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# Aluminium in Acid Soils: Chemistry, Toxicity and Impact on Maize Plants

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## 1. Introduction

Soil acidity is a limiting factor affecting the growth and yield of many crops all over the world. The basic problems concerning chemical properties of more acid soils are, besides acidity itself, the presence of toxic compounds and elements, such as soluble forms of Al, Fe and Mn, nitrites and various toxic organic acids. Aluminium (Al) toxicity is one of the major constraints on crop productivity on acid soils, which occur on up to 40% of the arable lands of the world. Al is the third most abundant element in the earth's crust and is toxic to plants when solubilised into soil solution at acidic pH values (Kochian, 1995). A total of 3950 million hectares of land is classed as having acidic soil, of which 15% is used for planting of annual and perennial crops (von Uexküll & Mutert, 1995).

Northern belt of acid soils occurring in the humid northern temperate zone is comprised of predominantly organic acid soils and supports coniferous forests. A southern belt of mineral acid soils occurs in the humid tropics. Currently approximately 12% of land in crop production is acidic (Uexküll & Mutert, 1995), however, the nutrient content of acid soil is increasing world-wide. Mineral acid soils result from parent materials that are acidic and naturally low in the basic cations (Ca, Mg, K and Na), or because these elements are leached from the soil, reducing pH and the buffering capacity of the soil. As soil pH decreases, aluminum (Al) is solubilized and the proportion of phytotoxic aluminium ions increases in the soil solution. In most mineral soils there is sufficient Al present to buffer the soil to around pH 4. Organic acid soils, consisting of large amounts of humic acids and partially decomposed plant matter, typically have little Al buffering and the pH of these soils can fall rather below pH 4 (Kidd, 2001).

A number of factors contribute to acid soil toxicity transdepending on soil composition. In acid soils with a high mineral content, the primary factor limiting plant growth is Al toxicity. The Al released from soil minerals under acid conditions occurs as  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})$  and  $\text{Al}(\text{H}_2\text{O})^{3+}$ , the latter commonly referred to as Al (Kinraide, 1991). For most agriculturally important plants, Al ions rapidly inhibit root growth at micromolar concentrations.

The primary target of Al toxicity is the root apex. Aluminium affects a host of different cellular functions, frustrating attempts to identify the principal effect(s) of Al toxicity. Exposure to Al causes stunting of the primary root and inhibition of lateral root formation. Affected root tips are stubby due to inhibition of cell elongation and cell division. The resulting restricted root system is impaired in nutrient and water uptake, making the plant more susceptible to drought stress. Plants sensitive to Al toxicity have greatly reduced yield and crop quality (Samac & Tesfaye, 2003; Jovanovic et al., 2006; 2007).

The influence of physical-chemical characteristics of soil on distribution of some elements and availability for plants in vertisols of Serbia are confirmed (Krstic et al., 2004; Krstic et al., 2007; Dugalic et al., 2010; Jelic et al., 2010; Milivojevic et al., 2011). Aim of this study was testing of soil pH, exchangeable acidity and mobile aluminium (Al) status in profiles of pseudogley soils of Čačak–Kraljevo basin.

### 1.1 Aluminium chemistry in the soil

Aluminium, bound as oxides and complex aluminosilicates, ranks third in abundance among the elements in the Earth's crust. Despite much research since Hartwell and Pember first postulated, nearly 90 years ago, that soluble aluminium is a major inhibitor of plant growth in acid soils, the mechanism of aluminium phytotoxicity is not yet fully understood. Aluminium can inhibit root growth at the organ, tissue, and cellular levels at micromolar concentrations (Ciamporová, 2002). Acid soils, present mostly in humid tropical and subtropical areas of the world, are characterized by having excess  $H^+$ ,  $Mn^{2+}$ , and  $Al^{3+}$ , with deficiencies of  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $PO_4^{3-}$ . Additionally, sulfur dioxide and other air pollutants cause acid soil stress in areas other than the tropics (Foy, 1984). In acidic soils, hydroxyl-rich aluminium compounds solubilize to an extent in the soil solution. Forty percent of the arable land globally is acidic because of solubilization of the abundantly present aluminium, greatly limiting crop productivity.

