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Influence of Fertilization and Agronomic Practices on Acrylamide Formation: Review for Potato and Grain Crops

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Efforts to reduce acrylamide formation would be greatly facilitated by the development of crop varieties with lower concentrations of free asparagine or reducing sugars, and of best agronomic practice to ensure that concentrations are kept as low as possible. Examinations have shown that 134 kg N ha^{-1} and 168 kg K_2O ha^{-1} are the best fertilizer rates for balancing tuber yields with a range of tuber quality attributes, including acrylamide- forming potential. The influence of potassium fertilizer source (K_2SO_4 and KCl) on potato yield and quality under pot experimental conditions was studied by some authors. Fertilizer importance was also proved by comparing five commercial rye varieties grown under a range of fertilization regimes to investigate the effects of genotype and nutrient (nitrogen and sulphur) availability on the accumulation of acrylamide precursors. From the above evidence, conclusions can be made that usage of agro-technical measures can reduce the toxic substances in grains and potato. Also, the appropriate ratio of applied fertilizers and basic nutrient metabolism for acrylamide creation can be adjusted to obtain predefined quantities of reducing sugars and asparagine as the main precursors.

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1. INTRODUCTION

Providing crops with adequate levels of nutrients ensures that the best yield possible is obtained, but attention is not always paid to the effect which plant nutrition has on crop composition and the consequences for food quality and safety [1]. Safety aspects are also influenced by acrylamide formation. Maintaining high safety standards, as well as the expected quality, requires systematic research based on an integrated approach including all relevant variables, e.g., raw material properties, processing conditions and equipment concepts [2]. Wheat and potato are especially interesting, considering that quality has been found to vary when grown under different agricultural and environmental conditions. Efforts to reduce acrylamide formation would be greatly facilitated by the development of crop varieties with lower concentrations of free asparagine or reducing sugars, and of best agronomic practice, to ensure that concentrations are kept as low as possible [3].

2. INFLUENCE OF FERTILIZATION AND AGRONOMIC PRACTICES ON ACRYLAMIDE FORMATION FOR POTATO AND GRAIN CROPS

2.1 Potato Crops

The quality of the potato has been found to vary, when grown under different agricultural and environmental conditions, i.e. different levels of fertilization. Consequently, these factors may influence acrylamide formation during the preparation of French fries [4]. To examine how sulphur deprivation may affect acrylamide formation in cooked potatoes, Elmore et al., [5] have examined three varieties of potato under conditions of either severe sulphur deprivation, or an adequate supply of sulphur. In all three varieties the sulphur deprivation led to a decrease in acrylamide formation, even though the levels of sugars, which are acrylamide precursors, were higher in tubers of the sulphur-deprived plants. In one variant the concentration of free asparagine, the other precursor for acrylamide, was also higher. There was a very close correlation between the concentration of asparagine in the tubers expressed as a proportion of the total free amino acid pool and the formation of acrylamide upon cooking (Fig. 1), whereas sugars were poorly correlated with acrylamide [5].

The influence of potassium fertilizer (K_2SO_4 and KCl) on potato yield and quality under pot experimental conditions was studied by Manolov et al. [6]. The experiments included increased quantities of the potassium fertilizers, providing 200, 400 and 600 mg/kg soil K_2O. Data indicated no statistical differences in potato yield as a result of potassium fertilizer.

In contrast, all studied quality parameters except for reducing sugars (Table 1) were influenced by potassium source. Increased rates of KCl resulted in decreasing mostly dry matter, starch and vitamin C contents in potato tubers which were diminished by 15%, 46% and 50% by K600 (600 mg K_2O kg^{-1} soil) treatment respectively when compared to control.

Reducing sugars are critical precursors for acrylamide formation during frying, which is considered carcinogenic and neurotoxic for humans. On the other hand, in their study, neither potassium source nor the rate influenced the level of reducing sugars in potato tubers. The contents of reducing sugars in the samples of all treatments were not found to be significantly different from each other. In most cases, increases of K rates led to a lower amount of reducing sugars. The differences between their observation and some published studies may be due to additional factors such as genetic variations and environmental impact like growing- and tuber storage conditions [6]. Gause [7] has also shown that 134 kg N ha^{-1} and 168 kg K_2O ha^{-1} are the best fertilizer rates for balancing tuber yields with a range of tuber quality attributes, including acrylamide- forming potential. Viklund et al., [8] examined the impact of harvest year, information on weather conditions during growth, temperature, precipitation and light, together with analytical data on the concentrations of free amino acids and sugars in five potato clones and acrylamide contents in potato chips (commonly known as crisps in Europe). The study was conducted for 3 years (2004 – 2006). The contents of acrylamide precursors differed among the clones; the glucose level was up to 4.2 times higher in 2006 than in 2004 and 2005, and the levels of fructose were 5.6 times higher, whereas the levels of asparagine varied to different extents. The high levels of sugars in 2006 were probably due to the extreme weather conditions during the growing season, and this was also reflected in acrylamide content that was approximately twice as high as in the preceding years [8].

