertilizers based on waste phosphate from the production of polyols is the lower cost and the possibility of using waste that has not been used so far [19]. The great advantage of this phosphorus source is the low content of impurities, especially cadmium, which is a big problem in phosphate rock deposits. Fertilizer regulations are introducing more and more restrictive parameters regarding this contamination, which results in limited use of some phosphate rock deposits. Moreover, the fertilizer industry in Europe is almost 90% dependent on the import of this raw material. That is why it is important to diversify its source as much as possible [19]. This confirms the validity of using a waste source of phosphorus in the form of waste from the production of polyols.

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Article

The Impact of Suspension Fertilizers Based on Waste Phosphorus Salts from Polyol Production on the Content of Macronutrients in Maize Grown for Green Fodder

Paulina Bogusz [1,2,*], Marzena Sylwia Brodowska [2] and Paweł Muszyński [3]

[1] Fertilizers Research Group, Łukasiewicz Research Network—New Chemical Syntheses Institute, Al. Tysiąclecia Państwa Polskiego 13a, 24-110 Puławy, Poland

[2] Department of Agricultural and Environmental Chemistry, University of Life Sciences in Lublin, Akademicka 13, 20-950 Lublin, Poland; marzena.brodowska@up.lublin.pl

[3] Department of Chemistry, University of Life Sciences in Lublin, Akademicka 13, 20-950 Lublin, Poland; pawel.muszynski@up.lublin.pl

* Correspondence: paulina.bogusz@ins.lukasiewicz.gov.pl

Abstract: Mineral phosphorus is a non-renewable resource that is constantly decreasing due to intensive fertilizer production. In total, 90% of mined phosphate ore is used for fertilizer purposes, so the demand for phosphorus is the highest in this sector. In this respect, it is advisable to strive to close the phosphorus cycle. In addition, economically viable phosphate-bearing deposits are concentrated in just a few locations worldwide. This comes down to the fact that most countries are simply dependent on imports of this raw material. This and the growing amount of waste have contributed to the search for alternative sources of phosphorus. One example of such phosphorus-containing waste that has fertilizer potential is sodium–potassium phosphate waste from polyol production. This article describes the effect of suspension fertilizers based on polyol production waste on the content of macronutrients in maize intended for green fodder. Fertilizers containing only basic nutrients (NPK) and fertilizers enriched with secondary components (S, Mg) and micronutrients (Zn, Mn, B) were evaluated. The conducted studies confirmed the effectiveness of the tested suspension fertilizers. The content of macronutrients in the dry mass of maize was at a similar level compared with the results obtained in the control, in which Fosdar was used for fertilization, which confirms the suitability of these products for agricultural use.

Keywords: maize green fodder; suspension fertilizer; management of waste phosphorus

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1. Introduction

The population is growing at a very fast pace and in order to meet its requirements, plant growth intensifiers are necessary. Phosphorus, alongside nitrogen and potassium, plays a key role here. As a building block of living organisms, it is one of the most important nutrients for plants and animals [1–3]. It is necessary to supplement its deficiencies in the soil [1,2]. Phosphorus deficiency in soil is often the main factor limiting plant growth. Its insufficient amount, especially in the early stages of development of annual plants, can result in reduced yield. Later correction of its dose is not able to restore proper plant growth [3].

The main source of phosphorus in agriculture is phosphates. These are sedimentary minerals made of calcium phosphate with an admixture of quartz, dolomite, glauconite, or aluminosilicates. They may contain significant amounts of organic substances, iron, aluminum, heavy metals, and radioactive substances, which make their processing difficult [1].

Phosphate ores are not equal in terms of phosphorus content and can contain from 12 to 38% P_2O_5. The current state of technology offers economically profitable exploitation of phosphate ores with a P_2O_5 content above 28%. The value of the raw material is also dependent on its chemical activity. Older phosphates, called hard, have lower chemical activity compared to younger (soft) ones [1]. The phosphorus contained in them has limited availability for plants, which is why they are processed using acids (mainly sulfuric acid) [4]. Their estimated extraction capacity is between 165 and 195 million tons per year. Experts have reported different estimates of the time of use of such resources, but they agree on one thing—they are a non-renewable source and will be exhausted sooner or later [5]. Another problematic issue is the uneven distribution of economically important phosphate mines on a global scale [5,6]. More than two-thirds of the raw material extracted there comes from Morocco, China, and the United States [2,3]. Europe is almost entirely dependent on these imports [2,3,7]. The importance of this raw material for agricultural production is proven by the fact that over 80% of its resources are used for fertilizing purposes, where it is the basis for the production of almost all phosphate fertilizers [2,6].

In order to obtain an effective fertilizer, phosphates are extracted with mineral acid to obtain phosphoric acid (V), which is called EKF-extraction phosphoric acid. Depending on the acid used, the calcium ion from phosphates goes into solution (hydrochloric or nitric acid) or precipitates in the form of a sparingly soluble salt, e.g., calcium sulfate (VI), using sulfuric acid [1]. By treating ground phosphate rock with sulfuric acid, we obtain the most popular phosphate fertilizer, called superphosphate. Unprocessed phosphate rock in the form of flour can also be applied as a fertilizer, provided that it is the so-called soft phosphate rock [7].

The distribution and availability of phosphate ores are not the only problem for the fertilizer industry and its beneficiary—the agricultural sector. Contamination accompanying phosphate deposits raises great concerns. Cadmium is particularly dangerous, with which mainly phosphate minerals of sedimentary origin are contaminated. This applies to deposits located in northern and eastern Africa and the Middle East. Lesser contamination is observed in minerals of volcanic origin (deposits in Finland, Russia, and the Republic of South Africa) [6]. When it enters the soil via fertilizers, it migrates easily and accumulates in plants [2,3,8]. Consuming contaminated crops is the main route of exposure for humans [8]. Cadmium is a toxic and mutagenic nutrient [3,8]. In the human body, it damages the kidneys and causes bone diseases and anemia [8]. The combination of the highly negative impact of cadmium on human health and its high content in phosphates has forced legal regulations limiting its amount in fertilizer products [2].

Sustainable phosphorus management also affects the natural environment. Intensive agriculture generates excess phosphorus in the soil, which can then migrate to nearby rivers and lakes. This is particularly true for highly permeable sandy soils, steeply sloping fields, and areas saturated with water [6]. Excess phosphates in surface waters cause eutrophication and disturb the biological balance. This has a negative impact on the diversity of species and the suitability of water for human use. Repairing such a situation can take years, especially since phosphorus accumulating in bottom sediments, after their agitation, causes the eutrophication process to resume [6].

The bad news is that there is no substitute for phosphorus, which is a non-renewable resource; the good news is that phosphorus does not disappear after use [4,9]. The basic scenario assumes its uptake from the ore and dispersion in the environment as a result of fertilization [9]. The key to maintaining the continuity of its flow is sustainable management and its effective recovery from the waste stream [9]. The question of how long natural phosphorus resources will last can therefore be answered in a rather divergent way. The fact is, however, that they are constantly shrinking and a preventive plan needs to be prepared. This is particularly important due to the growing demand for fertilizers, stimulated by the constant growth of the population [9]. The risk of deficits in the fertilizer market determines the threat to food production [8].

Since fertilizer production consumes nearly 90% of all extracted phosphorus resources, there is no way to compensate for its shortage in this sector by shifting resources from other industries [6]. The Food and Agriculture Organization of the United Nations (FAO) predicts that global demand for fertilizers will increase as populations grow and dietary habits change [6].

Rational phosphorus management is particularly important for European countries, where economically viable resources of this raw material are small. As a result, dependence on its importation reaches 90% [3,8]. In order to minimize the impact of external markets, European Union countries have turned to searching for alternative sources of phosphorus, including from waste materials. This corresponds to the assumptions of a circular economy, which assumes minimization and recycling of waste and extension of the life cycle of economic products [2]. In addition, to emphasize its high economic importance and high supply risk, phosphorus and phosphate rock have been included in the list of critical natural resources [4,8].

New EU regulations limit the cadmium content in fertilizer products, which significantly limits the use of contaminated phosphates for fertilizer purposes. On the other hand, they legally regulate and recommend the processing of waste raw materials rich in phosphorus, transforming its circulation into a closed cycle.

Phosphorus losses concern not only the waste of natural resources but also water, energy, and other resources used in the phosphorus processing cycle [6]. Thus, the production of fertilizers powered by waste materials has both ecological and economic benefits. Taking this course of action in the long term will allow the closure of the phosphorus cycle [2].

In recent years, there has been a significant increase in the share of corn in the crop structure, which makes it necessary to cultivate this species on less fertile soils. Especially in these conditions, it is important to properly balance mineral fertilization in order to maximize the yield potential of modern corn varieties [10]. It is classified as an intensive plant with high nutritional and fertilization requirements, much higher than other cereal plants [11,12]. It generates a huge amount of biomass in a short time. Optimal mineral fertilization and effective photosynthesis contribute to its rapid growth, which directly translates into higher yields of both grain and vegetative parts [10].

To ensure proper nutrition of maize grown for silage, it is essential to provide adequate amounts of essential nutrients such as nitrogen, phosphorus, potassium, sulfur, magnesium, zinc, and boron [10]. To produce one ton of green corn mass for silage, the plant needs about 3.5–4.1 kg of nitrogen (N), 1.3–1.5 kg of phosphorus (P_2O_5), 6.3–7.7 kg of potassium (K_2O), and 0.7–0.9 kg of magnesium (MgO) [13]. In the case of corn cultivation, starter fertilization is important, which provides the necessary nutrients in the early growth period, when its root system is poorly developed [10].

Understanding the periods of greatest demand for specific nutrients in corn is important for proper plant nutrition. Deficiencies or errors in fertilization lead to a decrease in the final yield, even if the availability of nutrients is at an appropriate level in the later period. Plants such as corn, characterized by high yield potential, may experience periodic nutrient deficiencies caused by, among other factors, limited nutrient uptake from the soil as a result of unfavorable conditions, such as drought, excess moisture, low temperatures, or chemical phenomena occurring in the soil (e.g., antagonistic interaction of ions, chemical sorption) [13].

The nutritional needs of maize increase as the plant develops, especially in the case of nitrogen, most of which is taken up during the generative development phase [11]. The key period in the development of corn is the stage of switching the plant from the stage of nutrition from the kernel to nutrition through the root system, which is still insufficiently developed (4–8-leaf phase). During this period, the plant encounters difficulties in the uptake of water and nutrients, which affects its weakened growth and development. Especially at low temperatures prevailing in the spring period, problems with the uptake of phosphorus can be observed [10].

In addition, good nutrition of corn in the 4–10-leaf phase ensures an appropriate yield, because the maximum yield potential, i.e., the number of rows of kernels in the cob and their length, is established during this period. At this stage it is important to take care of adjusting fertilization to the nutritional needs of the corn. In the initial stages of development, the plant particularly needs nitrogen, easily assimilable phosphorus, and zinc. Other nutrients, such as potassium, magnesium, sulfur, calcium, and boron, are taken up by corn in later stages of growth [10].

Maize takes up most of its nutrients from 10 days before panicle shedding to 30 days after the onset of this process. During this period, the plant takes up about 70–75% of the nitrogen (N) and 60–70% of the potassium (K) for the entire growth period. A particularly important moment is the approximately two-week interval before panicle shedding, when the plants take up about 31% of their nitrogen (N), 28% of their phosphorus (P), and 38% of their potassium (K). This accounts for about half of the growth of leaf blades, which are an important photosynthetic apparatus [11].

Rational fertilization of corn with nitrogen, in addition to the dose of this nutrient, requires the correct timing of its application [10,14]. Due to the specific dynamics of nitrogen uptake by corn, it is beneficial to divide the dose of this component and apply it in two stages [11]. It is recommended that the first part of the nitrogen dose, applied before corn sowing, constitutes about 50–70% of the total demand of the plant for this nutrient. In the case of light soils with a weaker sorption complex, the nitrogen dose should be reduced accordingly [10,11]. The remaining nitrogen should be applied as a top dressing, no later than the 4–7-leaf stage. At this stage, the nutritional status of the plants can be assessed and, if necessary, fertilization can be corrected [10,11]. At this stage, it is recommended to use fast-acting nitrogen fertilizers [11]. It is important that the top dressing is not applied too late, because corn intensively absorbs nutrients from the 6-8-leaf stage until the end of flowering. A delay in applying the nitrogen dose can cause increased water content in the harvested crop [10]. It is also important to note that tall plants can, in the absence of appropriate equipment, make it difficult to apply fertilizer [11]. When applying fertilizer top dressing, the plants should be dry so that the fertilizer granules do not stick to the plants, leading to their damage. Otherwise, when the fertilizer dissolves on wet plants, it can cause them to burn [11]. In the case of corn cultivation on heavy or medium soils, a single dose of nitrogen can be applied, traditionally before corn sowing. In such a situation, it is best to apply slower-acting nitrogen fertilizers, such as urea or ammonium sulfate, about 2 weeks before corn sowing [11].

A beneficial approach is to apply phosphate fertilizers in autumn, preferably before pre-winter ploughing. The dose of phosphorus in maize cultivation can also be divided into a pre-sowing dose applied in autumn and a starter dose applied when sowing seeds [11]. It is best to apply potassium fertilizers in maize cultivation once, before sowing, during soil preparation work [11].

In corn cultivation, it is also important to properly prepare the site in terms of soil pH, especially when the soil pH is below 5.5. The dose and form of fertilizer for deacidification should be adapted to the needs of liming and the type of soil. In a corn rotation, it is best to apply liming after harvesting the previous crop. The long period from harvest to corn sowing allows the soil to reach the optimal pH for the cultivation of this plant [15].

The aim of this work was to determine the possibilities of using phosphorus, which is a waste product generated during the production of polyols in the fertilizer industry. The production of polyols, which are widely used in the plastics industry, is constantly increasing, and with it, so too is the amount of waste generated. Waste phosphorus in the form of sodium potassium phosphate contains a large amount of water, which limits the possibilities of its use. The production of granulated fertilizers based on it would require evaporation of water, which is a cost-intensive process. Therefore, it is economically justified to use such waste phosphorus in the production of suspension fertilizers, where the raw materials do not have to be completely soluble in water, thus achieving a high concentration of fertilizer components. The use of phosphorus from waste sources is particularly important because deposits of phosphate rocks, which are the main source of this nutrient for fertilizer purposes, are limited. In addition, there are no economically viable deposits in Europe, which is associated with the need to import it. Another important factor is the quality of the extracted phosphate rocks. Many of them are contaminated with cadmium, which, in light of increasingly stringent EU regulations, limits the possibilities of their use. This activity is in line with the strategy of the circular economy and sustainable development. On the one hand, it protects natural resources, and on the other, it eliminates waste. In addition, the method of using this waste in the production of suspension fertilizers is economically justified. Existing installations can be used to produce this type of fertilizer. These installations are much simpler than those used in the production of granulated fertilizers. The technological line is devoid of granulation, drying, and classification nodes. Therefore, the construction and operation of such an installation is relatively cheap.

In connection with the above, the aim of this research was to develop a relatively simple and cheap method of producing suspension fertilizers based on waste from polyol production and to test them in field crops. To achieve the assumed goals, corn was selected for field tests due to its great importance in food and feed production. For comparative purposes, the granulated phosphorus fertilizer Fosdar 40 was used due to its great popularity.

The article "The Possibility of Using Waste Phosphates from the Production of Polyols for Fertilizing Purposes" presents a detailed description of waste from polyol production [16]. The composition and form of the waste are described, along with reference to the new EU regulations on fertilizers. The article "Suspension Fertilizers Based on Waste Phosphates from the Production of Polyols" presents a method for producing suspension fertilizers based on waste from the production of polyols. The described studies present fertilizers dedicated to maize cultivation. The method of their production, the possibilities of stabilizing the produced suspensions, and the parameters determining the ease of their application are presented [17]. The article "The Impact of Suspension Fertilizers Based on Waste Phosphorus Salts from Polyol Production on the Yield of Maize Intended for Green Fodder" describes the course of the experiment and the results of the field experiment in terms of plant yield and biometric parameters [18].

This article presents the results of an analysis of macronutrient content in maize cultivated for silage, which was fertilized with innovative suspension fertilizers based on waste sodium potassium phosphate from polyol production. In the conducted field experiment, the effect of phosphorus from the waste source was compared with the commercially available granulated fertilizer Fosdar 40. Additionally, the impact of suspension fertilizers of different composition on the content of macronutrients in the test plant was also assessed. Fertilizers containing only basic macronutrients (NPK) and fertilizers enriched with secondary components (S, Mg) and micronutrients (Zn, Mn, B) were assessed.

2. Materials and Methods

A three-year field experiment was conducted on corn intended for feed, in which the effect of suspension fertilizers based on waste sodium potassium phosphate from polyol production was tested. For comparison with the effects of phosphorus from the waste source on control plots, fertilizers were used in which the phosphorus came from a commercial fertilizer—Fosdar 40. Table 1 presents the division of experimental objects in the conducted field experiment.

In the experiment, suspension fertilizers were tested with the composition of the main NPK fertilizer components differing in the amount of phosphorus: 9.5-4-11 and 9.5-6-11. Each of these fertilizers was prepared in three variants: without additives, with the addition of secondary fertilizer components (S and Mg) and with the addition of micronutrients (Zn, Mn, B). Fosdar 40 was used for fertilization on the control plots as a source of phosphorus, while the sources of nitrogen and potassium were as in the suspension fertilizers: urea–ammonium nitrate solution (RSM) and potassium salt. The control fertilizers, similarly to the tested suspension fertilizers, had two NPK compositions: 9.5-4-11 and 9.5-6-11. In the conducted experiment, the given fertilizers were applied in two nitrogen doses: 180 and 135 kg ha^{-1}. In addition, a trial without fertilization was conducted. Three repetitions were performed for each variant, which in total constituted 51 experimental plots. The experiment was conducted for three consecutive years from 2021 to 2023. The exact scheme of the field experiment and the methodology for its conduct were presented in a previous article on the yield and quantitative parameters of maize [18].

Table 1. Division of fertilizers used in the field experiment according to their composition and the nitrogen dose applied.

Main Fertilizer Components—NPK	Source of Phosphorus in Fertilizer	Secondary Fertilizer Components	Micronutrients	N Dose, kg·ha^{-1}	Number of Repetitions
9.5-**4**-11	Polyol waste	0	0	180	3
				135	3
		Mg S	0	180	3
				135	3
		Mg S	Z, B, Mn	180	3
				135	3
	Fosdar 40	0	0	180	3
				135	3
9.5-**6**-11	Polyol waste	0	0	180	3
				135	3
		Mg S	0	180	3
				135	3
		Mg S	Z, B, Mn	180	3
				135	3
	Fosdar 40	0	0	180	3
				135	3
0	0	0	0	0	3
Total number of experimental objects					51

2.1. Chemical Analyses

The determination of nitrogen in the plant was carried out by the Kjeldahl method after mineralization of the plant material in concentrated sulfuric acid (VI) (H_2SO_4) with the addition of 30% H_2O_2. The determination of phosphorus was carried out by the molybdenum–vanadium method, while the determination of sulfate sulfur (VI) was carried out by the nephelometric method after extraction of the plant material with 2% CH_3COOH with the addition of activated carbon. Potassium, sodium, calcium, and magnesium were determined by atomic absorption spectrometry (ASA).