Aluminium chemistry is quite complex. It has a high ionic charge and a small crystalline radius, which gives it a level of reactivity that is unmatched by other soluble metals. When the pH of a solution is raised above 4.0,  $Al^{3+}$  forms the mononuclear species  $AlOH_2^+$ ,  $Al(OH)_2^+$ ,  $Al(OH)_3$ , and  $Al(OH)_4^+$ , and soluble complexes with inorganic ligands such as sulfate and fluoride,  $AlF_2^+$ ,  $AlF_3^+$ ,  $Al(SO)_4^+$ , and also with many organic compounds. Larger polynuclear hydroxyl aluminium species also form as metastable intermediates during  $Al(OH)_3$  precipitation. The mononuclear  $Al^{3+}$  species seems to be most toxic at low pH, at which it exists as an octahedral hexahydrate. With increasing pH,  $Al(H_2O)_6^{3+}$  undergoes repeated deprotonations to form insoluble  $Al(OH)_3$  at pH 7.0. At cytosolic pH, 7.4 aluminate ion,  $Al(OH)_4^-$ , is formed. In near neutral solutions, polynuclear forms of aluminium, which contain more than one aluminium atom, occurs. One of the most important polymer triskaidekaaluminium,  $AlO_4Al_{12}(OH)_{24}(H_2O)_{127}^+$  referred as  $Al_{13}$  (Parker & Bertsch, 1992), seems to be the most toxic Al specie.

## 2. Material and methods

### 2.1 General characteristics of the Čačak–Kraljevo Basin

Čačak–Kraljevo basin is part of western Serbia (Morava river area). It is narrow belt longitude approximately 70 km in NW–SE direction and width from 5 to 18 km. Kablar,

Ovčar, Troglav, Stolovi, Goč, Suvobor, Vujno and Kotlenik mountains are border toward SW and NE directions. Pseudogley soils of this area (approximately 32.000 hectares situated mainly in latitudes between 180 and 200 m above sea level) have been developed on diluvial-holocene terrace of Western Morava and its tributaries. Climate of this area is moderate continental characterizing mean annual air-temperature 11.2°C (winter 1.4°C, summer 20.5°C) and precipitation 715.8 mm (Kraljevo Weather Bureau; means 1961–1990).

2.2 Sampling and chemical analysis

Total 102 soil profiles were opened during 2008 at certain sites of the Čačak–Kraljevo basin. The tests encompassed 54 field, 28 meadow, and 20 forest profiles. From the opened profiles, samples of soil in the disturbed state were taken from the humus and Eg horizons (102 profiles); then from the B<sub>1</sub>tg horizon of 39 fields, 24 meadows and 15 forest profiles (total 78) and from the B<sub>2</sub>tg horizon of 14 fields, 11 meadows, and 4 forest profiles (total 29). Laboratory determination of exchangeable acidity was conducted in a suspension of soil with a 1.0 M KCl solution (pH 6.0) using a potentiometer with a glass electrode, as well as by Sokolov’s method, where the content of Al ions in the extract is determined in addition to total exchangeable acidity (H<sup>+</sup> + Al<sup>3+</sup> ions) (Jakovljevic et al., 1995).

3. Results and discussion

This mean pH (1M KCl) of tested soil profiles were 4.28, 3.90 and 3.80, for Ah, Eg and B<sub>1</sub>tg horizons, respectively. Also, soil pH of forest profiles was lower in comparison with meadows and arable lands (means: 4.06, 3.97 and 3.85, for arable lands, meadows and forest, respectively). Soil acidification is especially intensive in deeper horizons because 27% (Ah), 77% (Eg) and 87% (B<sub>1</sub>tg) soil profiles have pH lower than 4.0 (Table 1).