Research done by Muttucumaru et al., [9] on twenty potato (*Solanum tuberosum* L.) varieties grown in a field trial at Thorn Bank, Doncaster, North Lincolnshire, UK (Grid reference: SE723015; 53°30'20"N, 0°54'40"W; soil type: peaty sand) in 2011 revealed that free asparagine and total free amino acid concentrations correlated significantly ($r = 0.802$, $p < 0.001$, F-test) in potatoes fertilized with nitrogen at rates of 100 or 200 kg per hectare, suggesting that the stepwise change in the ratio observed between the Doncaster and Woburn sites in the present study was not caused by differences in nitrogen availability arising from the different soil types [9]. The same authors wrote that water availability may also affect the composition of the crop, with implications for processing properties and food safety. Five varieties of potatoes, including drought-tolerant and -sensitive types, which had been grown with and without irrigation, were analysed to show the effect of water supply on concentrations of free asparagine, other free amino acids, and sugars and on the acrylamide-forming potential of the tubers. Two varieties were also analysed under more severe drought stress in a glasshouse. Water availability had profound effects on tuber free amino acid and sugar concentrations, and it was concluded that potato farmers should irrigate only if necessary to maintain the health and yield of the crop, because irrigation may increase the acrylamide-forming potential of potatoes [10].

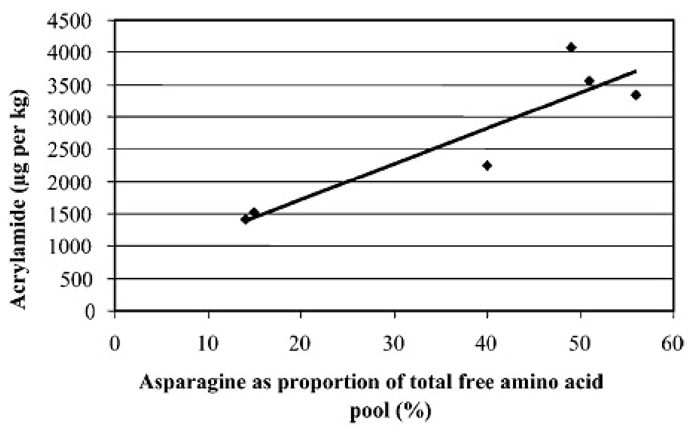

Fig. 1. The relationship between asparagine concentration expressed as a proportion of the total free amino acid pool and acrylamide formation in potato flour, after heating at 160 °C for 20 min ($R^2 = 0.8354$)

Source: Elmore et al., (2007)

Table 1. Quality parameters of potato tubers[1]

K level	K source	Dry matter (%)	Starch (%)	Reducing sugars (%)	Vitamin C (mg/100 g)	Crude protein (%)
1 K_0	Control	20.92a	10.05a	0.42a	11.4c	16.31b
2 K_{200}	K_2SO_4	18.99c	8.42d	0.40a	10.6d	15.38c
3 K_{400}	K_2SO_4	17.99e	9.42b	0.40a	14.9a	14.44e
4 K_{600}	K_2SO_4	20.36ab	9.40b	0.41a	12.3b	13.94f
5 K_{200}	KCl	19.68b	9.33c	0.40a	6.2e	13.88f
6 K_{400}	KCl	16.78d	8.11e	0.41a	5.2f	14.91d
7 K_{600}	KCl	17.59e	5.70f	0.40a	5.2f	18.97a

Source: Manolov et al., (2015)

[1] Values with different letters are with proved difference according to Duncan's multiple range test (p < 0.05).

2.2 Grain Crops

In wheat flour, the acrylamide formation is determined by asparagine levels and asparagine accumulation increases dramatically in response to sulphur deprivation and, to a much lesser extent, with nitrogen feeding [11]. Wheat flour from plants deficient in sulphur has been shown to contain substantially higher levels of free amino acids, particularly asparagine and glutamine, than flour from wheat grown where sulphur nutrition was sufficient. Elevated levels of asparagine resulted in acrylamide levels up to 6 times higher in sulphur-deprived wheat flour, compared with sulphur-sufficient wheat flour, for three varieties of winter wheat [12]. According to Halford et al., [3] asparagine levels appear to play a key role in determining acrylamide formation in processed wheat flour. Sulphur availability has been shown to be particularly important, with sulphur deprivation causing a dramatic increase in grain asparagine levels and acrylamide risk (Fig. 2). Also, sulphur deprivation led to huge increases in the concentrations of free asparagine and glutamine, and canonical variate analysis showed a clear separation of the grain samples as a result of treatment (environment, E) and genotype (G) and provided evidence of G x E interactions [3].