2.2. Statistical Analysis

The statistical results were developed using the Statistica 13 statistical package. For this purpose, ANOVA analysis of variance was used for factorial designs, determining the significance of differences using the Tukey test at the significance level of $\alpha = 0.05$ for each year of the study separately. The assumptions for the ANOVA test were examined using the Levene test (homogeneity of variance) and the Shapiro–Wilk test (normality of distribution).

For each parameter in each year, the impact of individual factors (marked with the letters A, B, and C) and the impact of their interaction effects (A × B, A × C, B × C, and A × B × C) were assessed. The measure of this impact was determined by calculating the coefficient—partial eta squared (η^2_p)—determining which factor explained the variability of the measured parameter to a greater extent.

The results of the analyses were developed in two ways. One table compares the effects of suspension fertilizers with a basic NPK composition and control fertilizers with the same composition. The main factor in this analysis was the source of phosphorus: waste phosphate from polyol production in suspension fertilizers and Fosdar 40 in control fertilizers. The subordinate factors in this analysis were the phosphorus rate (2 levels: 4% or 6%) and nitrogen rate (2 levels: 135 or 180 kg N·ha^{-1}). The obtained results were also compared with the control without fertilization. The Tukey test was used to determine homogeneous groups according to the average results from three replicates (marked with lower case letters: a, b, c, d or e). In the table, homogeneous groups are marked with capital letters for mean values depending on the phosphorus dose and phosphorus source (marked in green), mean values depending on the nitrogen dose and phosphorus source (marked in blue), and mean values depending only on the phosphorus source (marked in orange).

The second table compares the effect of the tested suspension fertilizers of different compositions. The factors in this analysis were the phosphorus dose (4% or 6%), the type of fertilizer (NPK, NKP + Mg + S or NPK + Mg + S + micro), and the nitrogen dose (135 or 180 kg N·ha^{-1}). The Tukey test distinguished homogeneous groups according to the average results from three replications (marked with lowercase letters: a, b, c, d or e). Capital letters mark homogeneous groups for the average results depending on the composition and amount of phosphorus in the fertilizer (marked in green), the average values depending on the nitrogen and phosphorus dose (marked in blue), and the average values depending only on the phosphorus dose in the fertilizer (marked in orange).

3. Results

3.1. Total Nitrogen Content

Table 2 presents the average total nitrogen content in maize depending on the type of phosphorus source in the fertilizer and its percentage content, divided into individual years of the research and the nitrogen dose applied.

Significant differences in the total nitrogen content in the maize plants in relation to the source of phosphorus used for fertilization were noted for the second year of the study. These differences were visible between the means, independent of the phosphorus content in the fertilizer. In the first and third year of the study, significantly lower results were noted on plots without fertilization, while no differences were observed in relation to the applied phosphorus fertilization, both in terms of the phosphorus dose and the type of phosphorus fertilizer.

The phosphorus dose did not statistically significantly affect the nitrogen content in maize plants in the field experiment.

In each year of the field study, the nitrogen dose had a significant effect on the total nitrogen content in the maize. The greatest effect of this factor was noted in the first year of the study ($\eta^2{}_p$ = 70.37%), where the average total nitrogen content in plant material at a dose of 135 kg N·ha^{-1} was 11.82 g·kg^{-1} d.m. of the plant, while at a dose of 180 kg N·ha^{-1}, it was 14.33 g·kg^{-1} d.m. of the plant, which was a significant difference. In the second year of the study, the total nitrogen content in maize plants showed an upward trend in accordance with the increasing nitrogen dose, with statistically significant differences noted between plants from control plots without fertilization and plants fertilized with the highest nitrogen dose (180 kg N·ha^{-1}). In the third year of the field study, similar relationships were noted, with the effect of nitrogen fertilization being higher than in the second year of the study ($\eta^2{}_p$ = 48.28%).

Table 3 presents the average total nitrogen content in maize depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of the research and the nitrogen dose applied.

In the first year of field tests, the variation in total nitrogen content in the test plant was influenced by the type of fertilizer ($\eta^2{}_p$ = 31.56%). This relationship referred only to the difference between the micronutrient fertilizer with 4% P content (12.23 g·kg $^{-1}$) and the fertilizer with secondary components with 6% P content (14.15 g·kg^{-1}).

The applied dose of phosphorus in suspension fertilizers had no significant effect on the total nitrogen content.

In all years of the field experiment, a significant effect of the nitrogen dose used in fertilization on the total nitrogen content in the maize was noted. Increasing the dose of this macronutrient resulted in an increase in the concentration of total nitrogen in the test plants. In the first year of the study, the average total nitrogen content in plants from plots where nitrogen fertilization was applied at a dose of 135 kg N·ha^{-1} was 11.90 g·kg^{-1} d.m. of plants, while at a dose of 180 kg N·ha^{-1}, it was 14.35 g·kg^{-1} d.m. of plants, which is a 20.59% difference. In the second year of the study, the effect of the applied nitrogen dose was lower compared with the first and third years of the study ($\eta^2{}_p$ = 37.61%) and the difference in total nitrogen content between doses of 180 kg N·ha^{-1} and 135 kg N · ha^{-1} was 9.88%. In the third year of the study, the total nitrogen content in plant material collected from plots fertilized with a higher nitrogen dose (180 kg N·ha^{-1}) was higher by 15.13% compared with the maize fertilized with a dose of 135 kg N·ha^{-1}.

Table 2. Average content of total nitrogen (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the source of phosphorus and its percentage content in the fertilizer.

Year	**N Dose, kg N·ha^{-1} (C)**	**Source of Phosphorus in Fertilizer (A)**						**Control without Fertilization**
		Polyol Waste			**Fosdar 40 (Control)**			
		Percentage of P (B)						
		4%	**6%**	**Avg.**	**4%**	**6%**	**Avg.**	
I	180	14.28 cd	14.84 d	14.56 B	13.36 bcd	14.84 d	14.10 B	10.53 a
	135	11.19 ab	12.01 abc	11.60 A	11.66 abc	12.43 abcd	12.04 A	A
	avg.	12.73 A	13.43 A		12.51 AB	13.63 A		B
	avg.	13.08 A			13.07 A			B
	A—s.i. B—$\eta^2{}_p$ = 23.77%		C—$\eta^2{}_p$ = 70.37%		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.	
II	180	11.75 ab	11.85 b	11.80 B	11.11 ab	10.83 ab	10.97 AB	9.80 a
	135	10.83 ab	11.11 ab	10.97 AB	10.31 ab	9.97 ab	10.14 A	A
	avg.	11.29 A	11.48 A		10.71 A	10.40 A		A
	avg.	11.39 B			10.55 A			A
	A—s.i. B—s.i.		C—$\eta^2{}_p$ = 32.13%		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.	
III	180	10.35 bc	9.68 abc	10.01 B	9.61 abc	10.48 c	10.04 B	8.12 ab
	135	8.03 a	8.77 abc	8.40 A	8.40 abc	9.63 abc	9.01 AB	A
	avg.	9.19 A	9.23 A		9.01 A	10.05 A		A
	avg.	9.21 AB			9.53 B			A
	A—s.i. B—s.i.		C—$\eta^2{}_p$ = 48.28%		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.	

Table 3. Average content of total nitrogen (g · kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ in relation to the type of suspension fertilizer and the percentage of phosphorus.

Year	N Dose, kg N·ha^{-1} (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**	**NPK**	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**
I	180	14.28 Bcde	15.03 de	13.07 abcde	14.12 B	14.84 cde	15.49 e	13.21 abcde	14.52 A
	135	11.19 A	11.35 ab	11.39 ab	11.48 A	12.01 abc	12.81 abcde	12.15 abcd	12.32 A
	avg.	12.73 AB	13.44 AB	12.23 A		13.43 AB	14.15 B	12.68 AB	
	avg.	12.80 A				13.42 A			
	A—η^2_p = 31.56% B—s.i.		C—η^2_p = 69.15%		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.		
II	180	11.74 a	10.60 A	11.49 a	11.28 AB	11.85 a	11.67 a	12.00 a	11.84 B
	135	10.83 a	10.00 A	10.91 a	10.58 A	11.11 a	9.99 a	10.27 a	10.45 A
	avg.	11.29 A	10.30 A	11.20 A		11.48 A	10.83 A	11.13 A	
	avg.	10.93 A				11.15 A			
	A—s.i. B—s.i.		C—η^2_p = 37.61%		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.		
III	180	10.35 bc	10.00 abc	11.47 c	10.61 C	9.68 abc	9.80 abc	10.32 abc	9.93 BC
	135	8.03 a	9.29 abc	9.24 abc	8.85 A	8.77 ab	8.72 ab	9.47 abc	8.99 AB
	avg.	9.19 A	9.65 A	10.35 A		9.23 A	9.26 A	9.89 A	
	avg.	9.73 A				9.64 A			
	A—η^2_p = 26.66% B—s.i.		C—η^2_p = 52.46%		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.		

3.2. Total Protein Content

Figures 1–3 contain graphs showing the content of total protein in corn in the individual years of the field tests, taking into account the nitrogen dose and phosphorus content in the fertilizer. The scales in all graphs have been unified to illustrate the differences between the individual years of the tests.

Comparing the obtained total protein contents from individual years, a clearly visible downward trend in the protein content in plant material was observed, progressing with subsequent years of conducting field experiments. The effect of nitrogen dose was most visible in the first year of research, where the white content increased proportionally to the amount of nitrogen applied with the fertilizer.

Figures 4–6 contain graphs showing the content of total protein in corn in the individual years of the field tests, taking into account the nitrogen dose and type of fertilizer. The scales in all graphs have been unified in order to illustrate the differences between the individual years of the tests.

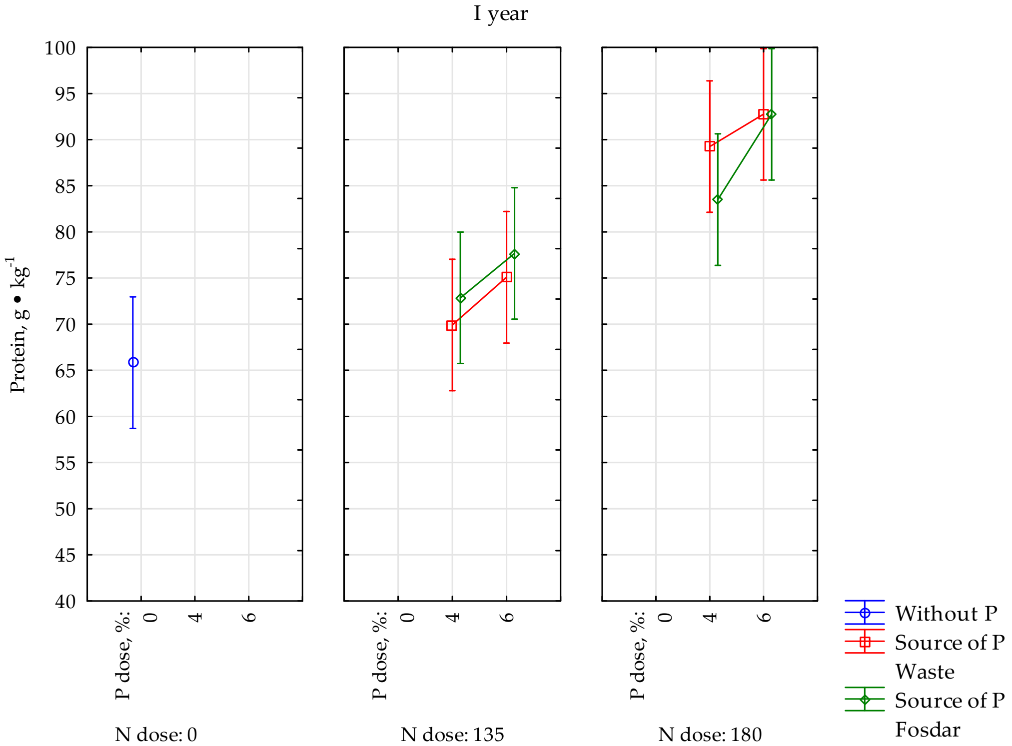

Figure 1. A graph showing the distribution of protein content in corn plant material in relation to the nitrogen dose applied in the first year of field tests, taking into account different phosphorus fertilization. Vertical bars indicate 0.95 confidence intervals.

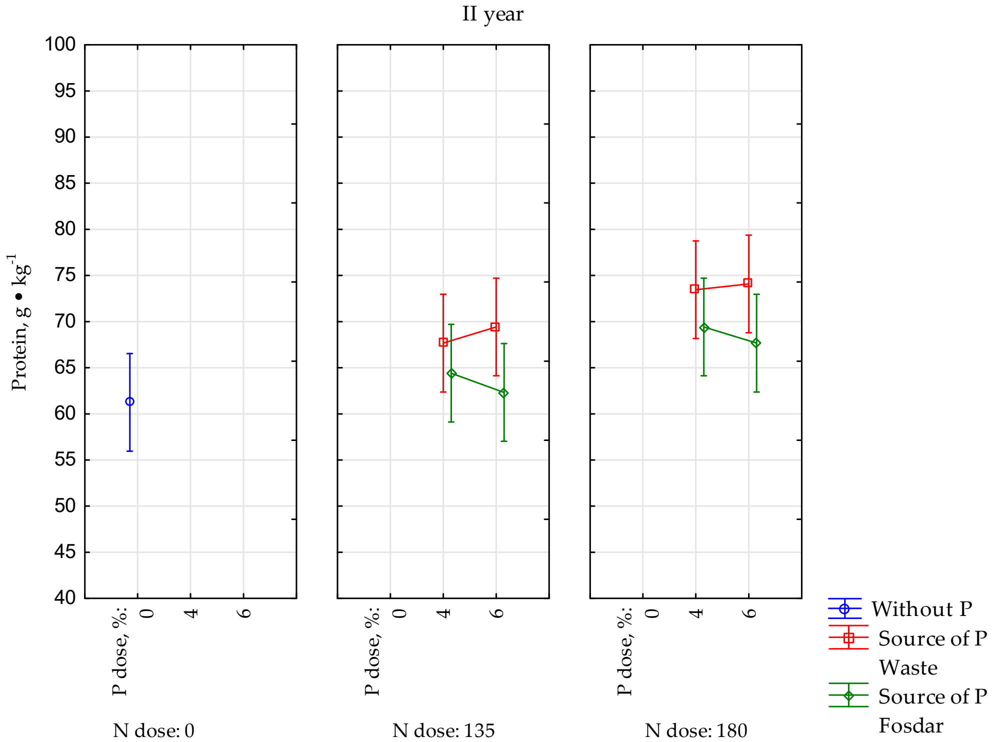

Figure 2. A graph showing the distribution of protein content in corn plant material in relation to the nitrogen dose applied in the second year of field tests, taking into account different phosphorus fertilization. Vertical bars indicate 0.95 confidence intervals.

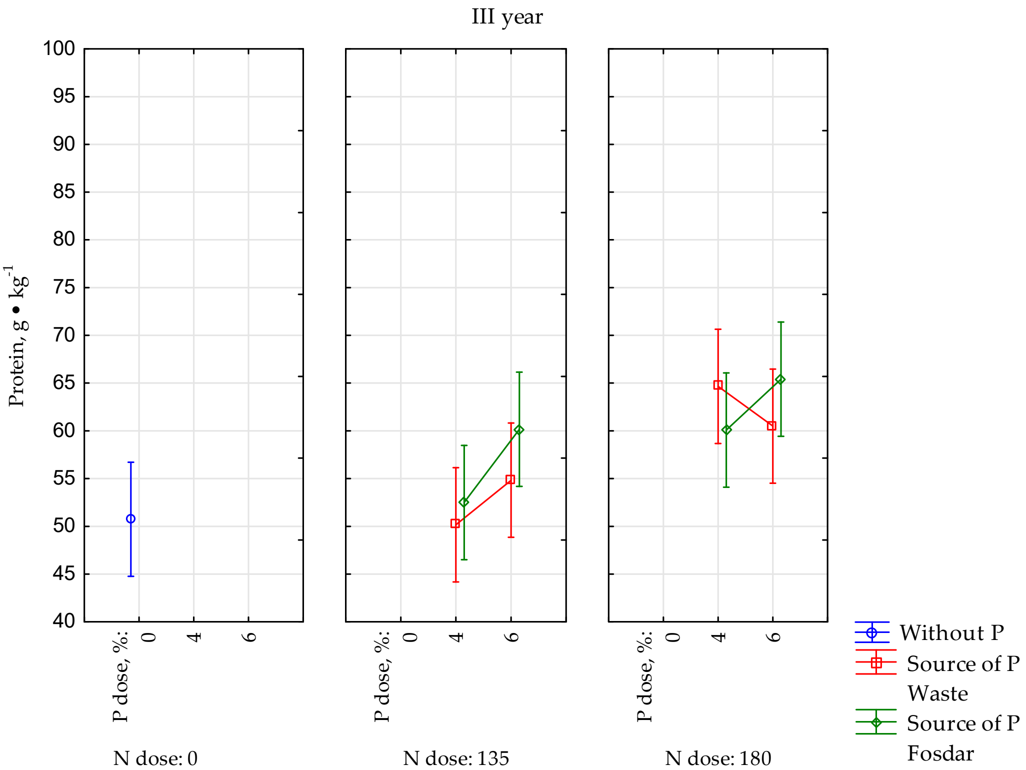

Figure 3. A graph showing the distribution of protein content in corn plant material in relation to the nitrogen dose applied in the third year of field tests, taking into account different phosphorus fertilization. Vertical bars indicate 0.95 confidence intervals.

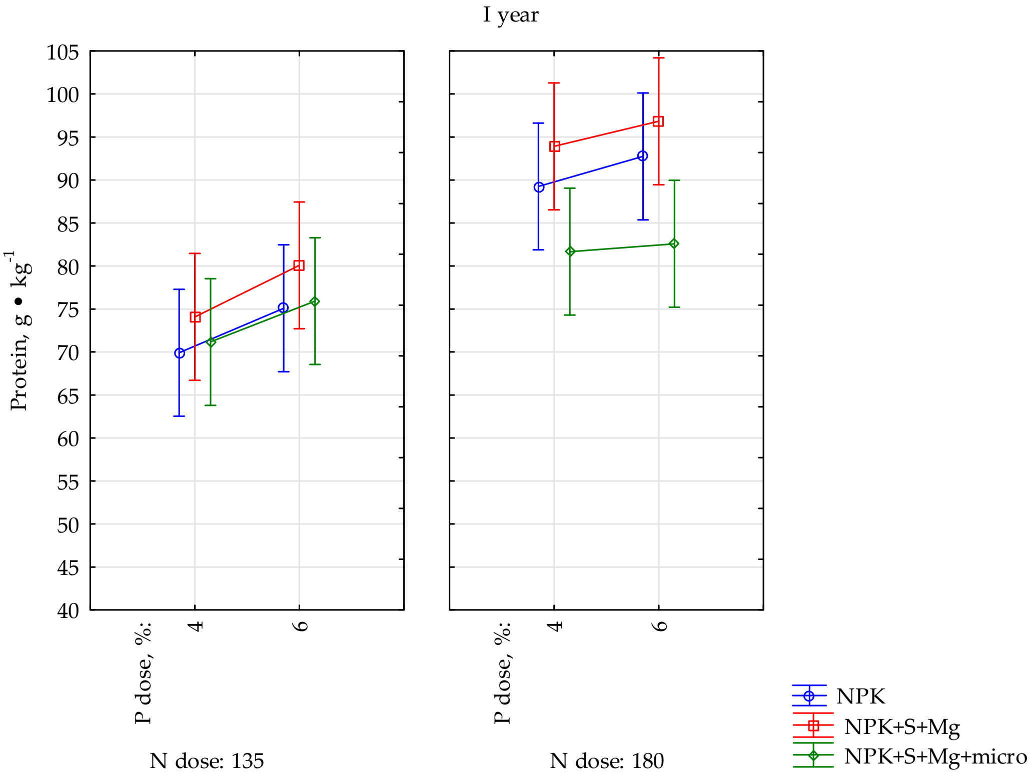

Figure 4. Graph showing the distribution of protein content in corn plant material depending on the nitrogen dose applied in the first year of field tests, taking into account various types of fertilizers. Vertical bars indicate 0.95 confidence intervals.