Distribution of pH (1M KCl) in soil profiles (a=arable land; m=meadow; f=forest)								
Horizons	n	pH (1M KCl)					pH values	
		< 4.0	4.1–4.5	4.6–5.1	> 5.1	Sum	Mean	Range
		pH (1M KCl) in % of total (n) tested profiles						
Ah (a)	54	18.5	57.5	22.2	1.8	100	4.33	3.7–5.2
Ah (m)	24	20.8	75.0	4.2	0.0	100	4.25	3.9–4.8
Ah (f)	20	55.0	30.0	5.0	10.0	100	4.18	3.6–5.3
Ah (total)	98	26.5	56.1	14.3	3.1	100	4.28	3.6–5.3
Eg (a)	54	64.8	27.8	7.4	0.0	100	3.99	3.6–5.1
Eg (m)	24	91.7	8.3	0.0	0.0	100	3.89	3.6–4.5
Eg (f)	20	90.0	10.0	0.0	0.0	100	3.69	3.4–4.1
Eg (total)	98	76.5	19.4	4.1	0.0	100	3.90	3.4–5.1
B <sub>1</sub> tg (a)	39	76.9	20.5	2.6	0.0	100	3.86	3.5–4.6
B <sub>1</sub> tg (m)	20	95.0	5.0	0.0	0.0	100	3.78	3.6–4.4
B <sub>1</sub> tg (f)	17	100.0	0.0	0.0	0.0	100	3.69	3.5–4.0
B <sub>1</sub> tg (total)	76	86.9	11.8	1.3	0.0	100	3.80	3.5–4.6
B <sub>2</sub> tg (total)	31	90.2	6.6	3.2	0.0	100	3.83	3.6–4.8

Table 1. Distribution of pH (1M KCl) in soil profiles

Mean total exchangeable acidity (TEA) of tested soil profiles were 1.55, 2.33 and 3.40 meq 100g<sup>-1</sup>, for Ah, Eg and B<sub>1</sub>tg horizons, respectively. However, it is considerably higher in forest soils (mean 3.39 meq 100g<sup>-1</sup>) than in arable soils and meadows (means 1.96 and 1.93, respectively).

The deeper horizons (Eg and B<sub>1</sub>tg) of meadows and forest soil profiles have especially high TEA values. Especially high frequencies of the high TEA values (over 3.0 meq 100g<sup>-1</sup>) were found in forest soil profiles (Table 2).

Total exchangeable acidity (TEA) in soil profiles (a=arable land; m=meadow; f=forest)								
Horizons	n	TEA (meq 100g <sup>-1</sup> )					TRA (meq 100g <sup>-1</sup> )	
		<1.0	1-2	2-3	>3.0	Sum	Mean	Range
		TEA in % of total (n) tested profiles						
Ah (a)	53	86.8	13.2	0.0	0.0	100	0.96	0.07-1.84
Ah (m)	27	85.2	14.8	0.0	0.0	100	0.90	0.22-1.58
Ah (f)	20	55.0	20.0	5.0	20.0	100	2.79	0.09-5.49
Ah (total)	100	80.0	15.0	1.0	4.0	100	1.55	0.07-5.49
Eg (a)	53	35.8	37.8	22.6	3.8	100	1.80	0.16-3.44
Eg (m)	27	18.5	63.0	11.1	7.4	100	1.85	0.37-3.33
Eg (f)	20	10.0	20.0	30.0	40.0	100	3.34	0.58-6.09
Eg (total)	100	26.0	41.0	21.0	12.0	100	2.33	0.16-6.09
B <sub>1</sub> tg (a)	37	24.3	18.9	24.3	32.5	100	3.12	0.23-6.01
B <sub>1</sub> tg (m)	23	8.7	21.7	39.2	30.4	100	3.05	0.60-5.49
B <sub>1</sub> tg (f)	14	0.0	21.4	28.6	50.0	100	4.03	1.36-6.69
B <sub>1</sub> tg (total)	74	14.8	20.3	29.6	35.3	100	3.40	0.23-6.69
B <sub>2</sub> tg (total)	29	14.8	27.6	36.5	21.1	100	2.62	0.70-5.54

Table 2. Distribution of total exchangeable acidity (sum of H<sup>+</sup> and Al<sup>3+</sup>) in soil profiles

Mean mobile Al contents of tested soil profiles were 11.02, 19.58 and 28.33 mg Al 100 g<sup>-1</sup>, for Ah, Eg and B<sub>1</sub>tg horizons, respectively. Soil pH and TEA in forest soils are considerably higher (mean 26.08 meq Al 100 g<sup>-1</sup>) than in arable soils and meadows (means 16.85 and 16.00 Al 100 g<sup>-1</sup>, respectively). The Eg and B<sub>1</sub>tg horizons of forest soil profiles have especially high mobile Al contents (means 28.50 and 32.95 mg Al 100 g<sup>-1</sup>, respectively). Frequency of high levels of mobile Al is especially high in forest soils because 35% (Ah), 85.0% (Eg) and 93.3% (B<sub>1</sub>tg) of tested profiles were in range above 10 mg Al 100 g<sup>-1</sup> (Table 3).