Low grain sulphur and high free asparagine concentration were closely associated with increased risk of acrylamide formation [13]. Nitrogen availability is also a factor, with increasing nitrogen availability causing grain asparagine levels and acrylamide risk to rise [14]. Nitrogen fertilization resulted in elevated amino acid and protein contents, thus increasing acrylamide levels from 10.6 to 55.6 mug/kg in breads [15]. The influence of different nitrogen (N) fertilizers (calcium ammonium nitrate, CAN; urea ammonium sulfate solution, UAS, applied according to the CULTAN method; urea; urea ammonium nitrate, UAN; ammonium nitrate sulfate containing the nitrification inhibitor 3,4-dimethyl pyrazole phosphate, Entec 26®; and a combination of liquid manure and CAN) at a nitrogen level of 180 kg N ha^{-1} and an additional sulphur (S) supply on grain yield, quality, Asn concentration, and the potential of acrylamide formation of winter wheat were studied in a 2-year field experiment. Grain yields varied between 61 und 104 dt ha^{-1} dry matter depending on cultivar (cv), fertilization and year. Quality demands concerning crude protein concentration and sedimentation value were reached when CAN, CAN+S, urea, or a combination of liquid manure and CAN were applied. Asparagine concentrations in flours varied from 2.6 to 13.6 mg per 100 g flour dry matter depending on cultivar, fertilization, and year. In both years, a close nonlinear correlation between crude protein concentration and the concentration of free Asn with $r^2_{2004} = 0.93$ and $r^2_{2005} = 0.94$ was observed. Nitrogen fertilizers leading to high crude protein concentrations caused significantly increased Asn concentrations. In both years, a correlation between the concentration of free Asn and the potential of AA formation with $r^2_{2004} = 0.72$ and $r^2_{2005} = 0.84$ was found [16]. Curtis et al., [17] revealed that wheat responds dramatically to sulphur deprivation by accumulating high levels of free asparagine in the grain. This increases the risk of acrylamide formation, and ensuring that wheat has an adequate supply of sulphur is a key factor for the mitigation of acrylamide risk in wheat products. However, in their study, grain sulphur concentration in rye was not related to the availability of sulphur in the soil, even when soil sulphur levels were as low as 4.1 mg/kg, suggesting that the rye plants were able to acquire enough sulphur even when soil levels were relatively low. Consequently, none of the grain samples had a sulphur concentration under 1.0 g/kg, a level that has been associated with very high levels of free asparagine and acrylamide formation in wheat [17]. Furthermore, the grain sulphur concentration did not correlate with the concentrations of free amino acids, including asparagine, or with acrylamide formation. On the other hand, high concentrations of nitrogen were associated with high concentrations of free amino acids, including asparagine and sugars, and with acrylamide risk, as in wheat grain (Fig. 3). In later study same author has shown that samples with the highest concentration of acrylamide were the samples with the least sulphur in the grain. This is a very important finding as it would suggest that the higher the sulphur in the grain, the lower the acrylamide formed in the grain will be. However, there will be a level when the addition of more sulphur does not result in a change in the level of asparagine [18].

This was also proved by Postles et al., [19] by comparing five commercial rye varieties grown under a range of fertilization regimes to investigate the effects of genotype and nutrient (nitrogen and sulphur) availability on the accumulation of acrylamide precursors. A strong correlation was established between the free asparagine concentration of grain and the acrylamide formed upon heating. The five rye varieties accumulated different concentrations of free asparagine in the grain, indicating that there is genetic control of this trait and that variety selection could be useful in reducing acrylamide levels in rye products. High levels of nitrogen fertilization were found to increase the accumulation of free asparagine, showing that excessive nitrogen application should be avoided in order not to exacerbate the problem of acrylamide formation [19]. Same author states that free asparagine concentration has been shown to correlate positively with nitrogen availability in the grain of barley (*Hordeum vulgare* L.), wheat and rye, while deficiencies in other minerals become important when there is a plentiful supply of nitrogen. Sulphur deficiency, in particular, can cause a massive (up to 30-fold) increase in free asparagine accumulation in wheat, barley and maize (*Zea mays* L.), although in the rye the response is much less dramatic, at least under field conditions [20].