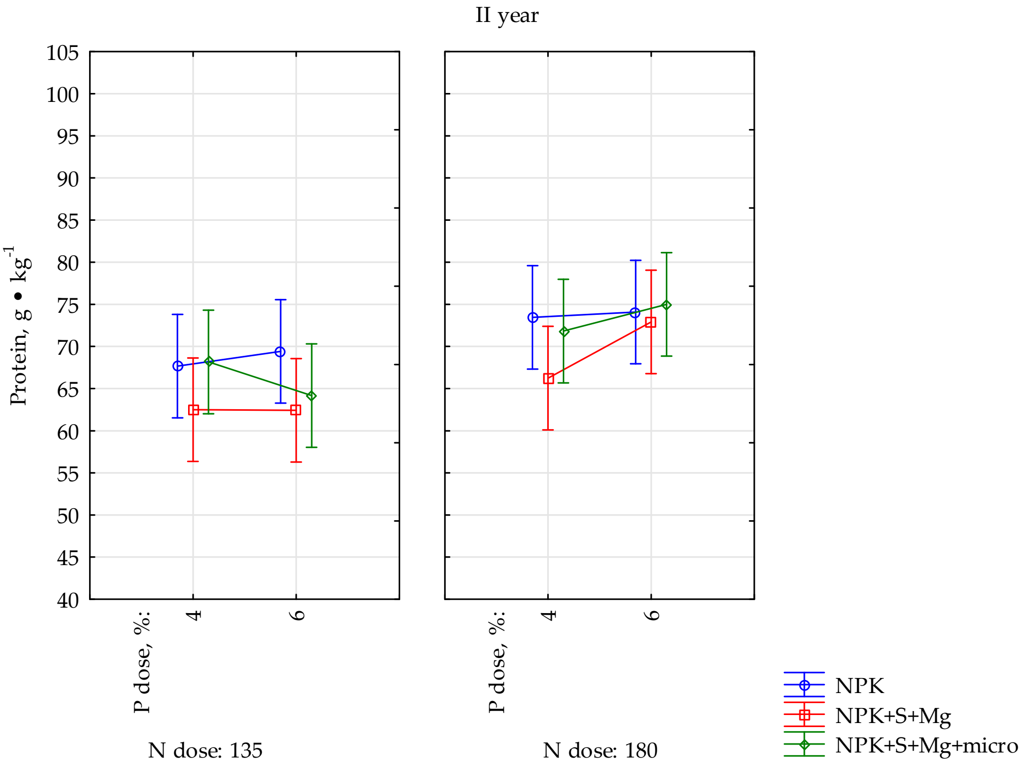

Figure 5. Graph showing the distribution of protein content in corn plant material depending on the nitrogen dose applied in the second year of field tests, taking into account various types of fertilizers. Vertical bars indicate 0.95 confidence intervals.

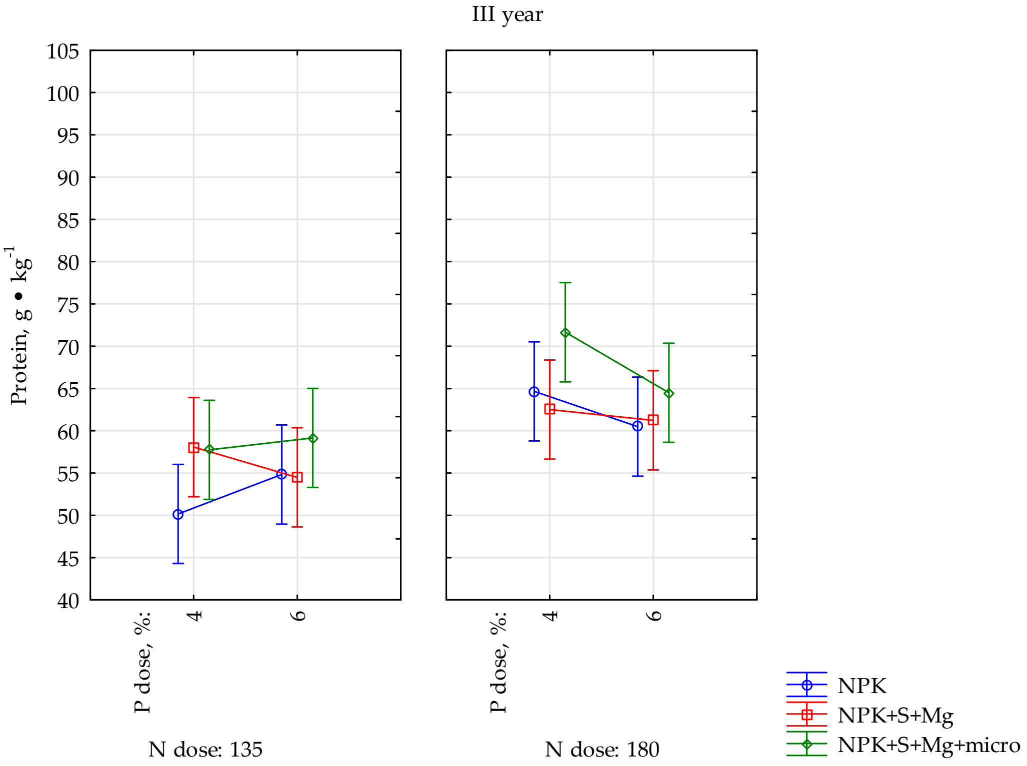

Figure 6. Graph showing the distribution of protein content in corn plant material depending on the nitrogen dose applied in the third year of field tests, taking into account various types of fertilizers. Vertical bars indicate 0.95 confidence intervals.

In the conducted studies, the type of fertilizer did not clearly differentiate the plant material samples in terms of total protein content.

3.3. Phosphorus Content

Table 4 presents the average phosphorus content in maize biomass depending on the type of phosphorus source in the fertilizer and its percentage content, divided into individual years of the research and the applied nitrogen dose.

Table 4. Average phosphorus content ($g\cdot kg^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the phosphorus source and its percentage in the fertilizer.

Year	N Dose, kg N·ha^{-1} (C)	Source of Phosphorus in Fertilizer (A)						Control without Fertilization
		Polyol Waste			Fosdar 40 (Control)			
		Percentage of P (B)						
		4%	6%	Avg.	4%	6%	Avg.	
I	180	2.69 e	3.09 F	2.89 D	2.28 bcd	2.45 de	2.37 C	1.41 a
	135	2.05 bc	2.39 cde	2.22 BC	1.93 b	2.32 cd	2.13 B	A
	avg.	2.37 C	2.74 D		2.11 B	2.39 C		A
	avg.	2.56 C			2.25 B			A
	A—η^{2}_{p} = 66.03% B—η^{2}_{p} = 67.58%	C—η^{2}_{p} = 80.67%			A × B—s.i. A × C—η^{2}_{p} = 48.33%		B × C—s.i. A × B × C—s.i.	
II	180	1.53 ab	1.78 c	1.66 B	1.56 ab	1.65 bc	1.61 B	1.41 a
	135	1.62 bc	1.71 bc	1.67 B	1.38 a	1.53 ab	1.46 A	A
	avg.	1.58 B	1.75 C		1.47 AB	1.59 B		A
	avg.	1.66 C			1.53 B			A
	A—η^{2}_{p} = 53.16% B—η^{2}_{p} = 58.50%	C—η^{2}_{p} = 25.15%			A × B—s.i. A × C—η^{2}_{p} = 29.19%		B × C—s.i. A × B × C—s.i.	
III	180	2.02 abc	2.19 bc	2.12 C	1.55 a	1.70 ab	1.63 AB	1.55 a
	135	1.82 ab	2.05 abc	1.93 BC	1.91 abc	2.34 c	2.13 C	A
	avg.	1.93 BC	2.12 C		1.73 AB	2.02 BC		A
	avg.	2.03 B			1.88 B			A
	A—s.i. B—η^{2}_{p} = 38.02%	C—η^{2}_{p} = 21.25%			A × B—s.i. A × C—η^{2}_{p} = 55.49%		B × C—s.i. A × B × C—s.i.	

In the first and second years of field tests, the application of waste phosphorus in fertilization significantly affected the phosphorus content in the plant material. In the first year, the use of the waste phosphorus source contributed to a 13.78% higher phosphorus content, and in the second year to a 8.5% higher content compared with fertilization with Fosdar 40. In all years of the tests, control samples without fertilization produced significantly lower results for phosphorus content compared with plots fertilized with both Fosdar 40 and waste phosphate.

A higher dose of phosphorus, both in the case of fertilization with Fosdar 40 and waste phosphate, significantly increased the content of this component in the test plants in each year of field tests.

In the first year of the tests, a clear effect of a higher dose of nitrogen on the content of phosphorus in plants was observed. The highest index was obtained from plots fertilized with waste phosphate and nitrogen application at the level of 180 (2.89 g·kg^{-1}), while the lowest was obtained with fertilization with Fosdar 40 and a nitrogen dose of 135 (2.13 g·kg^{-1}).

In the following years, this trend was not so pronounced. In the second and third years of the study, the nitrogen dose significantly differentiated the phosphorus content only in the case of fertilization with Fosdar 40, while a higher result was obtained in the second year with the use of a nitrogen dose of 180 kg N·ha^{-1}, and in the third year with a dose of 135 kg N·ha^{-1}.

Table 5 lists the average phosphorus content in corn depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of the research and the nitrogen dose applied.

The type of fertilizer used significantly differentiated the phosphorus content in maize only in the second year of the study. Statistically higher phosphorus content was noted in plants where NPK fertilizer was used compared with plants fertilized with fertilizer with micronutrients.

During all years of the field experiment, a significant relationship was confirmed regarding the increase in phosphorus content in the plant material and the increase in the amount of phosphorus in the fertilizer.

Table 5. Average phosphorus content (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the type of suspension fertilizer and the percentage of phosphorus.

Year	**N Dose, kg N·ha^{-1} (C)**	**Percentage of P (A)**							
		4%				**6%**			
		Type of Fertilizer (B)							
		NPK	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**	**NPK**	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**
I	180	2.69 bcd	2.12 ab	2.10 ab	2.31 A	3.09 d	3.05 d	2.97 cd	3.04 B
	135	2.05 a	2.72 cd	2.68 bcd	2.49 A	2.39 abc	3.01 d	3.01 d	2.80 B
	avg.	2.37 A	2.42 AB	2.39 AB		2.74 BC	3.03 C	2.99 C	
	avg.		2.40 A				2.92 B		
	A—s.i. B—s.i.		C—η^2_p = 71.43%		A × B—s.i. A × C—η^2_p = 65.38%		B × C—η^2_p = 28.15% A × B × C—s.i.		
II	180	1.53 abc	1.65 bcd	1.49 abc	1.56 AB	1.78 de	1.96 f	1.61 abcd	1.78 C
	135	1.62 abcd	1.38 A	1.38 A	1.46 A	1.71 cd	1.44 ab	1.70 cd	1.62 B
	avg.	1.58 ABC	1.52 AB	1.43 A		1.75 D	1.70 CD	1.65 BCD	
	avg.		1.51 A				1.70 B		
	A—η^2_p = 35.02% B—η^2_p = 67.35%		C—η^2_p = 49.87%		A × B—s.i. A × C—η^2_p = 65.93%		B × C—s.i. A × B × C—η^2_p = 35.07%		

Table 5. *Cont.*

Year	N Dose, kg N·ha^{-1} (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg Micro	Avg.	NPK	NPK S Mg	NPK S Mg Micro	Avg.
III	180	2.04 abc	1.84 ab	1.96 abc	1.95 A	2.19 c	2.03 abc	2.16 bc	2.13 B
	135	1.82 a	1.78 a	1.85 ab	1.82 A	2.05 abc	2.18 c	2.09 abc	2.11 B
	avg.	1.93 ABC	1.81 A	1.90 AB		2.12 C	2.11 BC	2.13 C	
	avg.		1.88 A				2.12 B		
	A—s.i. B—η^2_p = 61.95%		C—s.i.		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.		

In all years of the field experiment, no statistically significant differences were noted in the phosphorus content in relation to the applied nitrogen dose.

3.4. Potassium Content

Table 6 lists the average potassium content in corn depending on the type of phosphorus source in the fertilizer and its percentage, broken down into individual years of the research and the nitrogen dose applied.

Table 6. Average potassium content (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the source of phosphorus and its percentage content in the fertilizer.

Year	N Dose, kg N·ha^{-1} (C)	Source of Phosphorus in Fertilizer (A)						Control without Fertilization
		Polyol Waste			Fosdar 40 (Control)			
		Percentage of P (B)						
		4%	6%	Avg.	4%	6%	Avg.	
I	180	18.32 ab	21.60 b	19.96 B	24.20 b	22.27 b	23.23 B	13.73 a
	135	23.40 b	24.28 b	23.84 B	21.82 b	22.80 b	22.31 B	A
	avg.	20.86 B	22.94 B		23.01 B	22.53 B		A
	avg.	21.19 B			22.77 B			A
	A—s.i. B—s.i.		C—s.i.		A × B—s.i. A × C—η^2_p = 26.18%		B × C—s.i A × B × C—s.i.	
II	180	13.22 d	11.67 bcd	12.45 B	12.87 bcd	12.87 bcd	12.87 B	9.67 a
	135	11.13 abc	10.97 ab	11.05 A	12.92 cd	11.93 bcd	12.43 B	A
	avg.	12.18 BC	11.32 B		12.89 C	12.40 BC		A
	avg.	11.75 B			12.65 C			A
	A—η^2_p = 37.57% B—η^2_p = 25.46%		C—η^2_p = 38.61%		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—η^2_p = 20.80%	

Table 6. *Cont.*

Year	N Dose, kg N·ha^{-1} (C)	Source of Phosphorus in Fertilizer (A)						Control without Fertilization
		Polyol Waste			Fosdar 40 (Control)			
		Percentage of P (B)						
		4%	6%	Avg.	4%	6%	Avg.	
III	180	11.98 a	10.53 a	11.26 A	10.53 a	10.02 a	10.28 A	8.30 a
	135	9.42 a	10.78 a	10.10 A	10.70 a	10.73 a	10.72 A	A
	avg.	10.70 A	10.66 A		10.62 A	10.38 A		A
	avg.	10.68 A			10.50 A			A
	A—s.i. B—s.i.	C—s.i.			A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.	

The source of phosphorus used in the fertilizer significantly differentiated the potassium content in the plant material only in the second year of field tests, where in the case of fertilization with Fosdar 40, its content was higher by 7.66% compared with maize fertilized with fertilizer based on a waste source of phosphorus.

In the field study, the dose of phosphorus and nitrogen in the fertilizer had no significant effect on the potassium content in the test plants.

Table 7 shows the average potassium content in corn depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of the research and the nitrogen dose applied.

The type of fertilizer significantly differentiated the potassium content in the plant material only in the first year of the study, where significant differences were noted in the case of fertilization with fertilizers with a basic NPK composition (21.90 g K·kg^{-1} plant) and fertilizers with the addition of micronutrients (24.33 g K·kg^{-1} plant) without division into the applied P dose.

Significant differences were noted in the first year of the study in relation to the applied dose of phosphorus—plants fertilized with a higher dose of phosphorus were characterized by a higher potassium content. These relationships were not noted in the next two years of field experiments.

Table 7. Average potassium content (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ in relation to the type of suspension fertilizer and the percentage of phosphorus.

Year	N Dose, kg N·ha^{-1} (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg Micro	Avg.	NPK	NPK S Mg	NPK S Mg Micro	Avg.
I	180	18.32 a	20.08 ab	21.15 ab	19.85 A	21.60 ab	24.00 ab	25.35 b	23.65 B
	135	23.40 ab	22.75 ab	24.53 ab	23.56 B	24.28 ab	22.45 ab	26.30 b	24.34 B
	avg.	20.86 A	21.42 A	22.84 AB		22.94 AB	23.23 AB	25.83 B	
	avg.		21.71 A				24.00 B		
	A—η^{2}_{p} = 25.58% B—η^{2}_{p} = 28.58%		C—η^{2}_{p} = 26.99%		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.		

Table 7. *Cont.*

Year	N Dose, kg $N{\cdot}ha^{-1}$ (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**	**NPK**	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**
II	180	13.22 ab	12.43 ab	11.40 a	12.35 AB	11.67 a	14.63 b	11.90 a	12.73 B
	135	11.13 a	11.87 a	12.88 ab	11.96 AB	10.97 a	11.03 a	12.70 ab	11.57 A
	avg.	12.18 AB	12.15 AB	12.14 AB		11.32 A	12.83 B	12.30 AB	
	avg.	12.16 A				12.15 A			
	A—s.i. B—s.i.		C—η^{2}_{p} = 25.00%		A × B—s.i. A × C—η^{2}_{p} = 51.35%		B × C—s.i. A × B × C—η^{2}_{p} = 30.95%		
III	180	11.98 a	12.55 a	10.17 a	11.57 A	10.53 a	10.23 a	11.12 a	10.63 A
	135	9.42 a	10.80 a	12.10 a	10.77 A	10.78 a	9.43 a	11.13 a	10.45 A
	avg.	10.70 A	11.68 A	11.13 A		10.66 A	9.83 A	11.13 A	
	avg.	11.17 A				10.54 A			
	A—s.i. B—s.i.		C—s.i.		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.		

In the case of potassium, differentiated nitrogen fertilization had an effect on its content in the plants only in the second year of field tests at a phosphorus fertilization level of 6%.

3.5. Sulfate Sulfur Content

Table 8 lists the average sulfate sulfur content in corn depending on the type of phosphorus source in the fertilizer and its percentage, divided into individual years of the research and the nitrogen dose applied.

Regardless of the phosphorus source used in the fertilizer, the content of sulfate sulfur in the plant material remained at a similar level of 0.06–0.2 $g{\cdot}kg^{-1}$, with the median value being 0.087 $g{\cdot}kg^{-1}$ dry matter of the plant. No statistically significant differences were found in comparison to maize harvested from control plots without fertilization.

The doses of phosphorus and nitrogen did not significantly affect the content of sulfate sulfur in the field study.

Table 9 lists the average sulfate sulfur content in corn depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of the research and the nitrogen dose applied.

Comparing the effects of the type of fertilizer used on the content of sulfate sulfur in the plant material, significant differences were found in the second year of the study. In that year, the content of sulfate sulfur was higher in the plant material from the plots where a higher dose of phosphorus (6%) had been applied. For the remaining years of the study, this relationship could not be confirmed.

Table 8. Average sulfate sulfur content (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the source of phosphorus and its percentage content in the fertilizer.