Increased TEA is characteristics of soils in which acidification processes are rather for advanced, the reaction of their soil solutions being fairly acidic, which pH values are lower than 5.0. This is typical for pseudogley which is the most widely disseminated type of soil in the Čačak-Kraljevo basin. Due to the fact that Al ions in an increased concentration are

much more dangerous for plants than  $H^+$  ions in the same concentration at the same value of TEA, plants increasingly suffer if a higher share of Al ions is present in it. Already at the content of 6–10 mg 100 g<sup>-1</sup> of readily mobile Al in the soil, plant growth is retarded to a greater or lesser extent depending on the species (Rengel, 2004). High TEA, created predominantly by Al ions, is among the most important causes of the low productive capacity of pseudogley in the indicated basin where, despite of fertilizer use and application of different agrotechnical measures, average yields of cultivated plants are low and vary fairly greatly depending on weather conditions of the year.

Mobile aluminum contents in soil profiles (a = arable land; m = meadow; f = forest)								
Horizons	n	Mobile aluminum (mg Al 100 g <sup>-1</sup> )					mg Al 100 g <sup>-1</sup>	
		<3.0	3.1–6.0	6.1–10	>10	Sum	Mean	Range
		Mobile aluminum in % of total						
Ah (a)	54	63.0	18.5	11.1	7.4	100	8.15	0.2 – 16.1
Ah (m)	28	64.4	17.8	7.1	10.7	100	8.10	1.0 – 15.2
Ah (f)	20	40.0	10.0	15.0	35.0	100	16.80	0.4 – 33.2
Ah (total)	102	58.8	16.3	10.8	14.1	100	11.02	0.2 – 33.2
Eg (a)	54	20.4	13.0	12.9	53.7	100	15.40	0.5 – 30.3
Eg (m)	28	10.7	7.1	21.4	60.8	100	14.85	0.3 – 29.4
Eg (f)	20	0.0	15.0	0.0	85.0	100	28.50	3.5 – 53.5
Eg (total)	102	13.7	11.8	12.8	61.7	100	19.58	0.3 – 53.5
B <sub>1</sub> tg (a)	39	12.8	12.8	7.7	66.7	100	27.00	1.0 – 53.0
B <sub>1</sub> tg (m)	24	0.0	8.3	12.5	79.2	100	25.05	3.2 – 46.9
B <sub>1</sub> tg (f)	15	0.0	0.0	6.7	93.3	100	32.95	7.9 – 58.0
B <sub>1</sub> tg (total)	78	6.4	9.0	8.9	75.7	100	28.33	1.0 – 58.0
B <sub>2</sub> tg (total)	29	0.0	14.2	13.5	72.3	100	20.50	3.6 – 37.4

Table 3. Distribution of mobile aluminium in soil profiles

3.1 Aluminium Influence on maize plants

Al ions translocate very slowly to the upper parts of plants (Ma et al., 1997). Most plants contain no more than 0.2 mg Al g<sup>-1</sup> dry mass. However, some plants, known as Al accumulators, may contain over 10 times more Al without any injury. Tea plants are typical Al accumulators: the Al content in these plants can reach as high as 30 mg g<sup>-1</sup> dry mass in old leaves (Matsumoto et al., 1976). Approximately 400 species of terrestrial plants, belonging to 45 families, have so far been identified as hyperaccumulators of various toxic metals (Baker et al., 2000).



The main aluminum toxicity symptom is inhibition of root elongation with simultaneous induction of  $\beta$ -1,3-glucan (callose) synthesis, which is apparent after even a short exposure time. Aluminium causes extensive root injury, leading to poor ion and water uptake (Barcelo & Poschenrieder, 2002). One of the hypothesis is that the sequence of toxicity starts with perception of aluminum by the root cap cells, followed by signal transduction and a physiological response within the root meristem. However, recent work has ruled out a role of the root cap and emphasizes that the root meristem is the sensitive site. Root tips have been found to be the primary site of aluminum injury, and the distal part of the transition zone has been identified as the target site in maize (*Zea mays*) (Sivaguru & Horst, 1998). Root cell division results in root elongation. Aluminum is known to induce a decrease in mitotic activity in many plants, and the aluminum-induced reduction in the number of proliferating cells is accompanied by the shortening of the region of cell division in maize (Panda, 2007).