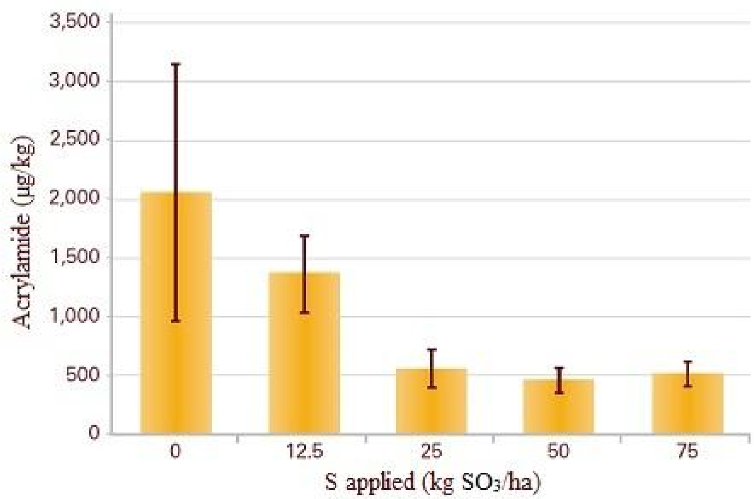

Fig. 2. Effect of S on acrylamide formation in heated flour samples. The acrylamide-forming potential of wheat grown at six S-deficient sites was minimized by applying 50 kg SO_3/ha
Source: HGCA, Information sheet 28, spring 2014 [21]

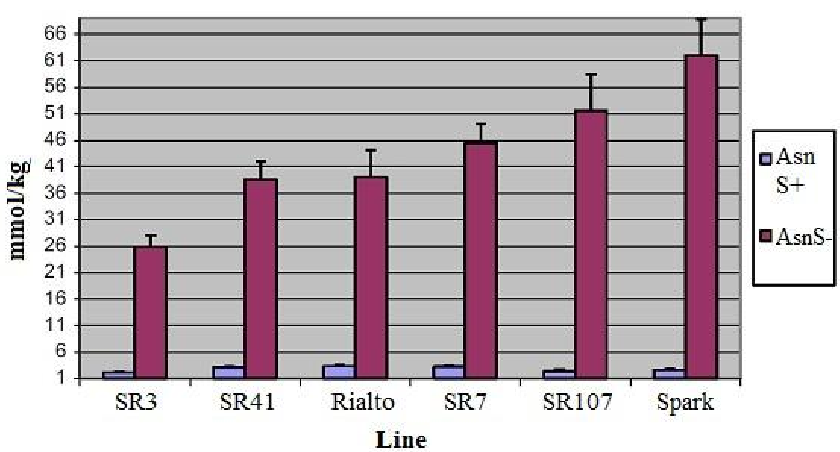

Fig. 3. Asparagine concentration (mmol/kg) under sulphur-sufficient (blue AsnS+) and sulphur-deficient (red AsnS−) treatments of wheat; Spark and Rialto parental varieties and four DH lines: SR3, SR41, SR7, and SR107
Source: Curtis et al., (2016)

3. CONCLUSION

Reducing sugars and asparagine are critical precursors to acrylamide formation during frying, which is considered carcinogenic and neurotoxic to humans. This review reveals differences in research and published studies on the effects of fertilization and agronomic practices for the acrylamide formation in potato due to additional factors such as genetic variation and environmental impact, growing- and tuber storage conditions. Research on soil type shows that free asparagine and the total concentration of free amino acid correlates significantly with potatoes fertilized with nitrogen, indicating that an upward shift in the relationship was not caused by differences in the availability of nitrogen resulting from different types of soil. Also the availability of water can affect the composition of the culture, with implications for the processing properties and food safety. From the analysis made during drought stress in the glasshouse we can also conclude that water availability has profound effects on free amino acid and sugar concentrations in potatoes.

The influence of fertilization and agronomic practices for acrylamide formation in cereal crops as subjects in this review, show that wheat should be provided with an adequate supply of sulphur, which is a key factor in reducing the risk of acrylamide in wheat products. This finding is very important because it suggests that the higher the sulphur in the grain, the smaller the acrylamide content formed in the grain. Several authors have stated that free asparagine concentration proved to be positively correlated with the availability of nitrogen in grain of barley, wheat and rye, and deficiencies in other minerals become important when there is a plentiful supply of nitrogen. Lack of sulphur in particular can cause a massive increase in accumulation of free asparagine in wheat, barley and rye, though this kind of response comes from field conditions.

From the above stated evidence, conclusions can be made that usage of agro-technical measures can reduce the toxic substances in grains and potato. Also, the appropriate ratio of applied fertilizers and basic nutrient metabolism for acrylamide creation can be adjusted to obtain predefined quantities of reducing sugars and asparagine as the main precursors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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