Year	**N Dose, kg N·ha^{-1} (C)**	**Source of Phosphorus in Fertilizer (A)**						**Control without Fertilization**
		Polyol Waste			**Fosdar 40 (Control)**			
		Percentage of P (B)						
		4%	**6%**	**Avg.**	**4%**	**6%**	**Avg.**	
I	180	0.085 a	0.098 a	0.092 A	0.104 a	0.067 a	0.085 A	0.071 a
	135	0.095 a	0.074 a	0.085 A	0.086 a	0.074 a	0.080 A	A
	avg.	0.090 A	0.086 A		0.095 A	0.070 A		A
	avg.	0.088 A			0.083 A			A
	A—s.i. B—s.i.	C—s.i.			A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—s.i.	
II	180	0.089 a	0.125 a	0.107 A	0.086 a	0.083 a	0.085 A	0.082 a
	135	0.079 a	0.108 a	0.094 A	0.139 a	0.196 a	0.168 A	A
	avg.	0.084 A	0.117 A		0.113 A	0.140 A		A
	avg.	0.100 A			0.126 A			A
	A—s.i. B—s.i.	C—s.i.			A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—s.i.	
III	180	0.082 a	0.088 a	0.085 A	0.087 a	0.082 a	0.084 A	0.088 a
	135	0.134 a	0.091 a	0.113 A	0.089 a	0.086 a	0.088 A	A
	avg.	0.108 A	0.090 A		0.088 A	0.084 A		A
	avg.	0.099 A			0.086 A			A
	A—s.i. B—s.i.	C—s.i.			A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—s.i.	

Table 9. Average sulfate sulfur content (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the type of suspension fertilizer and the percentage of phosphorus.

Year	**N Dose, kg N·ha^{-1} (C)**	**Percentage of P (A)**							
		4%				**6%**			
		Type of Fertilizer (B)							
		NPK	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**	**NPK**	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**
I	180	0.085 a	0.091 a	0.119 a	0.099 A	0.098 a	0.093 a	0.065 a	0.085 A
	135	0.095 a	0.107 a	0.090 a	0.097 A	0.074 a	0.087 a	0.091 a	0.084 A
	avg.	0.090 A	0.099 A	0.105 A		0.086 A	0.090 A	0.078 A	

Table 9. *Cont.*

Year	N Dose, kg N·ha^{-1} (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg Micro	Avg.	NPK	NPK S Mg	NPK S Mg Micro	Avg.
I	avg.	0.098 A				0.085 A			
	A—s.i. B—s.i.	C—s.i.			A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—s.i.		
II	180	0.089 a	0.077 a	0.100 a	0.089 A	0.125 a	0.117 a	0.095 a	0.112 A
	135	0.079 a	0.088 a	0.081 a	0.083 A	0.108 a	0.101 a	0.117 a	0.109 A
	avg.	0.084 A	0.083 A	0.091 A		0.117 A	0.109 A	0.106 A	
	avg.	0.086 A				0.111 B			
	A—$\eta^2{}_p$ = 15.41% B—s.i.	C—s.i.			A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—s.i.		
III	180	0.082 a	0.086 a	0.113 a	0.094 A	0.088 a	0.112 a	0.107 a	0.102 A
	135	0.134 a	0.092 a	0.095 a	0.107 A	0.091 a	0.112 a	0.086 a	0.096 A
	avg.	0.108 A	0.089 A	0.104 A		0.090 A	0.112 A	0.096 A	
	avg.	0.100 A				0.099 A			
	A—s.i. B—s.i.	C—s.i.			A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—s.i.		

3.6. Magnesium Content

Table 10 lists the average magnesium content in corn depending on the type of phosphorus source in the fertilizer and its percentage, broken down into individual years of the research and the nitrogen dose applied.

Significant differences in magnesium content in plant material were observed only in the first year of field tests. Significantly higher magnesium concentration was obtained in corn from plots fertilized with Fosdar 40.

Table 11 lists the average magnesium content in corn depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of the research and the nitrogen dose applied.

The magnesium content in maize plants fertilized with suspension fertilizers was in the range of 0.17–1.73 g·kg^{-1}, with the median value being 0.63. The type of fertilizer and the nitrogen dose did not significantly affect the content of this macronutrient in maize plants in the conducted experiment.

Table 10. Average magnesium content (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the source of phosphorus and its percentage in the fertilizer.

Year	N Dose, kg N·ha^{-1} (C)	Source of Phosphorus in Fertilizer (A)						Control without Fertilization
		Polyol Waste			Fosdar 40 (Control)			
		Percentage of P (B)						
		4%	6%	Avg.	4%	6%	Avg.	
I	180	0.17 a	0.17 a	0.17 A	0.92 c	0.42 abc	0.67 B	0.19 a
	135	0.22 ab	0.17 a	0.20 A	0.42 abc	0.77 bc	0.59 B	A
	avg.	0.20 A	0.17 A		0.67 C	0.59 BC		AB
	avg.	0.18 A			0.63 B			A
	A—η^2_p = 63.07% B—s.i.		C—s.i.		A × B—s.i. A × C—s.i.		B × C—η^2_p = 24.69% A × B ×C—η^2_p = 30.19%	
II	180	0.56 a	0.57 a	0.57 A	0.47 a	0.51 a	0.49 A	0.50 a
	135	0.72 a	0.57 a	0.65 A	0.68 a	0.78 a	0.73 A	A
	avg.	0.64 A	0.57 A		0.58 A	0.65 A		A
	avg.	0.61 A			0.61 A			A
	A—s.i. B—s.i.		C—s.i.		A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—s.i.	
III	180	1.90 a	1.55 a	1.73 A	1.52 a	1.73 a	1.63 A	2.10 a
	135	1.33 a	1.65 a	1.49 A	1.65 a	2.20 a	1.93 A	A
	avg.	1.62 A	1.60 A		1.58 A	1.97 A		A
	avg.	1.61 A			1.78 A			A
	A—s.i. B—s.i.		C—s.i.		A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—s.i.	

Table 11. Average magnesium content (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the type of suspension fertilizer and the percentage of phosphorus.

Year	N Dose, kg N·ha^{-1} (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg Micro	Avg.	NPK	NPK S Mg	NPK S Mg Micro	Avg.
I	180	0.17 a	0.17 A	0.26 a	0.20 A	0.17 a	0.14 a	0.23 a	0.18 A
	135	0.22 a	0.17 A	0.20 a	0.20 A	0.17 a	0.19 a	0.29 a	0.22 A
	avg.	0.20 A	0.17 A	0.23 A		0.17 A	0.16 A	0.26 A	

Table 11. *Cont.*

Year	N Dose, kg N·ha^{-1} (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg Micro	Avg.	NPK	NPK S Mg	NPK S Mg Micro	Avg.
I	avg.		0.20 A				0.20 A		
	A—s.i. B—s.i.		C—s.i.		A × B—η^{2}_{p} = 3.17% A × C—s.i.		B × C—s.i. A × B ×C—s.i.		
II	180	0.56 a	0.53 a	0.89 a	0.66 A	0.57 a	0.89 a	0.99 a	0.82 A
	135	0.72 a	0.72 a	0.59 a	0.68 A	0.57 a	0.54 a	0.58 a	0.56 A
	avg.	0.64 A	0.63 A	0.74 A		0.57 A	0.71 A	0.78 A	
	avg.		0.67 A				0.69 A		
	A—s.i. B—s.i.		C—s.i.		A × B—η^{2}_{p} = 3.83% A × C—s.i.		B × C—η^{2}_{p} = 22.89% A × B ×C—s.i.		
III	180	1.90 a	1.63 a	1.48 a	1.67 A	1.55 a	1.72 a	1.57 a	1.61 A
	135	1.33 a	1.60 a	1.50 a	1.48 A	1.65 a	1.67 a	1.73 a	1.68 A
	avg.	1.62 A	1.62 A	1.49 A		1.60 A	1.69 A	1.65 A	
	avg.		1.58 A				1.65 A		
	A—s.i. B—s.i.		C—s.i.		A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—s.i.		

3.7. Calcium Content

Table 12 lists the average magnesium content in corn depending on the type of phosphorus source in the fertilizer and its percentage, broken down into individual years of the research and the nitrogen dose applied.

Phosphorus raw material did not have a significant impact on the differentiation of calcium content in maize plants in the conducted field experiment. In the third year of the study, the average calcium content in the tested plants was higher compared with the two previous years of the study.

Table 13 lists the average magnesium content in corn depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of research and the nitrogen dose applied.

The calcium content in maize plants fertilized with suspension fertilizers was in the range of 1.36–4.26 g·kg^{-1} of plants.

In the group of fertilizers with the same P content, no significant effect was noted in relation to the type of fertilizer used and the calcium content.

In the first year of the study, significant differences were noted in calcium content depending on the phosphorus dose, with a higher dose of phosphorus in the fertilizer resulting in higher calcium content in the corn. A similar relationship was also observed in the second year of the study. However, in the third year of the study, no significant differences were noted, although the obtained calcium concentrations in the test plant were higher than in the previous years of the field experiment.

Table 12. Average calcium content (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the source of phosphorus and its percentage content in the fertilizer.

Year	N Dose, kg N·ha^{-1} (C)	Source of Phosphorus in Fertilizer (A)						Control without Fertilization
		Polyol Waste			Fosdar 40 (Control)			
		Percentage of P (B)						
		4%	6%	Avg.	4%	6%	Avg.	
I	180	1.36 a	2.41 b	1.89 A	1.98 b	2.07 b	2.02 AB	2.05 b
	135	1.99 b	2.01 b	2.00 AB	2.13 b	2.43 b	2.28 B	AB
	avg.	1.67 A	2.21 B		2.06 B	2.25 B		AB
	avg.	1.94 A			2.15 A			A
	A—η^2_p = 25.51% B—η^2_p = 51.25%	C—η^2_p = 21.27%			A × B—s.i. A × C—s.i.		B × C—η^2_p = 24.91% A × B ×C—η^2_p = 42.87%	
II	180	1.87 a	1.79 a	1.83 A	1.99 a	2.03 a	2.01 A	1.81 a
	135	1.87 a	2.13 a	2.00 A	2.19 a	2.11 a	2.15 A	A
	avg.	1.87 A	1.96 A		2.09 A	2.07 A		A
	avg.	1.91 A			2.08 A			A
	A—s.i. B—s.i.	C—s.i			A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—s.i.	
III	180	4.26 b	3.59 ab	3.92 B	3.78 ab	3.82 ab	3.80 B	3.64 ab
	135	3.09 a	2.99 a	3.04 A	3.72 ab	2.98 a	3.35 AB	AB
	avg.	3.67 A	3.29 A		3.75 A	3.40 A		A
	avg.	3.64 A			3.58 A			A
	A—s.i. B—η^2_p = 28.59%	C—η^2_p = 56.91%			A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—η^2_p = 25.24%	

Table 13. Average calcium content (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the type of suspension fertilizer and the percentage of phosphorus.

Year	N Dose, kg N·ha^{-1} (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg Micro	Avg.	NPK	NPK S Mg	NPK S Mg Micro	Avg.
I	180	1.36 a	1.81 ab	1.92 ab	1.70 A	2.41 b	2.57 b	2.07 ab	2.35 B
	135	1.99 ab	1.54 a	2.12 ab	1.88 A	2.01 ab	1.97 ab	2.08 ab	2.02 AB
	avg.	1.67 A	1.68 A	2.02 AB		2.21 B	2.27 B	2.07 AB	

Table 13. *Cont.*

Year	N Dose, kg N·ha^{-1} (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg Micro	Avg.	NPK	NPK S Mg	NPK S Mg Micro	Avg.
I	avg.		1.79 A				2.19 B		
	A—η^2_p = 44.92% B—s.i.		C—s.i.		A × B—η^2_p = 23.56% A × C—η^2_p = 26.51%		B × C—η^2_p = 25.46% A × B × C—s.i.		
II	180	1.87 a	2.03 ab	1.91 ab	1.93 A	1.79 a	2.39 b	2.40 b	2.19 B
	135	1.87 a	2.00 ab	1.97 ab	1.95 A	2.13 ab	1.85 a	2.00 ab	2.00 AB
	avg.	1.87 A	2.01 AB	1.94 AB		1.96 AB	2.12 AB	2.20 B	
	avg.		1.94 A				2.09 B		
	A—s.i. B—η^2_p = 22.64%		C—s.i.		A × B—s.i. A × C—η^2_p = 31.59%		B × C—s.i. A × B ×C—η^2_p = 32.48%		
III	180	4.26 a	3.55 a	3.14 a	3.65 A	3.59 a	3.54 a	4.05 a	3.72 A
	135	3.09 a	3.57 a	3.93 a	3.53 A	2.99 a	4.11 a	3.94 a	3.68 A
	avg.	3.67 A	3.56 A	3.54 A		3.29 A	3.82 A	3.99 A	
	avg.		3.59 A				3.70 A		
	A—s.i. B—s.i.		C—s.i.		A × B—s.i. A × C—η^2_p = 38.76%		B × C—s.i. A × B × C—s.i.		

3.8. Sodium Content

Table 14 lists the average sodium content in corn depending on the type of phosphorus source in the fertilizer and its percentage, divided into individual years of the research and the nitrogen dose used.

In the first year of the study, the source of phosphorus used in the fertilizer significantly affected the sodium content in the plant material. A 16.7% higher sodium concentration was noted in plants from plots fertilized with waste from polyol production compared with fertilization with Fosdar 40. For the subsequent years of the field experiment, no such relationship was found.

Table 15 lists the average sodium content in corn depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of research and the nitrogen dose applied.

Sodium content in maize plants fertilized with suspension fertilizers was in the range of 0.107–0.402 g·kg^{-1} plant, with the median value being 0.314 g·kg^{-1} plant.

The type of applied suspension fertilizer significantly differentiated the sodium content in the plants only in the second year of the study. Fertilizers with micronutrients influenced the higher sodium content in comparison with the other fertilizers. In the first and second year of the study, no significant differences were found in the sodium content in the plants as a result of the application of different fertilizers.

Table 14. Average sodium content (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the source of phosphorus and its percentage content in the fertilizer.

Year	**N Dose, kg N·ha^{-1} (C)**	**Source of Phosphorus in Fertilizer (A)**						**Control without Fertilization**
		Polyol Waste			**Fosdar 40 (Control)**			
		Percentage of P (B)						
		4%	**6%**	**Avg.**	**4%**	**6%**	**Avg.**	
I	180	0.132 b	0.107 ab	0.120 B	0.099 a	0.101 a	0.100 A	0.083 a
	135	0.110 ab	0.097 a	0.104 AB	0.094 a	0.090 a	0.092 A	A
	avg.	0.121 B	0.102 AB		0.097 A	0.096 A		A
	avg.	0.112 B			0.096 A			A
	A—η^{2}_{p} = 40.59% B—η^{2}_{p} = 21.72%		C—η^{2}_{p} = 29.96%		A × B—s.i. A × C—s.i.		B × C—s.i. A × B ×C—s.i.	
II	180	0.322 b	0.319 b	0.321 B	0.342 bc	0.354 bc	0.348 BC	0.249 a
	135	0.357 bc	0.391 c	0.374 C	0.345 bc	0.372 bc	0.359 C	A
	avg.	0.339 B	0.355 B		0.344 B	0.363 B		A
	avg.	0.347 B			0.353 B			A
	A—s.i. B—s.i.		C—η^{2}_{p} = 42.27%		A × B—s.i. A × C—η^{2}_{p} = 24.31%		B × C—s.i. A × B × C—s.i.	
III	180	0.340 b	0.333 b	0.337 C	0.319 b	0.331 b	0.325 BC	0.246 a
	135	0.299 ab	0.290 ab	0.295 AB	0.319 b	0.324 b	0.322 BC	A
	avg.	0.320 B	0.312 B		0.319 B	0.327 B		A
	avg.	0.316 B			0.323 B			A
	A—s.i. B—s.i.		C—η^{2}_{p} = 24.76%		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.	

Table 15. Average sodium content (g·kg^{-1}) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 in relation to the type of suspension fertilizer and the percentage of phosphorus.

Year	**N Dose, kg N·ha^{-1} (C)**	**Percentage of P (A)**							
		4%				**6%**			
		Type of Fertilizer (B)							
		NPK	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**	**NPK**	**NPK S Mg**	**NPK S Mg Micro**	**Avg.**
I	180	0.132 a	0.131 a	0.117 a	0.127 A	0.107 a	0.114 a	0.099 a	0.107 A
	135	0.110 a	0.146 a	0.345 a	0.200 A	0.097 a	0.093 a	0.130 a	0.107 A
	avg.	0.121 A	0.139 A	0.231 A		0.102 A	0.104 A	0.114 A	

Table 15. *Cont.*

Year	N Dose, kg N·ha^{-1} (C)	Percentage of P (A)							
		4%				6%			
		Type of Fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg Micro	Avg.	NPK	NPK S Mg	NPK S Mg Micro	Avg.
I	avg.	0.163 A				0.107 A			
	A—s.i. B—s.i.		C—s.i.		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.		
II	180	0.322 abc	0.349 abcd	0.285 a	0.319 A	0.319 abc	0.328 abcd	0.379 bcd	0.342 AB
	135	0.357 abcd	0.340 abcd	0.473 e	0.390 C	0.391 cd	0.306 ab	0.402 de	0.366 BC
	avg.	0.339 AB	0.345 ABC	0.379 BC		0.355 ABC	0.317 A	0.391 C	
	avg.	0.354 A				0.354 A			
	A—η^2_p = 53.69% B—s.i.		C—η^2_p = 56.43%		A × B—s.i. A × C—η^2_p = 58.21%		B × C—η^2_p = 24.11% A × B × C—η^2_p = 51.02%		
III	180	0.340 a	0.369 a	0.313 a	0.341 A	0.333 a	0.327 a	0.391 a	0.351 A
	135	0.299 a	0.344 a	0.335 a	0.326 A	0.290 a	0.341 a	0.342 a	0.324 A
	avg.	0.320 A	0.357 A	0.324 A		0.312 A	0.334 A	0.367 A	
	avg.	0.333 A				0.338 A			
	A—s.i. B—s.i.		C—s.i.		A × B—s.i. A × C—s.i.		B × C—s.i. A × B × C—s.i.		

3.9. Summary of Key Results

Figures 7–13 summarize the key results of the study comparing the effects of suspension fertilizers based on polyol waste phosphates with those of a commercial fertilizer, Fosdar 40, used as the phosphorus source. For comparison, the results for the unfertilized control are also summarized.

The analysis of the average content of macronutrients in the plant material from maize did not show any significant differences depending on the source of phosphorus used in fertilization, which was confirmed in the three consecutive years of the experiment. The greatest differences were observed in the average content of phosphorus. In the first two years of the field experiment, a significantly higher content of this nutrient was confirmed in the plant material from the plots fertilized with suspension fertilizers—by 14% and 8.5%, respectively.