Blancaflor et al. (1998) have studied Al-induced effects on microtubules and actin microfilaments in elongating cells of maize root apices, and related the Al-induced growth inhibition to stabilization of microtubules in the central elongation zone. With respect to growth determinants (auxin, gibberellic acid and ethylene), Al apparently interacts directly and/or indirectly with the factors that influence organization of the cytoskeleton, such as cytosolic levels of  $\text{Ca}^{2+}$  (Jones et al., 2006),  $\text{Mg}^{2+}$  and calmodulin (Grabski et al., 1998), cell-surface electrical potential (Takabatake & Shimmen, 1997), callose formation (Horst et al., 1997) and lipid composition of the plasma membrane.

Genetic variability for Al resistance in maize has been reported (Jorge & Arruda, 1997; Pintro et al., 1996) and Al-resistant maize cultivars have been selected for acidic soils (Pandey & Gardner, 1992). Maize grain-yield increase has been obtained on acid soils through selection for tolerant cultivars in tropical maize populations. Most breeding work designed at increasing productivity on acid soil, focused on tolerance to Al toxicity (Garvin & Carver, 2003).

Al resistance mechanisms can be grouped into two categories, exclusion of Al from the roots, and detoxification of Al ions in the plant (Taylor, 1991; Heim et al., 1999; Kochian et al., 2005; Zhou et al., 2007). Exclusion mechanisms include binding of Al in the cell wall, a plant-induced rhizosphere pH barrier, and root exudation of Al-chelating compounds. Organic acids have been reported to play a role both in Al exclusion, via release from the root and Al detoxification in the symplasm, where organic acids such as citric acid and malic acid could chelate Al and reduce or prevent its toxic effects at the cellular level, in particular protecting enzyme activity internally in the plant from the deleterious effect of Al (Delhaize et al., 1993). Genetic adaptation of plants to Al toxicity may provide a sustainable strategy to increase crop yield in the tropics at relatively low costs and low environmental impacts. This approach is particularly interesting for maize, where Al tolerant germplasm is available for selection and for genetic studies. A number of studies have been carried out to elucidate the genetic control of Al tolerance in maize, resulting in controversial results. However, a consensus among the authors has shown that the trait is quantitatively inherited under the control of few genes (Lima et al., 1995). Most of the genetics studies on aluminum tolerance in maize have evaluated the seminal root growth under nutrient solution as screening

technique. Nutrient solutions with high concentration of aluminum have proven to be an effective way to discriminate tolerant and susceptible maize genotypes (Martins et al., 1999; Cancado et al., 1999). Although a large number of studies have been conducted, the genetic basis and the molecular mechanisms responsible for the genetic variability in maize Al tolerance are still poorly understood.

### 3.2 Al toxicity and root growth

High Al concentrations are particularly difficult to interpret in terms of physiological responses. A high proportion of Al in the nutrient growth medium might become inert by precipitation (e.g., with phosphate) or by polymerisation and complexation. Thus, the concentration of free Al promoting toxicity in plant metabolism can be much lower than that existing in the growth medium (Mengel & Kirkby, 1987). Low concentrations of Al can also lead to a stimulation of root growth in tolerant genotypes of *Zea mays* L.

In non-accumulators plant species the negative effects of Al on plant growth prevail in soils with low pH (Marschner, 1995), the reduction in root growth being the most serious consequence (Tabuchi & Matsumoto, 2001). This symptom of Al toxicity has been related to the linkage of Al to carboxylic groups of pectins in root cells (Klimashevsky & Dedov, 1975) or to the switching of cellulose synthesis into callose accumulation (Teraoka et al., 2002), to Al inhibition of mitosis in the root apex (Rengel, 1992; Delhaize & Ryan, 1995) implicating blockage of DNA synthesis, aberration of chromosomal morphology and structure occurrence of anaphase bridges and chromosome stickiness and to Al-induced programmed cell death in the root-tip triggered by reactive oxygen species (Pan et al., 2001).