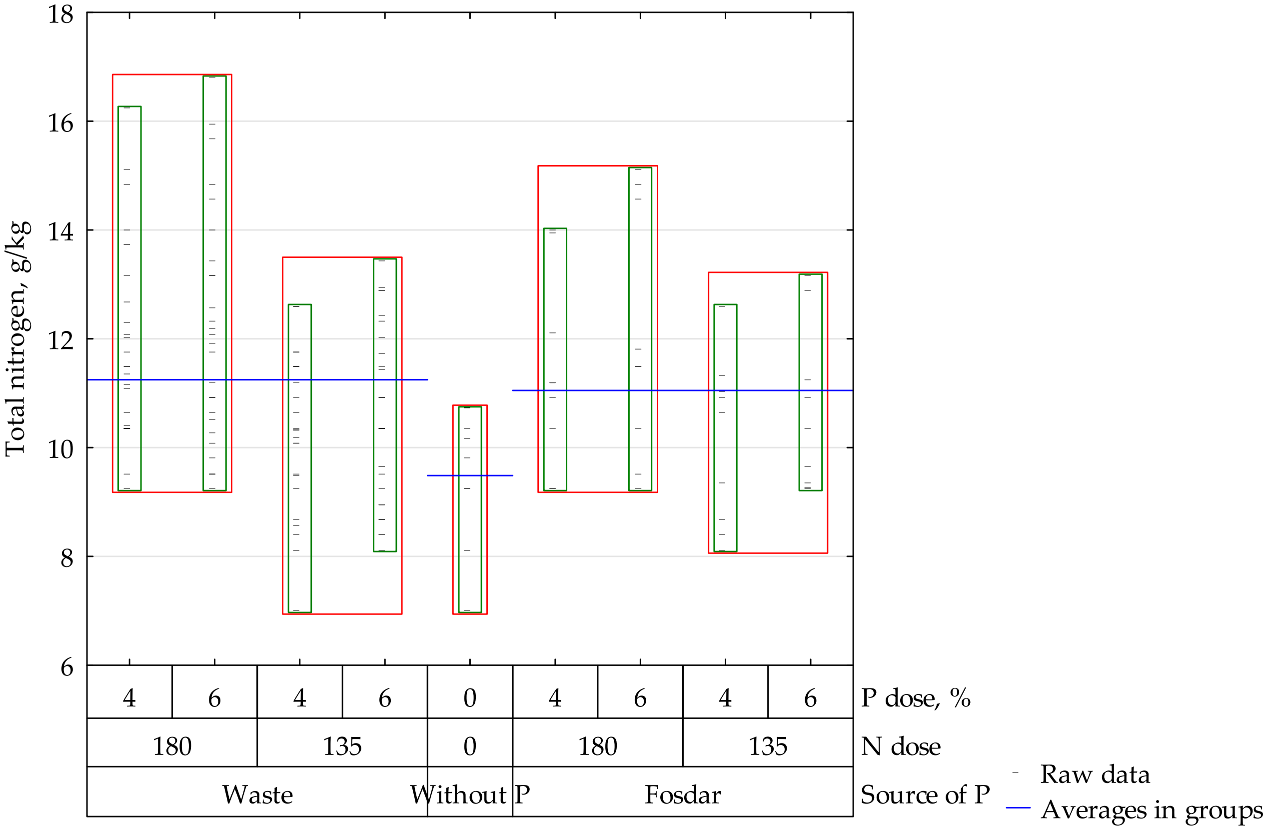

Figure 7. Graph showing the distribution of total nitrogen content in maize plant material in relation to nitrogen rate, amount, and source of phosphorus in fertilizers.

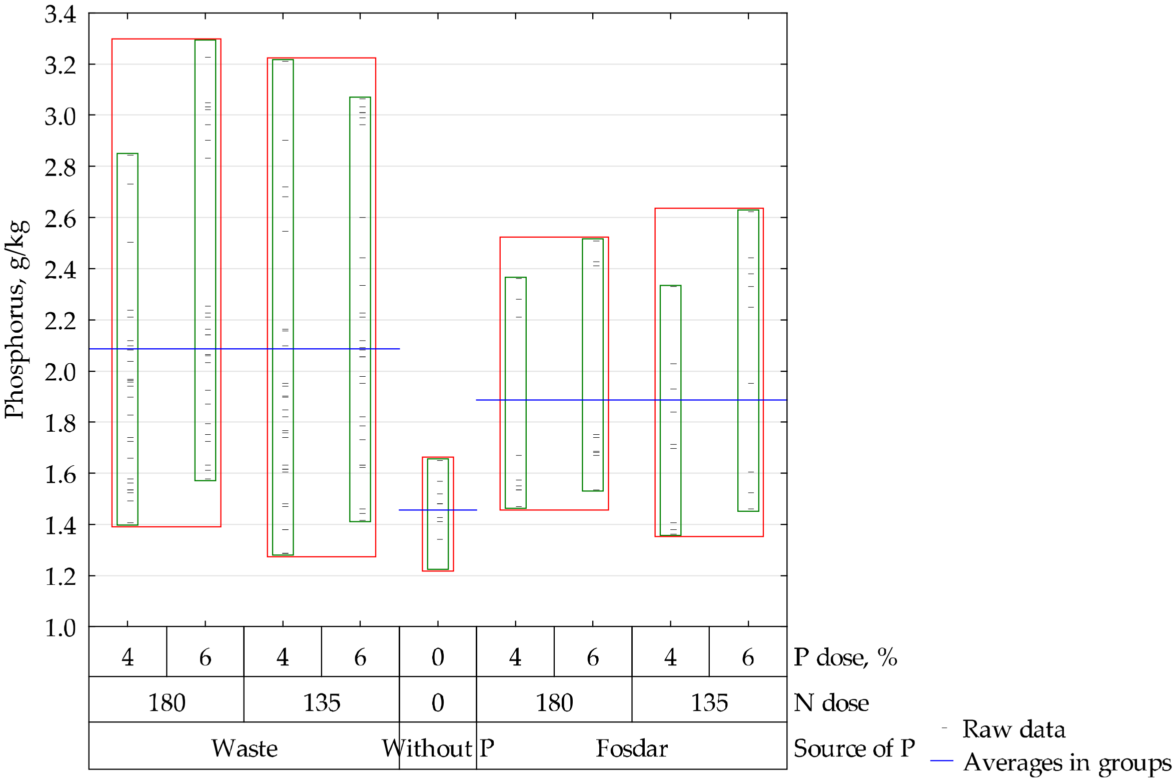

Figure 8. Graph showing the distribution of phosphorus content in maize plant material in relation to nitrogen rate, amount and source of phosphorus in fertilizers.

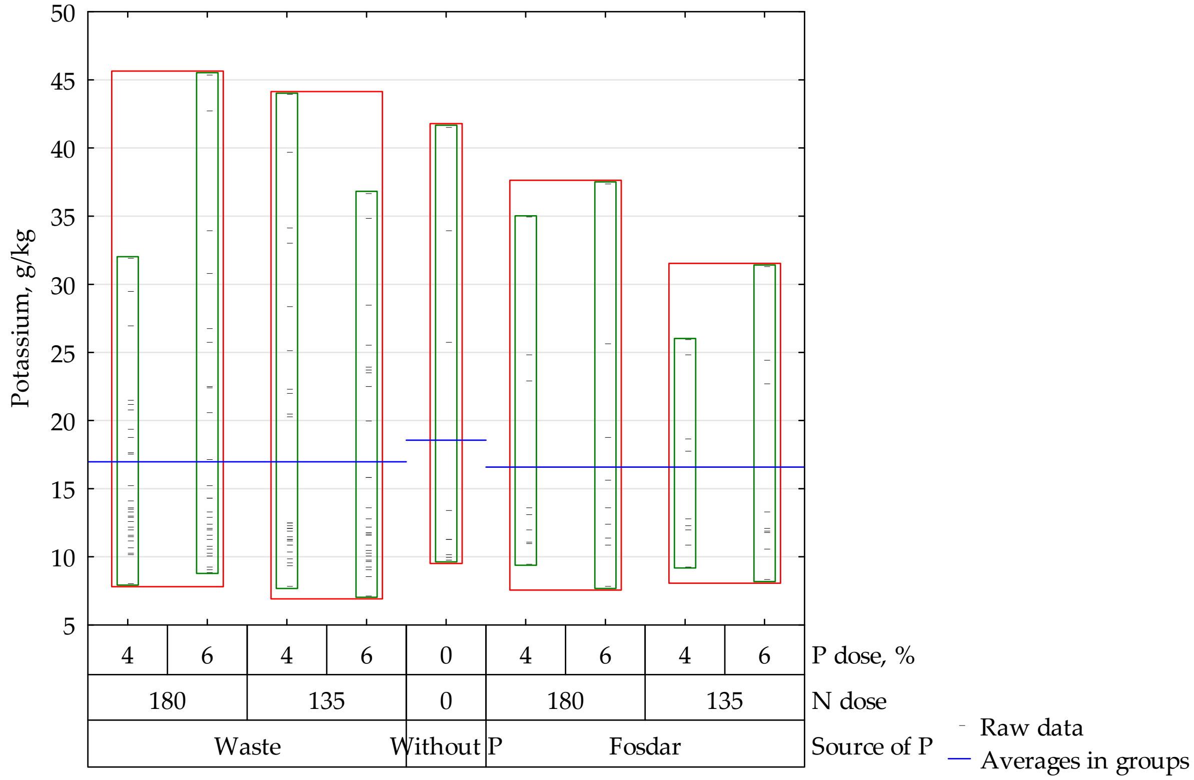

Figure 9. Graph showing the distribution of potassium content in maize plant material in relation to nitrogen rate, amount and source of phosphorus in fertilizers.

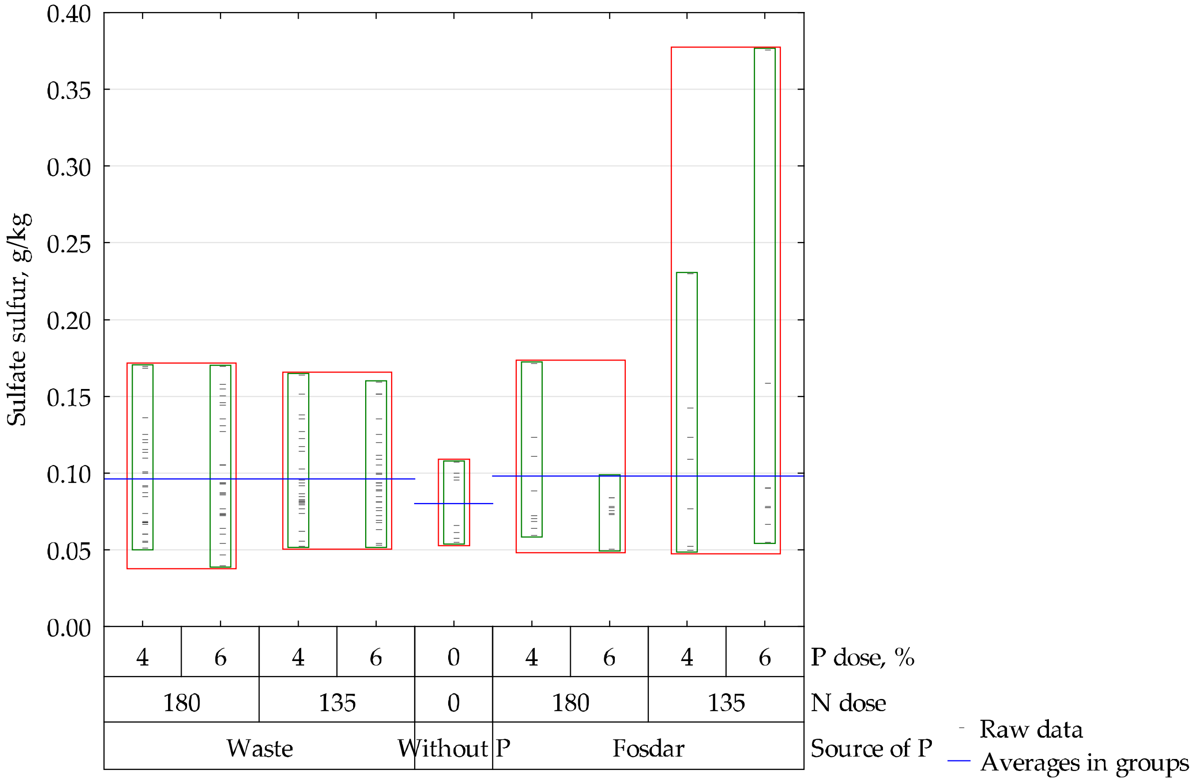

Figure 10. Graph showing the distribution of sulfate sulfur content in maize plant material in relation to nitrogen rate, amount and source of phosphorus in fertilizers.

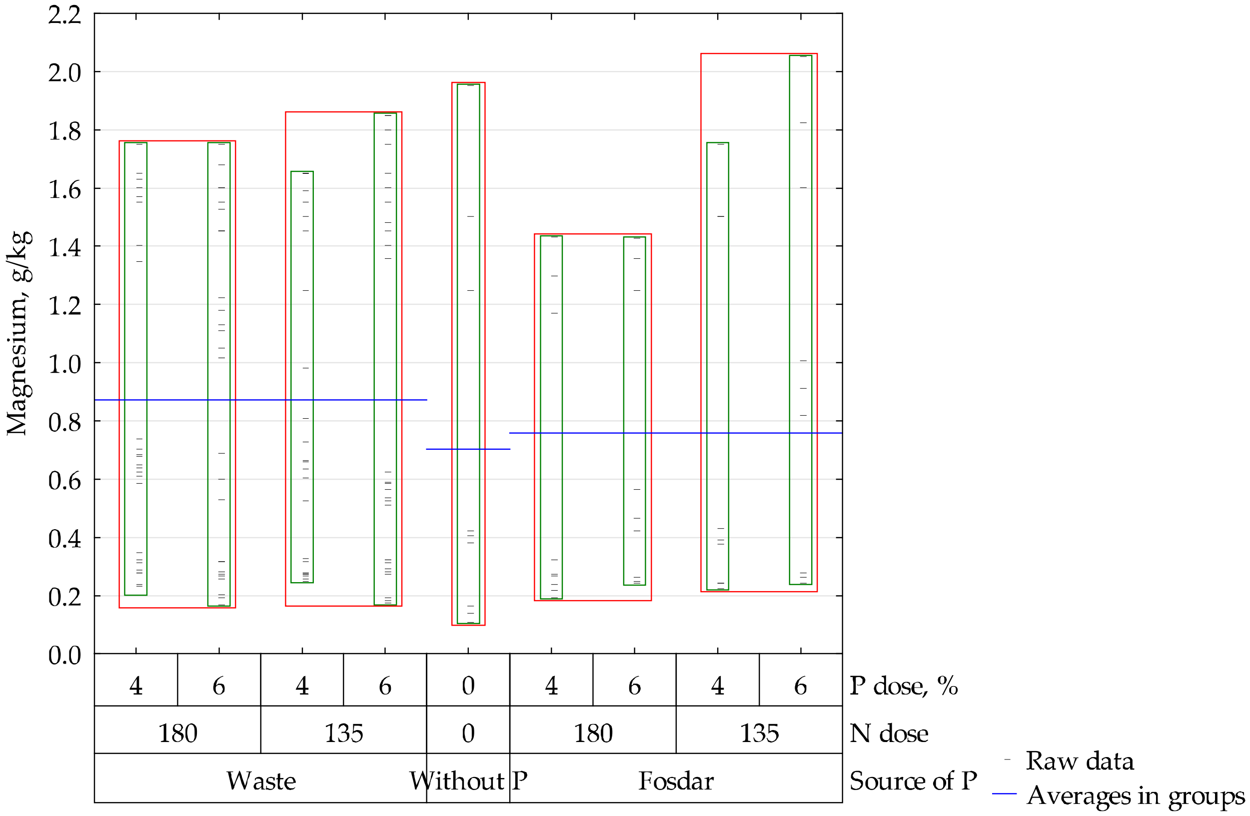

Figure 11. Graph showing the distribution of magnesium content in maize plant material in relation to nitrogen rate, amount and source of phosphorus in fertilizers.

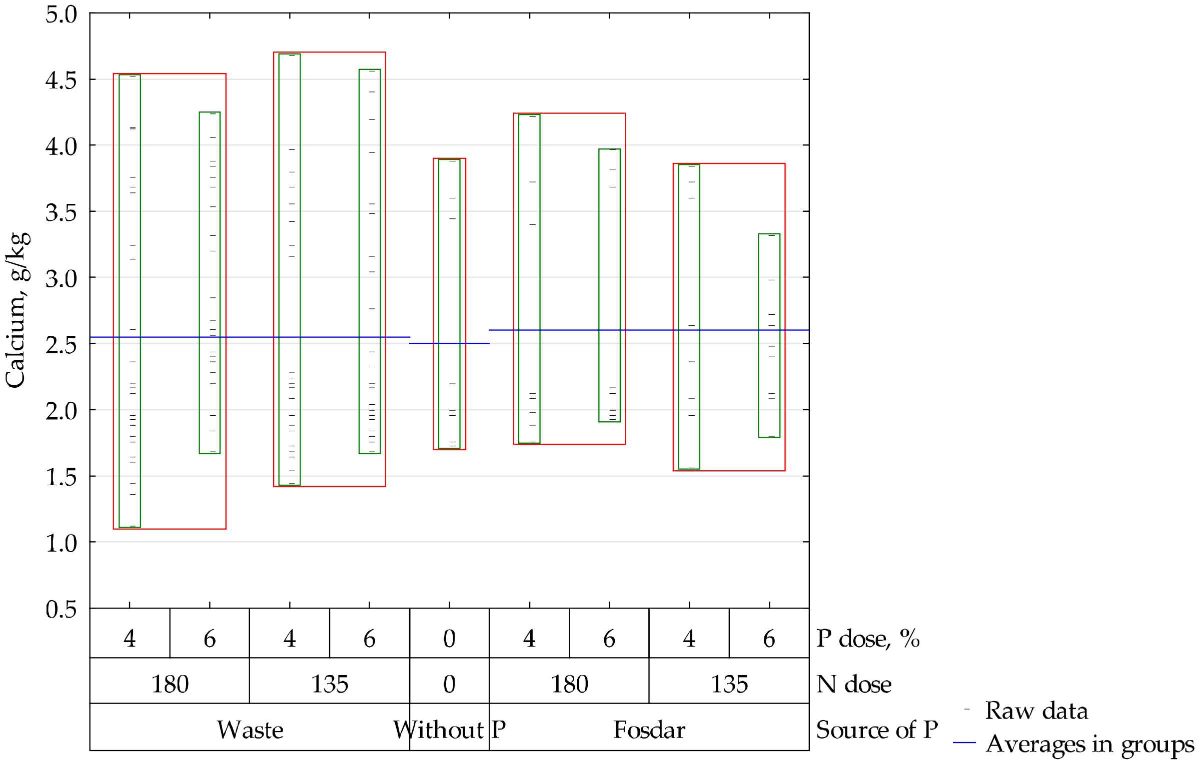

Figure 12. Graph showing the distribution of calcium content in maize plant material in relation to nitrogen rate, amount and source of phosphorus in fertilizers.

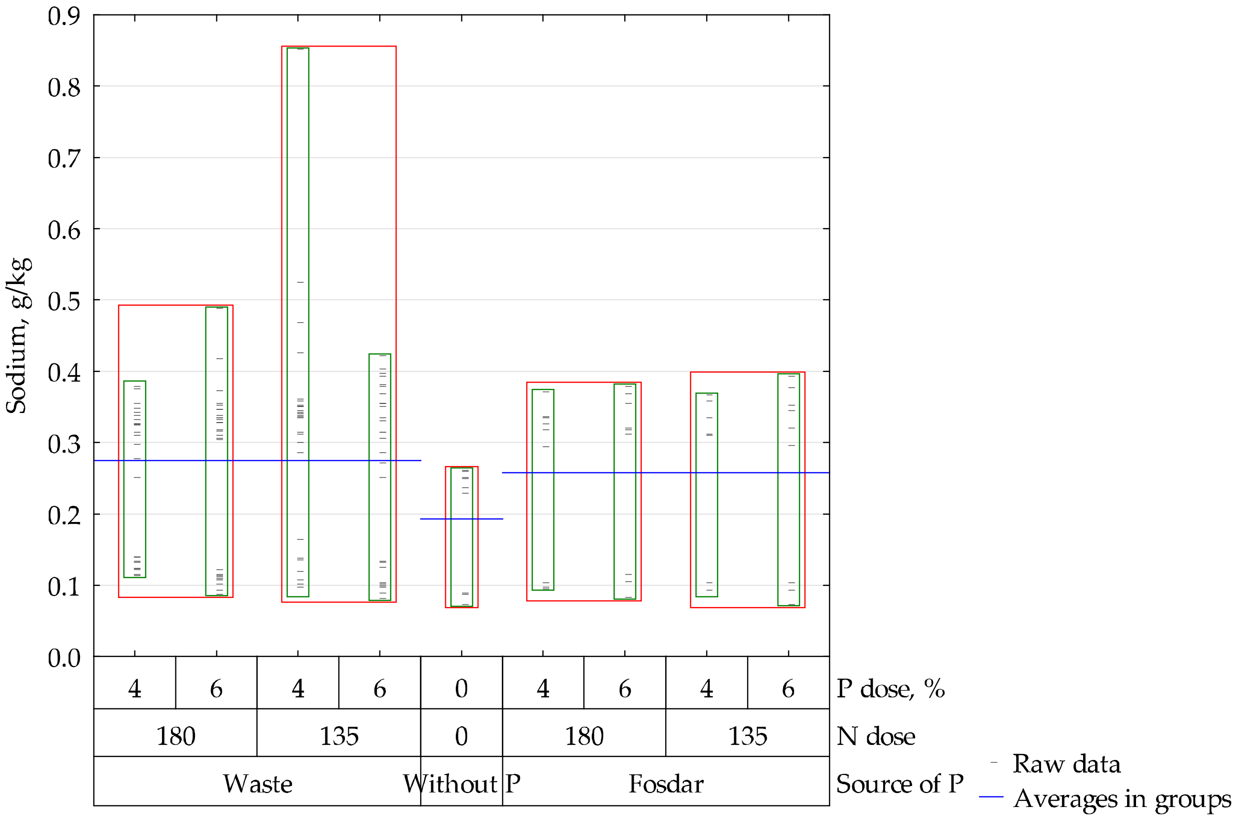

Figure 13. Graph showing the distribution of sodium content in maize plant material in relation to nitrogen rate, amount and source of phosphorus in fertilizers.

4. Discussion

The availability of nutrients to plants depends on their ability to absorb these nutrients and on the properties of the soil that enable the delivery of nutrients to the plant roots [19].

In order for plants to produce maximum yield, they must be adequately supplied with all the necessary nutrients. The average contents of basic macronutrients in corn grown for green mass are 17.0 g·kg^{-1} nitrogen, 2.7 g·kg^{-1} phosphorus, 19.7 g·kg^{-1} potassium, and 1.6 g·kg^{-1} magnesium [20]. Either an excess or a deficiency of essential nutrients significantly affects the growth and development of plants, which ultimately affects the quantity and quality of the obtained crop [21].

Under the conditions of the conducted research, the total nitrogen content in the vegetative parts of maize ranged from 7.0 to 16.8 g kg^{-1} and depended mainly on the nitrogen dose, because fertilization with this component in larger amounts increased its concentration. However, no effect of the type of fertilizer was demonstrated in this respect. Variable weather conditions meant that the maize cultivated in the third year of the research contained the least nitrogen, while the most was present in the first year. The difference between the general averages in these years was 36.35%.

Also, in the studies conducted by Księżak et al. (2012) [22] and Filipek-Mazur et al. (2013) [23], it was found that different levels of nitrogen fertilization and weather conditions during the growing season influenced the accumulation of this nutrient in plants.

The growth and productivity of corn are strongly dependent on appropriate nitrogen fertilization throughout the growing season [10]. Nitrogen is an essential component of a wide range of biological chemicals that play a key role in the physiological and metabolic functions of plants [24–27]. This nutrient is crucial for increasing soil productivity and crop efficiency [28–31]. The availability of nitrogen for plants affects the growth of biomass and the yield of maize grain, among other things, through the development of the leaf surface and maintaining the appropriate photosynthetic efficiency [27,29,32]. The right amount of nitrogen ensures maximum plant emergence and improves plant elongation and yield [24]. It can dramatically increase protein content and reduce fiber content [33].

Insufficient nitrogen in plant cultivation has the greatest impact on corn yield and its ability to absorb nutrients [15]. The lack of sufficient nitrogen reduces the plant's phosphorus uptake by almost half, which negatively affects the development of the root system [10,15]. This results in limited development in the early stages of maize growth [10,25]. Nitrogen deficiency also reduces potassium uptake by almost two-thirds compared with sites that have sufficient nitrogen available to plants [15].

Insufficient nitrogen at the 8-leaf stage causes an irreversible reduction of kernels in the cob by up to 30%. Until the flowering stage, corn grows intensively, which requires a significant amount of nitrogen [10,34]. With nitrogen deficiency during this period, corn may not reach its full growth potential, which leads to a less efficient photosynthesis process and lower yields and quality [10,25].

At low temperatures below 5 °C, corn plants reduce their nitrogen uptake, which is indicated by yellowing leaves and slower growth. In later stages of growth, deficiency symptoms include pale green and narrower leaves [35]. Nitrogen is a key nutrient influencing yield; therefore, its deficiency leads to slower growth, reduced yields, and delayed ripening. Insufficient nitrogen can also cause poorly developed and grained cobs [10,35].

Over-fertilizing corn with nitrogen negatively affects the quality of feed, increasing the content of nitrates in the biomass. This is not only uneconomical but also ecologically irresponsible, because it can lead to environmental pollution. In addition, too high doses of nitrogen can affect plant lodging [15,35]. Applying nitrogen fertilization in close proximity to the seeds simultaneously with sowing may cause a local increase in the fertilizer concentration, disrupting plant emergence [15].

The classic model of nitrogen uptake by corn consists of accumulating from 65% to 100% of the required nitrogen in the vegetative growth phase. In the grain filling phase, the process of remobilization of previously accumulated nitrogen compounds takes place, and there is a small level of uptake from the soil at the same time [15,34]. For classic varieties, the nitrogen and other nutrient remobilization indices are positive—in the grain filling phase, plants use primarily the resources accumulated in the vegetative growth phase [15,34,35]. However, in the case of "stay-green" varieties, the behavior is different—in the grain filling phase, the main sources of nitrogen are the resources available in the soil. A lack of sufficient nitrogen in the soil during the ripening period of "stay-green" corn makes it impossible to use the full yield potential of the plant. There-fore, in the case of "stay-green" corn cultivation, it is recommended to use slow-acting nitrogen fertilizers such as urea or ammonium sulphate. Also, the use of divided doses of nitrogen fertilizer at different stages of corn growth allows maximum grain yield to be achieved [25,36].

The choice of nitrogen fertilizer for corn should primarily take into account the price of the pure component, because corn is not demanding in terms of its form. It is important not to use too high doses of nitrogen in the ammonium form (NH_4) shortly before sowing corn, especially on alkaline soils. Under such conditions, this form can easily transform into ammonia (NH_3), which results in losses of this component and can disrupt plant emergence [15].

In the case of urea, it is easy to apply and mix with the soil, which prevents nitrogen losses in the form of ammonia and protects the soil from drying out. In recent years, urea on the market has been enriched with urease inhibitors, which slow down the release of nitrogen. This allows for a significant reduction in nitrogen losses in the form of ammonia [2].

In the conducted studies, the value of phosphorus in dry matter of maize was in the range of 1.23–3.29 $g \cdot kg^{-1}$. The median value was 2.00 $g \cdot kg^{-1}$. Weather conditions significantly diversified its content. The highest average concentration of this component was obtained in the first year of the study, similarly to nitrogen, and amounted to 2.49 $g \cdot kg^{-1}$. The lowest average phosphorus content was recorded in the second year of the study, at 1.57 $g \cdot kg^{-1}$. The use of waste sodium potassium phosphate in phosphorus fertilization increased the concentration of phosphorus in maize, which was confirmed in the first and second years of field studies. In comparison with fertilization with Fosdar 40, a higher P index of 13.8% was obtained in the first year, while in the second year it was 8.5%. A higher dose of P in both suspension fertilizers and Fosdar 40 resulted in a higher content of this nutrient in the plant.

Phosphorus is an essential ingredient in the process of growing corn, playing a key role in the development of the root system, flowering, and seed formation. Proper root development increases the resistance of plants to low temperatures, drought, and some diseases [10,15]. It has a direct impact not only on the ripening and quality of grain, but also on its quantity. When plants are properly supplied with this macronutrient, annual fluctuations in yields resulting from unfavorable weather conditions are smaller. In addition, this nutrient affects the proper development of generative organs and increases the stiffness of stems and blades, which effectively counteracts lodging [15].

Corn has specific phosphorus uptake dynamics. This nutrient is taken up in larger quantities from the beginning of vegetation, when the phosphorus reserves in the grain are exhausted after germination. As the vegetation period progresses, uptake increases and lasts until the grain is fully mature (grain filling). Hence, the critical phases of demand for this nutrient fall in the period of initial development, i.e., from germination to the 6–8-leaf phase and during the ripening period [10,15]. As plants age and in cases of water stress, the concentration of phosphorus in plant tissues decreases [37,38].

Many soils have low levels of available phosphorus despite large reserves of total phosphorus [37,39]. Applying phosphate fertilizers or slurry to these types of soils can increase crop yields [37,39,40].

Corn has low tolerance to phosphorus deficiency. Phosphorus starvation is more severe in soils with lower phosphorus content or acidic pH and in cases of one-sided nitrogen fertilization [10,15]. One way to increase the availability of phosphorus for corn is to maintain a soil pH between slightly acidic and neutral [15].

The rate of phosphorus uptake depends on the form in which the plant takes up nitrogen. When the plant is supplied with ammonium nitrogen ($N\text{-}NH_4$), H^+ ions are released from the cells into the soil solution, which causes soil acidification. Acidification usually increases the concentration of phosphorus and the rate of its absorption. However, when supplied with nitrate ($N\text{-}NO_3$), plant cells release HCO_3^- and OH^- ions, leading to an alkaline soil environment and reducing phosphorus absorption. In the case of phosphorus deficiency in the soil, plants take up a small amount of nitrogen, while in the case of phosphorus excess, nitrogen uptake is limited. Therefore, the correct N:P ratio is important for the proper growth and development of plants. The best N:P ratio occurs in ammonium phosphate (Polidap) [15].

Corn, despite being a late-sown plant, is sensitive to low temperatures in the early stages of growth. This sensitivity affects the limited uptake of nutrients, especially phosphorus. Low soil temperature negatively affects root activity, reduces the permeability of cell membranes and increases water viscosity, which results in limited uptake of phosphorus. This can be counteracted by increasing the concentration of phosphorus in the immediate vicinity of the roots through the use of starter fertilization. For corn to effectively absorb phosphorus, relatively high temperatures, exceeding 10–12 °C, are necessary [10,15].

In addition to nitrogen stress, phosphorus deficiency is a common problem in cereal crops worldwide [39]. Among crop plants, corn is the most sensitive to the deficiency of this nutrient [10]. This is manifested by stunted plant growth, stiffened leaves, thin stems, and limited root development. The cobs are small and twisted, with underdeveloped grains [15]. Especially at low temperatures, problems with phosphorus uptake can be observed, manifested by blue-purple discoloration progressing from the edges of the leaves [10,15].

For corn, it is recommended to use superphosphates as phosphate fertilizers on most soils. On lighter soils, magnesium superphosphate can be used [15]. For starter fertilization, it is recommended to use two-component fertilizers that contain nitrogen and phosphorus, e.g., ammonium phosphate (Polidap). The combination of these two components contributes to increased phosphorus uptake by corn in the early stages of growth [15].

In the conducted studies, the value of potassium in dry matter of maize was in the range of 7.80–28.45 g kg^{-1}. The median value was 15.01 g kg^{-1}. Weather conditions signicantly differentiated its content. The highest average sulfur content was obtained in the first year of the study, where the average for all plots was 22.3 g kg^{-1}. On the other hand, the average values obtained in the second and third years of the study were 12.12 g kg^{-1} and 10.62 g kg^{-1}, respectively. The doses of phosphorus and nitrogen did not significantly differentiate the potassium content in maize plants. There were also no confirmed significant differences influenced by the type of fertilizer used, and this finding was repeated over the three years of conducting the field experiment.

In the period from the fifth leaf stage to the flowering stage, corn intensively takes up potassium, and the demand for this nutrient then gradually decreases. Before the appearance of stigmata, the relative potassium uptake is greater than the relative increase in the dry mass of the plant. In this period, corn shows high sensitivity to water deficiency. When both of these factors are negatively correlated, it leads to a drastic reduction in corn yields intended for both grain and silage. When the potassium content in the soil is high enough, corn is able to manage water effectively, which has a significant impact on the flowering and kernel formation processes [15].

Potassium deficiency has a negative effect on the photosynthesis process and impairs the plant's ability to regulate water management, especially during periods of drought, which significantly reduces grain yields and green mass. Additionally, it weakens the resistance of corn to diseases and unfavorable environmental conditions. This is manifested by inhibition of plant growth, unnaturally dark green coloration of leaves, the appearance of necrotic spots on the edges of leaves, poor grain filling and increased susceptibility to lodging, especially with intensive nitrogen fertilization [10,15]. The use of too high doses of potassium in maize cultivation leads to excessive accumulation of this nutrient in plants, which may contribute to the occurrence of diseases in farm animals fed with such feed [15].

Corn is a plant that requires large amounts of sulfur, which contributes to its ability to produce a significant amount of biomass [31]. The content of sulfate sulfur in maize plants in the three-year field study was in the range of 0.04–0.37 g kg^{-1}, while the median value was 0.089 g kg^{-1}. The mean values from individual years did not differ significantly and were 0.088 g kg^{-1}, 0.104 g kg^{-1}, and 0.096 g kg^{-1}, respectively.

In the studies conducted by Siwik-Ziomek and Lemanowicz (2011), it was found that the sulfur content in corn depended on nitrogen fertilization. High nitrogen doses increased the amount of sulfur in the above-ground parts of plants by about 35% compared with unfertilized plants [9]. In their studies, similar relationships were shown by Barczak et al. (2011) [41] and Filipek-Mazurek et al. (2013) [23]. In our own studies, no significant differences were found that were repeated in each year of the field experiment and were related to the doses of phosphorus and nitrogen in fertilizers.

Many of the literature reports refer to the positive effect of sulfur fertilization on the content of this nutrient in the plant [23,41,42]. In our own studies, we did not confirm a significant effect of the type of fertilizer applied, including fertilizers with added sulfur, on the content of this nutrient in maize plants. This may have been due to high nitrogen fertilization causing a large increase in green mass, while at the same time, insufficient sulfur fertilization resulted in the dilution of this nutrient [43].

In recent years, reducing sulfur dioxide emissions and using fertilizers without added sulfur have worsened the supply of this nutrient to plants. In addition, reducing the use of organic fertilizers, including manure, which provided about 8 kg of elemental sulfur at a dose of 10 t·ha^{-1}, has contributed to the depletion of soils in this important macronutrient [15]. In cases of sulfur deficiency, a decrease in the protein content of plants is observed and causes a significant inhibition of growth. In addition, it leads to a decrease in the efficiency of nitrogen use from fertilizers. Each missing 1 kg of sulfur per hectare means that on average about 15 kg of the applied nitrogen is not used by plants. Although corn is not a plant with a high demand for sulfur, it is a plant with high productivity, which absorbs significant amounts of nutrients, including sulfur in amounts of about 35–50 kg S·ha^{-1} [15]. Corn is not a typical indicator of sulfur deficiency, but the symptoms of this nutrient deficiency are noticeable. In young plants, it manifests itself in pale green or yellowish leaves and a slight inhibition of growth. In older plants, the deficiency of this nutrient is visible in young leaves with a pale green color, while the older leaves are intensely green. On the other hand, too high sulfur fertilization leads to lower yields and losses of this nutrient [15].

Corn has a high demand for magnesium. Adding magnesium to fertilization improves the effectiveness of the NPK fertilizer used and contributes to a greater increase in the mass of grains, which translates into higher yields [15,44]. In soils with a light structure and acidic pH, natural magnesium resources are usually insufficient to achieve even average yields [10,44]. Over the course of a year, corn absorbs from 30 to even 70–80 kg of MgO·ha^{-1}. The choice of the appropriate magnesium fertilizer depends on the soil pH and its content of this nutrient. On acidic soils, it is recommended to use calcium–magnesium fertilizers. On soils with a regulated pH but insufficient magnesium, magnesium–sulphate fertilizers are recommended, while on soils with an appropriate pH and medium magnesium content, it is recommended to use magnesium fertilizer together with basic NPK + Mg fertilization [10]. For foliar fertilization, it is best to use magnesium sulfate heptahydrate, also known as Epsom salts [15,44].

Foliar application of magnesium in the early stages of corn growth is more beneficial, while in full maturity, foliar and soil fertilization give similar effects, with a slight advantage for soil application. The foliar application method is exceptionally effective, allowing easy removal of magnesium deficiency symptoms in the plant. The best time to apply magnesium fertilizers to the soil is autumn, before winter plowing [15,44].

In the case of cereal crops, including corn, foliar application of magnesium is recommended at two key growth stages: in the 5–8-leaf stage and after flowering, until full maturity. In the first period, magnesium uptake is not correlated with the rapid growth rate of the plant, which causes its deficit. Then, application to the leaves in the form of a spray works quickly and is concentrated in places where the plant needs this nutrient. This explains the greater efficiency of foliar application of magnesium compared with soil fertilization in the early stages of corn growth. In the second key period of magnesium demand, assimilates produced in the leaves are transported as sucrose to the grains and used to produce starch. Therefore, the longer the leaves remain green with a larger surface area for absorbing sunlight, the longer it takes to transport nutrients to the grains [15,44].

Cereal plants, including corn, have a limited ability to take up magnesium from the soil and store it in the grain. Most of this nutrient comes from displacement from the vegetative parts of the plant, such as stems and leaves. Foliar fertilization with magnesium can therefore increase the generative yield of corn, e.g., by increasing the thousand-grain weight [11,15].

Corn is very sensitive to magnesium deficiency, and the plant's ability to absorb and assimilate it decreases drastically with decreasing soil pH. Its deficiency causes a reduced concentration of chlorophyll and a decrease in the rate of photosynthesis, because it plays a key role as a component of chlorophyll. In young plants, it manifests itself in light discolorations along the leaf veins, and at a later stage, it can lead to flowering and pollination disorders, limiting the formation of cobs and worsening their graining. Hence, magnesium deficiencies in the soil can lead to a decrease in grain weight. Therefore, during the period of setting and ripening of corn grain, the demand for magnesium reaches a critical phase. In a situation where corn suffers from a magnesium deficiency and high temperatures occur, the plants take on a withered appearance and the ripening process is delayed [10,15].

Calcium is a nutrient that occurs in the soil in sufficient quantities for corn. Calcium deficiency can only occur in cases of high NPK mineral fertilization, where it is manifested by rolling and sticking of leaf blades. However, liming fields is a procedure aimed at improving the soil structure, increasing the activity of microorganisms and facilitating the absorption of nutrients (e.g., increasing the availability of phosphorus in a slightly acidic and neutral reaction) [15].

5. Conclusions

The three-year field tests confirmed the effectiveness of suspension fertilizers based on waste sodium potassium phosphate from polyol production applied at similar levels to the commercial phosphorus fertilizer Fosdar 40. This confirms the justification for using waste from polyol production as a raw material for phosphorus in the fertilizer industry. This is justified from the economic and environmental protection point of view. On the one hand, we use waste, which is a cheaper raw material, and on the other, we also become independent from the importation of phosphates, which are a non-renewable source of phosphorus.