According to Comin et al. (1997) tolerant cultivars of *Zea mays* L. have different toxicity mechanisms, following monomeric or polymeric forms of Al supplied to the growth medium. Aluminum can easily polymerise, transforming the monomeric form ( $\text{Al}^{3+}$ ) into a polymeric form ( $\text{Al}_{13}$ ), which is much more phytotoxic in maize. Yet, although Bashir et al. (1996) had noticed Al nucleotypic effects on maize, a lack of nuclear DNA content variability was found among wheat isolines differing in Al response as well as four genes that ameliorate Al toxicity (Ezaki et al., 2001). Indeed, the general responses to Al excess by tolerant genotypes deal with the varying ability of plants to modify the pH of the soil-root interface (Mengel & Kirkby, 1987; El-Shatnawi & Makhadmeh, 2001).

## 4. Conclusion

Soil acidity and aluminium toxicity is certain one of the most damaging soil conditions which affecting the growth of most crops. In this paper soil pH, exchangeable acidity and mobile aluminium (Al) status in profiles of pseudogley soils of Western Serbia region were studied. Total 102 soil profiles were opened during 2008 in the Western Serbia. The tests encompassed 54 field, 28 meadow, and 20 forest profiles. From the opened profiles, samples of soil in the disturbed state were taken from the humus and Eg horizons (102 profiles); then from the B<sub>1</sub>tg horizon of 39 fields, 24 meadows and 15 forest profiles (total 78) and from the B<sub>2</sub>tg horizon of 14 fields, 11 meadows, and 4 forest profiles (total 29). Laboratory determination of exchangeable acidity was conducted in a suspension of soil with a 1.0 M



KCl solution (pH 6.0) using a potentiometer with a glass electrode, as well as by Sokolov's method, where the content of Al ions in the extract is determined in addition to total exchangeable acidity ( $H^+ + Al^{3+}$  ions). Mean pH (1M KCl) of tested soil profiles were 4.28, 3.90 and 3.80, for Ah, Eg and B<sub>1</sub>tg horizons, respectively. Also, soil pH of forest profiles was lower in comparison with meadows and arable lands (means: 4.06, 3.97 and 3.85, for arable lands, meadows and forest, respectively). Soil acidification is especially intensive in deeper horizons because 27% (Ah), 77% (Eg) and 87% (B<sub>1</sub>tg) soil profiles have pH lower than 4.0. Mean total exchangeable acidity (TEA) of tested soil profiles were 1.55, 2.33 and 3.40 meq 100g<sup>-1</sup>, for Ah, Eg and B<sub>1</sub>tg horizons, respectively. However, it is considerably higher in forest soils (mean 3.39 meq 100g<sup>-1</sup>) than in arable soils and meadows (means 1.96 and 1.93, respectively). Mean mobile Al contents of tested soil profiles were 11.02, 19.58 and 28.33 mg Al 100 g<sup>-1</sup>, for Ah, Eg and B<sub>1</sub>tg horizons, respectively. Soil pH and TEA in forest soils are considerably higher (mean 26.08 meq Al 100g<sup>-1</sup>) than in arable soils and meadows (means 16.85 and 16.00 Al 100 g<sup>-1</sup>, respectively). The Eg and B<sub>1</sub>tg horizons of forest soil profiles have especially high mobile Al contents (means 28.50 and 32.95 mg Al 100 g<sup>-1</sup>, respectively). Frequency of high levels of mobile Al is especially high in forest soils because 35% (Ah), 85.0 % (Eg) and 93.3% (B<sub>1</sub>tg) of tested profiles were in range above 10 mg Al 100 g<sup>-1</sup>.

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High Al concentrations are particularly difficult to interpret in terms of physiological responses. A high proportion of Al in the nutrient growth medium might become inert by precipitation (e.g., with phosphate) or by polymerisation and complexation. Thus, the concentration of free Al promoting toxicity in plant metabolism can be much lower than that existing in the growth medium.

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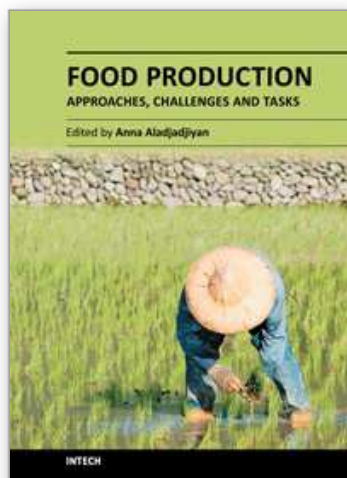
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