The difference for farmers is in the method of applying the fertilizers. Suspension fertilizers are applied with a spreader equipped with a mixing system. In addition, fertilizers of this type are usually prepared immediately before application to the field. Their application, in addition to providing the appropriate nutrients for plants, also introduces water into the soil, which promotes their better absorption, which is especially important during droughts. In addition, the fertilizer is distributed on the field in a more even manner than in the case of granulated fertilizers.

The topic of using waste phosphate from polyol production is very broad and offers many possibilities for further research. Research can be undertaken on the long-term effects of using these fertilizers. An interesting direction is to expand research towards using these fertilizers in other large-area crops as well as in horticulture and fruit growing.

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Content of micronutrients in maize grown for green fodder fertilized with suspension fertilizers based on waste phosphorus salts from the production of polyols

Paulina Bogusz [1 2]*, Marzena Sylwia Brodowska [2] and Paweł Muszyński [3]

[1] Fertilizers Research Group, Łukasiewicz Research Network–New Chemical Syntheses Institute, Al. Tysiąclecia Państwa Polskiego 13a, 24-110 Puławy, Poland; paulina.bogusz@ins.lukasiewicz.gov.pl
[2] Department of Agricultural and Environmental Chemistry, University of Life Sciences in Lublin, Akademicka 13, 20-950 Lublin, Poland
[3] Department of Chemistry, University of Life Sciences in Lublin, Akademicka 13, 20-950 Lublin, Poland

* Correspondence: paulina.bogusz@ins.lukasiewicz.gov.pl

Abstract: The need to import phosphorus raw materials for fertilization purposes in Europe and the need to manage the increasing amount of waste have contributed to the search for alternative sources of phosphorus. One such waste is sodium-potassium phosphate waste generated during polyol production. In addition, the current problem is to provide an adequate amount of food, where fertilizers play the main role. Due to the increase in meat consumption, the attractiveness of growing feed corn is increasing due to its high yield potential and rich composition. The article presents the effect of suspension fertilizers based on waste from polyol production on the content of micronutrients in corn intended for green fodder. In a 3-year field study, the impact of a waste phosphorus source was compared with a commercial granular phosphorus fertilizer – Fosdar 40. Additionally, suspension fertilizers were assessed in terms of their composition, examining fertilizers containing only basic nutrients (NPK) and fertilizers enriched with secondary components (S, Mg) and micronutrients (Zn, Mn, B). The tests confirmed the effectiveness of the suspension fertilizers tested. The content of micronutrients in the dry matter of maize was at a similar level to the control, where Fosdar 40 was used for fertilization.

Keywords: maize green fodder; suspension fertilizer; management of waste phosphorus

1. Introduction

The number of people and farm animals is systematically growing, which affects the growth of demand for food and feed. Due to land area limitations, optimization is necessary by increasing the quality and efficiency of feed crops [1].

Maize (*Zea mays L.*) is a popular forage plant because it grows quickly, accumulates a large amount of dry matter and has good taste [2]. Compared to other forage plants, it has high digestibility and the availability of sugars facilitates preservation in the form of silage [1]–[3].

Maize is very exhaustive in terms of fertilizers [1], [4]. Micronutrients nutrition of corn, in addition to basic microelement fertilization, contributes to increasing the quantity and quality of the crop [5]. They are of great importance due to their participation in the processes of synthesis and transformation of nutrients, as components of enzymes [2], [5]. Micronutrients take part in the most important processes in plants: photosynthetic activity, fruit and seed ripening, productivity, resistance to stress conditions [5], [6].

The availability of micronutrients for plants depends on the soil pH and decreases with its increase, which is mainly due to the high concentration of calcium and magnesium [6]–[8]. Increasing soil pH by one unit in the range of 4-9 results in a thousand-fold reduction in Fe solubility [7]. Therefore, Fe deficiencies occur mainly in limestone soils. The bioavailability of Zn, Mn and Cu decreases hundred-fold with each unit of soil pH increase [7], [9].

This paper presents an analysis of the content of selected micronutrients (Zn, Mn, Fe, Cu) in plant material from whole maize plants grown for feed. The tested plant samples came from a 3-year field experiment, in which suspension fertilizers based on waste sodium-potassium phosphate, generated during the production of polyols at PCC Rokita in Brzeg Dolny, were tested. For comparison, the control included fertilizers with the same composition of the main NPK nutrients, in which the phosphorus raw material was a commercially available granulated phosphorus fertilizer - Fosdar 40.

2. Materials and Methods

In a field experiment, the effect of 6 suspension fertilizers was tested, in which the source of phosphorus was sodium-potassium phosphate waste from polyol production. A detailed characterization of the polyol production waste is presented in the article “The Possibility of Using Waste Phosphates from the Production of Polyols for Fertilizing Purposes” [10], in the article “Suspension Fertilizers Based on Waste Phosphates from the Production of Polyols” [11] described the method of producing suspension fertilizers used in the experiment, while in the article "The Impact of Suspension Fertilizers Based on Waste Phosphorus Salts from Polyol Production on the Yield of Maize Intended for Green Fodder"[12] the course of the field experiment and the yields were described. In the article “The Impact of Suspension Fertilizers Based on Waste Phosphorus Salts from Polyol Production on the Content of Macronutrients in Maize Grown for Green Fodder” describes the influence of the developed suspension fertilizers on the content of macronutrients in plant material from maize [13].

Figure 1 shows the division of fertilizers used in the field experiment according to their composition.

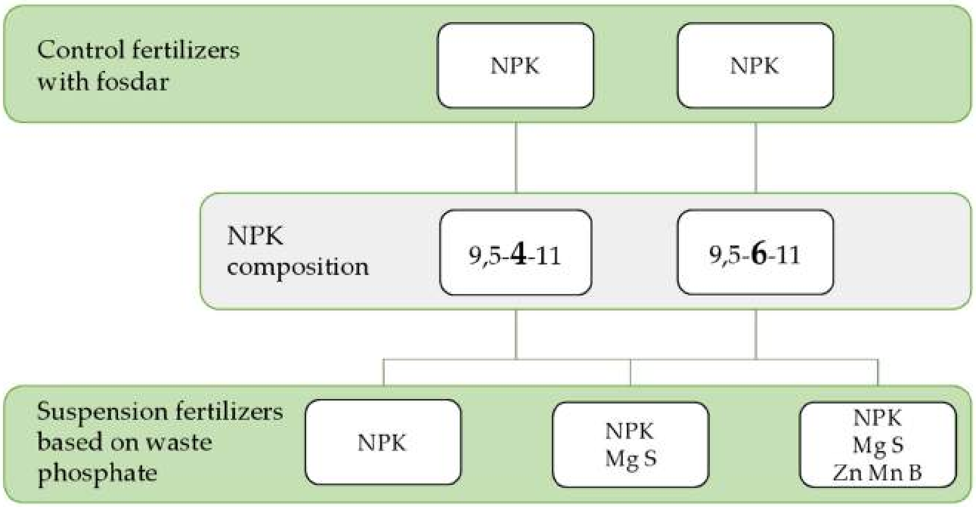

Fig 1. Division of fertilizers used in the field experiment according to their composition

Suspension fertilizers were prepared in two formulations of the main NPK nutrients, which differed in phosphorus content (4% and 6%). Each such fertilizer was tested in the basic NPK form, with the addition of secondary nutrients Mg and S and with the addition of micronutrients Zn, Mn and B. Two fertilizers with the same NPK composition as suspension fertilizers were proposed as controls, except that the commercial granular fertilizer Fosdar was used as a source of phosphorus. Each fertilizer was applied to the field in two nitrogen doses: 135 and 180 kg N · ha^{-1}.

A 3-year field study (2021, 2022, 2023) was conducted on medium-early Pioneer P8244 feed corn in Czesławice (eastern Poland). Fertilizer was applied in two doses: 70% pre-sowing and the remaining fertilizer at the 5-6 leaf stage. Corn was harvested at the milky-waxy maturity stage when corn moisture was in the range of 30-35%. For the study, 2m3 of whole plants were collected from the center of each plot, which were then cut, mechanically mixed and 500g samples were taken for chemical testing. The samples were placed in an air circulation oven set at 70°C until the plant biomass reached a constant weight.

Wet mineralization of plant material was carried out in a high-temperature mineralization block. From the dried and ground plant material, 2 g was weighed into glass test tubes, covered with 15 ml of concentrated (96%) sulfuric acid and left for 24 h. Mineralization was carried out for 5 h at a temperature of 350°C, which was achieved in stages: 80/ 120/ 200/ 350°C. The next day, hydrogen peroxide was added to the cold sample and heated at 350°C until the sample discolored. Then the mineralizate was quantitatively transferred to a volumetric flask and filled with water to the mark.

The results of the micronutrient content in plant material from maize presented in this paper were determined using the atomic absorption spectrometry (ASA) method.

2.2. Statistical analysis

The statistical results were prepared using the Statistica 13 program. For this pur-pose, ANOVA (analysis of variance) for factorial designs was used, and the significance of differences was determined using the Tukey test at a significance level of $\alpha = 0.05$ for each year of research separately. Assumptions for the ANOVA test were tested using the Levene test (homogeneity of variances) and the Shapiro–Wilk test (normality of distribution).

For each parameter in individual years, the impact of individual factors (marked with the letters A, B and C) and the impact of their interaction effects (A × B, A × C, B × C and A × B × C) are presented. The measure of this influence was determined by calculating the coefficient—partial eta squared (η^2_P)—which determines which factor explains to a greater extent the variability in the measured parameter.

The statistical analysis of the results was divided into two parts:

Part I—The effects of fertilizers were compared depending on the source of phospho-rus (superior factor, 2 levels: polyol waste or phosphorus fertilizer). The secondary factors in this analysis were the phosphorus dose (2 levels: 4% or 6%) and the nitrogen dose (2 levels: 135 or 180 kg N·ha^{-1}). The obtained results were compared after a control test with-out fertilization. Using the Tukey test, homogeneous groups were determined for individ-ual results (marked with lowercase letters: a or b) and homogeneous groups for mean val-ues regardless of the nitrogen dose (vertical) and mean values regardless of the phospho-rus dose (horizontal), marked with capital letters: A, B.

Part II—The effects of the produced suspension fertilizers were compared in terms of the dose of phosphorus (4% or 6%), the type of fertilizer (NPK, NKP + Mg + S or NPK + Mg + S + micro) and the dose of nitrogen (135 or 180 kg N·ha^{-1}). Using the Tukey test, homoge-neous groups were distinguished for individual results (marked with lowercase letters: a or b) and homogeneous groups for average values regardless of the nitrogen dose (vertical) and average values regardless of the type of fertilizer (horizontal), which were marked with uppercase letters: A, B.

3. Results

3.1. Soil pH in the experimental plots

Tables 1 and 2 present the average pH values of the soil in the objects for which the analysis of the content of individual micronutrients was carried out, due to its close connection with the availability of individual components for plants. The shape of the tables results from the methodology of analysis of the results of the content of the analyzed micronutrients.

Table 1. Average soil pH value due to the source of phosphorus and its percentage content in the fertilizer.

Year	N dose, kg N/ha (C)	Source of phosphorus in fertilizer (A)						Control without fertilization
		Polyol waste			Fosdar 40 (control)			
		Percentage of P (B)						
		4%	6%	avg.	4%	6%	avg.	
I	180	6.30	6.57	6.43	6.20	5.60	5.90	6.63
	135	6.73	6.60	6.67	6.23	6.57	6.40	
	avg.	6.52	6.58		6.22	6.08		
	avg.	6.55			6.15			
II	180	6.73	6.50	6.62	6.67	6.80	6.73	6.83
	135	6.90	6.73	6.82	6.73	6.93	6.83	
	avg.	6.82	6.62		6.70	6.87		
	avg.	6.72			6.78			
III	180	6.53	6.43	6.48	6.23	6.23	6.23	6.57
	135	6.53	6.47	6.50	6.47	6.70	6.58	
	avg.	6.53	6.45		6.35	6.47		
	avg.	6.49			6.41			

Table 2. Average soil pH value due to the type of suspension fertilizer and the percentage of phosphorus.

Year	N dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg micro	avg.	NPK	NPK S Mg	NPK S Mg micro	avg.
I	180	6.30	6.60	6.17	6.36	6.57	6.17	6.30	6.34
	135	6.73	6.23	6.43	6.47	6.60	6.53	6.43	6.52
	avg.	6.52	6.42	6.30		6.58	6.35	6.37	
	avg.	6.41				6.43			
II	180	6.73	6.70	6.80	6.74	6.50	6.30	6.83	6.54
	135	6.90	6.47	6.70	6.69	6.73	7.03	6.67	6.81
	avg.	6.82	6.58	6.75		6.62	6.67	6.75	
	avg.	6.72				6.68			
III	180	6.53	6.77	6.57	6.62	6.43	6.37	6.60	6.47
	135	6.53	6.40	6.57	6.50	6.47	6.47	6.50	6.48
	avg.	6.53	6.58	6.57		6.45	6.42	6.55	
	avg.	6.56				6.47			

In all the studied sites, the average soil pH value was in the range of 5.60 - 7.03, and the median value was 6.60, which classifies it as neutral.

3.2. *Zinc content*

Table 3 lists the average zinc content in corn depending on the type of phosphorus source in the fertilizer and its percentage, broken down into individual years of research and the nitrogen dose applied.

Table 3. Average zinc content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the source of phosphorus and its percentage content in the fertilizer.

Year	**N dose, kg N/ha (C)**	**Source of phosphorus in fertilizer (A)**						**Control without fertiliza-tion**
		Polyol waste			**Fosdar 40 (control)**			
		Percentage of P (B)						
		4%	6%	avg.	4%	6%	avg.	
I	**180**	10.47 cd	7.97 a-c	9.22 B	6.35 ab	8.65 b-d	7.50 AB	7.60 ab
	135	11.20 d	6.57 ab	8.88 B	5.75 a	8.05 a-c	6.90 A	AB
	avg.	10.83 C	7.27 AB		6.05 A	8.35 B		AB
	avg.	9.05 B			7.20 A			AB
	A – η^{2}_{p} = 53.82% B – s.i.		C - s.i.		AxB – η^{2}_{p} = 74.55% AxC – s.i.		BxC – s.i. AxBxC – s.i.	
II	**180**	8.73 c	8.33 c	8.53 B	8.77 c	7.83 bc	8.30 B	7.10 bc
	135	8.10 bc	7.55 bc	7.83 B	6.15 ab	4.87 a	5.51 A	B
	avg.	8.42 B	7.94 B		7.46 AB	6.35 A		AB
	avg.	8.18 B			6.90 A			AB
	A – η^{2}_{p} = 53.48% B – η^{2}_{p} = 30.71%		C – η^{2}_{p} = 68.41%		AxB – s.i. AxC – η^{2}_{p} = 43.42%		BxC – s.i. AxBxC – s.i.	
III	**180**	10.37 bc	11.17 c	10.77 B	9.87 a-c	7.85 a	8.86 A	9.80 a-c
	135	10.53 bc	9.17 a-c	9.85 AB	8.73 ab	9.33 a-c	9.03 A	AB
	avg.	10.45 B	10.17 B		9.30 AB	8.59 A		AB
	avg.	10.31 B			8.95 A			AB
	A – η^{2}_{p} = 49.39% B – s.i.		C – s.i.		AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – η^{2}_{p} = 42.92%	

All years of the study showed significant differences in zinc content in plant material due to the source of phosphorus in the fertilizer. Fertilization with phosphorus, in which phosphorus occurs in the form of calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$), resulted in lower zinc content than in the case of fertilization with waste sodium-potassium phosphate. Higher calcium content may result in lower zinc absorption. Higher zinc content was also observed at lower phosphorus doses, with significant differences shown only in the first year of the study.

Table 4 lists the average zinc content in corn depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of research and the nitrogen dose applied.

Table 4. Average zinc content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the type of suspension fertilizer and the percentage of phosphorus.

Year	**N dose, kg N/ha (C)**	**Percentage of P (A)**							
		4%				**6%**			
		Type of fertilizer (B)							
		NPK	**NPK S Mg**	**NPK S Mg micro**	**avg.**	**NPK**	**NPK S Mg**	**NPK S Mg micro**	**avg.**
I	**180**	10.47 bc	8.80 a-c	11.17 c	10.14 B	7.97 ab	7.05 a	9.51 a-c	8.18 A
	135	11.20 c	8.87 a-c	10.80 bc	10.29 B	6.57 a	8.73 a-c	9.50 a-c	8.27 A
	avg.	10.83 C	8.83 AB	10.98 C		7.27 A	7.89 AB	9.51 BC	
	avg.	10.22 B				8.22 A			
	A – η^2_p = 45.67% B – η^2_p = 58.03%		C – s.i.		AxB – η^2_p = 30.82% AxC – s.i.		BxC – s.i. AxBxC – s.i.		
II	**180**	8.73 bc	8.40 bc	11.13 d	9.42 B	8.33 bc	7.30 ab	9.71 cd	8.45 AB
	135	8.10 a-c	5.90 a	8.87 bc	7.61 A	7.55 a-c	7.95 a-c	9.20 b-d	8.23 A
	avg.	8.42 AB	7.15 A	9.98 C		7.94 A	7.63 A	9.46 BC	
	avg.	8.52 A				8.34 A			
	A – η^2_p = 69.65% B – s.i.		C – 38.70%		AxB – s.i. AxC – s.i.		BxC – η^2_p = 28.19% AxBxC – s.i.		
III	**180**	11.17 bc	10.50 bc	14.70 d	12.12 B	10.37 bc	7.47 a	11.30 bc	9.71 A
	135	9.17 ab	10.53 bc	12.57 cd	10.76 A	10.53 bc	10.19 a-c	10.60 bc	10.44 A
	avg.	10.17 AB	10.52 AB	13.63 C		10.45 AB	8.83 A	10.95 B	
	avg.	11.44 B				10.08 A			
	A – 66.78% B – η^2_p = 42.86%		C – s.i.		AxB – η^2_p = 38.03% AxC – η^2_p = 37.43%		BxC – η^2_p = 30.74% AxBxC – s.i.		

In the first and third year of field tests, significantly higher zinc content was confirmed in the plant material with a lower (4%) dose of phosphorus in the fertilizer. In all years of the tests, microelement fertilization, including zinc, influenced its higher content in the corn yield.

3.2. *Manganese content*

Table 5 lists the average manganese content in corn depending on the type of phosphorus source in the fertilizer and its percentage, broken down into individual years of research and the nitrogen dose applied.

Table 5. Average manganese content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the source of phosphorus and its percentage content in the fertilizer.

Year	N dose, kg N/ha (C)	Source of phosphorus in fertilizer (A)						Control without fertilization
		Polyol waste			Fosdar 40(control)			
		Percentage of P (B)						
		4%	6%	avg.	4%	6%	avg.	
I	180	7.67 a	10.67 ab	9.17 A	13.67 b	13.33 b	13.50 B	10.00 ab
	135	7.67 a	13.33 b	10.50 AB	11.00 ab	10.33 ab	10.67 AB	AB
	avg.	7.67 A	12.00 B		12.33 B	11.38 B		AB
	avg.	9.83 A			12.08 B			AB
	A – η^{2}_{p} = 31.96% B – η^{2}_{p} = 25.42%	C - s.i.			AxB – η^{2}_{p} = 35.14% AxC – η^{2}_{p} = 28.71%		BxC – s.i. AxBxC – s.i.	
II	180	11.00 a	9.33 a	10.17 A	9.33 a	8.67 a	9.00 A	9.67 a
	135	6.33 a	8.00 a	7.17 A	11.67 a	9.33 a	10.50 A	A
	avg.	8.67 A	8.67 A		10.50 A	9.00 A		A
	avg.	8.67 A			9.75 A			A
	A – s.i. B – s.i.	C – s.i.			AxB – s.i. AxC – η^{2}_{p} = 23.18%		BxC – s.i. AxBxC – s.i.	
III	180	2.33 ab	21.00 ab	20.67 AB	24.00 b	20.33 ab	22.17 B	17.67 ab
	135	16.67 a	17.00 a	16.83 A	18.00 ab	20.00 ab	19.00 AB	AB
	avg.	18.50 A	19.00 A		21.00 A	20.17 A		A
	avg.	18.75 A			20.58 A			A
	A – s.i. B – s.i.	C – η^{2}_{p} = 41.25%			AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – s.i.	

In the first year of the study, significantly higher manganese contents were noted in the plant material on the plots fertilized with phosphorus, however, this relationship was not confirmed in the next two years of the study. The results obtained in the third year of the study were significantly higher than in the previous years of the study, which may be influenced by weather conditions - higher temperature and lower waste in relation to previous years. The total manganese content is classified as low due to the high pH of the soil.

Table 6 lists the average manganese content in corn depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of research and the nitrogen dose applied.

Table 6. Average manganese content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the type of suspension fertilizer and the percentage of phosphorus.

Year	N dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg micro	avg.	NPK	NPK S Mg	NPK S Mg micro	avg.
I	180	7.67 ab	8.67 ab	9.67 ab	8.67 A	10.67 a-c	10.67 a-c	9.33 ab	10.22 AB
	135	7.67 ab	16.67 c	10.67 a-c	11.67 B	13.33 bc	11.33 bc	7.00 a	10.56 AB
	avg.	7.67 A	12.67 B	10.17 AB		12.00 B	11.00 B	8.17 A	
	avg.		10.17 A				10.39 A		
	A – η^2_p = 30.50% B – s.i.		C – η^2_p = 19.18%			AxB – η^2_p = 41.98% AxC – η^2_p = 26.51%		BxC – s.i. AxBxC – η^2_p = 26.51%	
II	180	11.00 ab	8.67 ab	7.33 ab	9.00 AB	9.33 ab	12.33 b	10.00 ab	10.56 B
	135	6.33 a	9.67 ab	9.33 ab	8.44 AB	8.00 ab	7.33 ab	8.33 ab	7.89 A
	avg.	8.67 A	9.17 A	8.33 A		8.67 A	9.83 A	9.17 A	
	avg.		7.72 A				9.22 A		
	A – s.i. B – s.i.		C – η^2_p = 19.91%			AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – η^2_p = 27.35%	
III	180	20.33 a-c	27.67 c	21.00 a-c	23.00 B	21.00 a-c	20.67 a-c	24.67 bc	22.11 AB
	135	16.67 a	23.00 a-c	20.33 a-c	20.00 AB	17.00 ab	20.33 a-c	20.33 a-c	19.22 A
	avg.	18.50 A	25.33 B	20.67 AB		19.00 A	20.50 A	22.50 AB	
	avg.		21.50 A				20.67 A		
	A – η^2_p = 39.37% B – s.i.		C – η^2_p = 31.80%			AxB – η^2_p = 30.85% AxC – s.i.		BxC – s.i. AxBxC – s.i.	

Despite fertilization with manganese in the plots where the fertilizer with micronutrients was applied, no significantly higher manganese content was noted in the plant material in all three years of the field experiment. This may be related to the antagonistic effect of boron and zinc, which were components of microelement fertilizers, on its absorption. The studies also did not note a significant effect of the phosphorus dose.

3.3. *Copper content*

Table 7 lists the average copper content in corn depending on the type of phosphorus source in the fertilizer and its percentage, broken down into individual years of research and the nitrogen dose applied.

Table 7. Average copper content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the source of phosphorus and its percentage content in the fertilizer.

Year	**N dose, kg N/ha (C)**	**Source of phosphorus in fertilizer (A)**						**Control without fertiliza-tion**
		Polyol waste			**Fosdar 40 (control)**			
		Percentage of P (B)						
		4%	6%	avg.	4%	6%	avg.	
I	**180**	2.97 a	3.53 a	3.25 A	4.57 a	2.27 a	3.47 A	3.67 a
	135	2.13 a	3.30 a	2.72 A	2.47 a	4.00 a	3.23 A	A
	avg.	2.55 A	3.42 A		3.52 A	3.13 A		A
	avg.	2.98 A			3.33 A			A
	A – η^2_p = 31.83% B – s.i.		C - s.i.		AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – s.i.	
II	**180**	5.33 a	4.73 a	5.03 A	6.27 a	5.57 a	5.92 A	6.03 a
	135	10.80 a	5.53 a	8.17 A	3.93 a	5.33 a	4.63 A	A
	avg.	8.07 A	5.13 A		5.10 A	5.45 A		A
	avg.	6.60 A			5.28 A			A
	A – s.i. B – s.i.		C – s.i.		AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – s.i.	
III	**180**	3.00 a	3.13 a	3.07 A	2.70 a	2.00 a	2.35 A	3.10 a
	135	2.43 a	2.10 a	2.27 A	3.47 a	3.47 a	3.47 A	A
	avg.	2.72 A	2.62 A		3.08 A	2.73 A		A
	avg.	2.67 A			2.91 A			A
	A – s.i. B – s.i.		C – s.i.		AxB – s.i. AxC – s.i.		BxC – η^2_p = 31.00% AxBxC – s.i.	

The copper content in maize plant material in 3-year field studies did not differ significantly depending on the phosphorus source used in the fertilizer.

Table 8 lists the average copper content in corn depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of research and the nitrogen dose applied.

Table 8. Average copper content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the type of suspension fertilizer and the percentage of phosphorus.

Year	N dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg micro	avg.	NPK	NPK S Mg	NPK S Mg micro	avg.
I	180	2.97 a	8.53 a	1.87 a	4.46 A	3.53 a	3.43 a	1.90 a	2.96 A
	135	2.13 a	5.93 a	2.33 a	3.47 A	3.30 a	4.00 a	5.17 a	4.16 A
	avg.	2.55 A	7.23 A	2.10 A		3.42 A	3.72 A	3.53 A	
	avg.	3.96 A				3.56 A			
	A – s.i. B – s.i.	C – s.i.		AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – s.i.			
II	180	5.33 a	4.27 a	4.73 a	4.78 A	4.73 a	4.53 a	6.97 a	5.41 A
	135	10.80 a	4.97 a	2.57 a	6.11 A	5.53 a	6.77 a	5.80 a	6.03 A
	avg.	8.07 A	4.62 A	3.65 A		5.13 A	5.65 A	6.38 A	
	avg.	5.44 A				5.72 A			
	A – s.i. B – s.i.	C – s.i.		AxB – s.i. AxC –s.i.		BxC – s.i. AxBxC – s.i.			
III	180	3.00 a	3.60 a	3.47 a	3.36 A	3.13 a	3.13 a	3.27 a	3.18 A
	135	2.43 a	2.43 a	3.83 a	2.90 A	2.10 a	2.20 a	1.63 a	1.98 A
	avg.	2.72 A	3.02 A	3.65 A		2.62 A	2.67 A	2.45 A	
	avg.	3.13 A				2.58 A			
	A – s.i. B – s.i.	C – s.i.		AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – s.i.			

The type of fertilizer used did not significantly affect the differences in copper content in plant material during the three-year field study.

3.4. Iron content

Table 9 lists the average iron content in corn depending on the type of phosphorus source in the fertilizer and its percentage, broken down into individual years of research and the nitrogen dose applied.

Table 9. Average iron content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the source of phosphorus and its percentage content in the fertilizer.

Year	N dose, kg N/ha (C)	Source of phosphorus in fertilizer (A)						Control without fertilization
		Polyol waste			Fosdar 40 (control)			
		Percentage of P (B)						
		4%	6%	avg.	4%	6%	avg.	
I	180	94.00 c	71.00 ab	82.50 C	66.33 ab	58.00 ab	62.17 A	64.33 ab
	135	73.33 bc	79.00 bc	76.17 BC	79.00 bc	51.33 a	65.17 AB	AB
	avg.	83.67 C	75.00 BC		72.67 BC	54.67 A		AB
	avg.	79.33 B			63.67 A			A
	A – s.i. B – s.i.		C - η^2_p = 23.53%		AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – s.i.	
II	180	99.67 ab	111.33 b	105.50 B	87.00 a	91.67 ab	89.33 A	84.67 a
	135	90.33 ab	96.00 ab	93.17 AB	84.00 a	94.33 ab	89.17 A	A
	avg.	95.00 AB	103.67 B		85.50 A	93.00 AB		A
	avg.	99.33 B			89.25 A			A
	A – η^2_p = 38.37% B – η^2_p = 28.57%		C – s.i.		AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – s.i.	
III	180	139.00 c-e	140.33 de	139.67 B	155.33 e	108.33 a	131.83 AB	129.33 a-d
	135	123.33 a-d	114.33 ab	118.83 A	131.33 b-d	117.67 a-c	124.50 A	AB
	avg.	131.17 BC	127.33 B		143.33 C	113.00 A		BC
	avg.	129.25 A			128.17 A			A
	A – s.i. B – η^2_p = 61.17%		C – η^2_p = 51.71%		AxB – η^2_p = 48.66% AxC – η^2_p = 19.74%		BxC – s.i. AxBxC – η^2_p = 39.15%	

In the first two years of the field experiment, the plant material showed significant differences in iron content in relation to the applied source of phosphorus in the fertilizer. Fertilization with waste phosphate in the first year of the study increased the iron content by 24.6% and in the second year of the study – 11.3% in relation to fertilization with phosphorus. In the third year, differentiated fertilization with phosphorus gave significant differences in relation to the dose of applied phosphate, where higher iron contents were observed at a lower dose of phosphorus (4%). Moreover, in the third year of the study, the iron content in the plant material was clearly higher in relation to previous years, which may result from the fact that the highest average temperatures were recorded in that year.

Table 10 lists the average iron content in corn depending on the type of suspension fertilizer and the percentage of phosphorus, divided into individual years of research and the nitrogen dose applied.

Table 10. Average iron content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for $\alpha = 0.05$ due to the type of suspension fertilizer and the percentage of phosphorus.

Year	N dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg micro	avg.	NPK	NPK S Mg	NPK S Mg micro	avg.
I	180	94.00 b-e	95.00 c-e	86.33 a-e	91.78 BC	71.00 a	83.33 a-d	68.67 a	74.33 A
	135	73.33 ab	103.67 de	70.33 a	82.44 AB	79.00 a-c	107.67 e	93.00 b-e	93.22 C
	avg.	80.67 AB	99.33 C	78.33 A		75.00 A	95.50 BC	80.83 A	
	avg.		87.11 A				83.78 A		
	A – $\eta^2_p = 66.59\%$ B – s.i.		C – s.i.		AxB – s.i. AxC – $\eta^2_p = 37.71\%$		BxC – $\eta^2_p = 58.06\%$ AxBxC – s.i.		
II	180	99.67 bc	92.33 a-c	85.00 a-c	92.33	111.33 c	73.33 ab	106.67 c	97.11 A
	135	90.33 a-c	98.33 a-c	71.00 a	86.56 A	96.00 a-c	86.33 a-c	72.33 ab	84.89 A
	avg.	95.00 BC	95.33 BC	78.00 A		103.67 C	79.83 AB	89.50 A-C	
	avg.		89.44 A				91.00 A		
	A – $\eta^2_p = 42.31\%$ B – s.i.		C – $\eta^2_p = 25.25\%$		AxB – $\eta^2_p = 37.97\%$ AxC – $\eta^2_p = 44.78\%$		BxC – s.i. AxBxC – s.i.		
III	180	139.00 bc	120.00 a-c	108.33 a	122.44 A	140.33 bc	131.00 a-c	113.00 ab	128.11 A
	135	123.33 a-c	178.33 e	171.67 de	157.78 B	114.33 ab	112.00 ab	146.33 cd	124.22 A
	avg.	131.17 AB	149.17 C	140.00 BC		127.33 AB	121.50 A	129.67 AB	
	avg.		140.11 B				126.17 A		
	A – s.i. B – $\eta^2_p = 43.18\%$		C – $\eta^2_p = 49.14\%$		AxB – $\eta^2_p = 28.34\%$ AxC – $\eta^2_p = 75.89\%$		BxC – $\eta^2_p = 60.05\%$ AxBxC – $\eta^2_p = 43.59\%$		

The differentiation of fertilization with respect to the applied additives did not show a clear effect on the iron content in the plant material from corn. In general, it can be stated that the content of this nutrient in corn in the conducted experiment was at an appropriate level.

4. Discussion

The nutrient uptake by maize presented in the literature data varies significantly depending on the cultivation conditions and harvest method [7].

Among the micronutrients, corn has the greatest demand for zinc [2], [5]. It is essential for proper growth because it is a component of many enzymes, it takes part in the synthesis of vitamins and the formation of chlorophyll [2], [5], [14]. It plays an important role in oxidation and reduction processes [2], [5], [14]. Zn is necessary for the synthesis of tryptophan - the precursor of growth hormone (auxin) [3], [6], [15]. It is a structural and functional component of many plant enzymes [16], [17]. Zinc deficiency disrupts photosynthesis, reduces protein synthesis, and destroys RNA [2], [6], [18].

Low availability of Zn in calcareous soils covers the largest range of biotic stresses in agriculture, especially in cereals [7]. In addition to the Zn concentration in the soil, soil pH and phosphorus content are the main factors determining Zn availability to plants [7], [16], [19]. High pH and P levels are strongly associated with a decrease in Zn content in the plant [7], [16], [19]. This effect is greatest in soils with a pH above 7 and low organic matter content [7], [19]. In such cases, Zn deficiency can be corrected by enriching the fertilization with water-soluble zinc (organic Zn complexes or chelates) [1], [7], [20]. Its availability, however, decreases over time as a result of the formation of stable forms with soil components. In such conditions, foliar application of Zn in the form of spraying is more effective [7].

Motesharezadeh et al. (2011) observed an increase in chlorophyll content and dry plant mass as a result of its use [21]. Azab (2015) showed an improvement in maize yields by using fertilizer containing zinc (1.5%) [22]. Adesh et al. (2021) found that zinc application improves yield parameters and properties of forage plants. In their study, they obtained higher green corn yield (519.20 q ha^{-1}), dry fodder yield (137.90 q ha^{-1}), protein content (10.27%) and crude fiber (58.33%) by applying 20 kg $ZnSO_4$ ha^{-1} to the soil and 0.5% $ZnSO_4$ to the leaves. [23]. Ramakrishna et al. (2022) in their study obtained the highest production of dry matter (104 q ha^{-1}), green forage yield (419 q ha^{-1}) and crude protein (9.3%) by using 1% $ZnSO_4$ as compared to the control. [24]. Sulthana et al. (2015) using 50 kg $ZnSO_4 \cdot ha^{-1}$ in soil and 0.2% $ZnSO_4$ foliarly in their experiments resulted in better parameters of green forage and higher yield (424 q ha^{-1}) and dry matter content (6695 K g ha^{-1}) [25]. Sewhag et al. (2022) reached similar conclusions, obtaining better quality and quantity of corn plant yield. They supported their conclusions with research, where they used 25 kg $ZnSO_4 \cdot ha^{-1}$ for fertilization in the basic dose + 1% in the form of spray, obtaining green forage yield (463.08 q ha^{-1}), dry feed yield (118.75 q ha^{-1}) and crude protein (9.90 %) [26].

Iron is an essential nutrient for all organisms. It participates in respiration, photosynthesis, chlorophyll biosynthesis, DNA and plant hormones [6], [7], [16], [18], [27]. Although Fe is abundant in the earth's crust, it is one of the most limiting nutrients for plant growth. This is due to the low solubility of the oxidized form of Fe (III) at alkaline soil pH. Fe deficiency is also associated with excessive irrigation, long-term moisture or poor soil drainage, and low temperature [7], [18]. More than one third of the world's soils are considered to be iron-poor [7].

Fe deficiencies in most plant species are manifested by Fe content below 10-80 mg kg^{-1} in leaves [9]. For maize leaves during the silking period, the sufficient Fe content is in the range of 21 – 250 mg kg^{-1} [7].

The presence of boron in the soil has a positive effect on the uptake of iron by plants [7]. According to research by Farshid (2012) the application of 6 kg ha^{-1} B resulted in an increase in Fe content in leaves by more than 12% [7]. Application of B in the form of spray directly onto leaves did not affect the Fe content in the plant [7]. Similar relationships were confirmed in their studies by Patel and Golakiya (1986), who applied 2 mg B kg^{-1} of soil and obtained higher contents of N, P, K, Fe and Cu in the plant [7].

Manganese affects corn yield by participating in the synthesis of respiratory and photosynthetic enzymes. It also prevents the accumulation of nitrates in plant tissues [6], [18].

Plants take up manganese in the form of Mn^{2+} ion and its optimal concentration range in plant tissues, according to the literature, is very wide: from 30 to > 1000 mg $\cdot$ kg^{-1} in dry matter [7]. Reuter and Robinson (1997) classified the Mn concentration range for maize leaves in the silk stage below 15 mg $\cdot$ kg^{-1} as deficiency, 16 to 19 mg $\cdot$ kg^{-1} as minimum range, 20 to 150 mg $\cdot$ kg^{-1} as optimum range, 151 to 200 mg $\cdot$ kg^{-1} as high range, while Mn content above 200 mg $\cdot$ kg^{-1} was considered toxic [7].

Manganese deficiency in plants is common in a wide range of soils and climatic conditions [7]. This is caused by oxidation of Mn to forms inaccessible to plants in soils with high pH and high oxygen concentration in the soil solution [7], [8]. However, in soils with pH lower than 5.5, high concentrations of easily mobile Mn^{2+} ions may be toxic [7]. In general, as soil pH increases, manganese forms fewer organic compounds and more amorphous and crystalline ones [7].

Aref (2012) in his study showed a negative effect of boron fertilization on manganese content in maize leaves. At the highest level of B fertilization (6 kg $\cdot$ ha^{-1} B) he obtained Mn concentration in maize leaves at the level of 124 mg $\cdot$ kg^{-1}, while in the control without B fertilization - 153.1 mg $\cdot$ kg^{-1}. The author also showed an antagonistic effect of zinc on manganese content in the plant. Application of 16 kg ha^{-1} Zn increased Mn content in leaves from 133 to 182 mg $\cdot$ kg^{-1} [7].

Copper is one of the essential trace nutrients, which is an essential part of the cofactor of molecules widely involved in basic metabolic processes, including photosynthesis, respiration, and cell wall lignification. However, in excessive amounts, it has a toxic effect, resulting in inhibition of plant growth [7], [28].

Copper present in soil is not very mobile because it strongly binds with organic matter. Soil pH plays a significant role in its bioavailability - as it increases, the content of Cu2+ ions in the soil solution decreases rapidly [7], [16]. Therefore, copper uptake can be regulated by liming the soil and fertilizing with manure. Corn shows moderate sensitivity to copper deficiency [7].

5. Conclusions

In most cases, no higher micronutrient contents were noted in maize plants by using suspension fertilizers with micronutrients, which could be mainly due to high soil pH and low rainfall. In such a case, foliar application of fertilizer in the form of spraying would be more beneficial.

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