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REVIEW ARTICLE

Plant polyphenol content, soil fertilization and agricultural management: a review

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Abstract The review deals with polyphenol content of vegetables and fruits under different experimental conditions. The effect of fertilizers, mainly nitrogen containing fertilizers, on qualitative and especially quantitative content of the polyphenols mixture, was reviewed. Soil nitrogen affects both anthocyanins and flavonoids content, and generally, a higher polyphenolic content is observed when less nitrogen fertilizer is added to the soil. Also the effect of different agricultural management (conventional, organic, biodynamic, integrate) is reviewed with respect to polyphenols. In this case, a major effect has pointed out in the case of vegetables, while agricultural practice affects in a minimal way fruits polyphenols content. The effect of different management is, however, hardly pointed out, since many environmental factors are involved and affect polyphenols biosynthetic pathway.

Keywords Flavonoids · Anthocyanins · N-fertilization · Conventional management · Organic management · Biodynamic management

Introduction

The great number of reviews, published in the last 20 years, substantiates the importance of polyphenols and the relevance of scientific studies on this subject. Taking into account the reviews published since 2008, a general overlook on the research topics can emphasize the main current fields in which the research is presently developed. The different subjects which may be inferred are: problems in the analytical assays of polyphenols [1–5], polyphenols composition of fruits and vegetables [6–10], the fate of polyphenols in postharvest technology [11, 12], chemistry and biochemistry [13–16], polyphenols and food [17–21], polyphenols and health [22–28]. From this short survey which takes into account only partly the last years, the great number and variety of researches on these plants metabolites can be pointed out. There is a lack of reviews on the relations between polyphenols content, fertilization and agriculture practice, with the exception of a recent review on the possibility of differentiating organic practice by means of secondary plant metabolites in carrots [29], and the review of Stefanelli et al. [18] focused on horticulture quality under minimal nitrogen and water supply.

The aim of this review is concerned with the relationships between polyphenols content, fertilization and agricultural practice correlated to soil management.

Effect of nitrogen and/or potassium fertilization

As summed up by Nguyen and Niemeyer [30], the carbon/nitrogen balance (CNB) pathways can be taken into account when studying the effect of nitrogen fertilization on phenolic content. Phenylalanine is the rate-limiting precursor for phenylpropanoid synthesis (e.g., lignin, flavonoids and condensed tannins), and at the same time, it is an essential amino acid for protein synthesis. Plant growth is heavily dependent on protein synthesis for the manufacture of photosynthetic, biosynthetic and regulatory enzymes, as well as for structural protein, and phenolic synthesis

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competes with growth for common substrate. When environmental conditions are favorable, vegetative growth generally receives resource priority over secondary metabolism and storage. In resource-rich environments, growth processes receive allocation priority for resources, decreasing the relative availability of carbon for the support of secondary metabolism and structural reinforcement. The CNB hypothesis predicts that concentrations of carbon-based secondary metabolites (e.g., terpenes, phenolics and other compounds that have only C, H and O as part of their structure) will inversely correlate with nitrogen availability. On the contrary, concentrations of nitrogen-based secondary metabolites (e.g., alkaloids, nonprotein amino acids, cyanogenic compounds, proteinase inhibitors and others having N as part of their structure) are predicted to be directly correlated with nitrogen availability of the plant. As pointed out by Stefanelli et al. [18], nitrogen fertilization causes a decrease in polyphenols amount in most cases. Also interactions with other inorganic fertilizers or environmental conditions have been taken into account. Low nitrogen availability during flowering of grape bloom (*Vitis vinifera* L.) significantly enhanced the formation of phenolics, particularly flavonol glycosides at the beginning of the berry-ripening period, while the N-induced differences became smaller for all classes of phenolics at later stage of maturity [31]. In grape fruits [32] with average levels of potassium fertilization, increased nitrogen supply caused a significant decrease in the content of total polyphenols, whereas when potassium supplies were high, the treatments with a higher nitrogen level resulted in higher concentrations of these compounds. A stronger accumulation of polyphenols in the fruit of vine with no nitrogen fertilization was observed, especially during the last weeks of ripening. Leaves of apple trees (Golden delicious and Rewena) [33], sugar maple (*Acer saccharum*) seedlings [34], red basil, *Ocimum basilicum* L. [30], broccoli [35] and tomato leaves [36] exhibited a decrease in flavonoids along with nitrogen fertilization. For tomato fruits, the effect of nitrogen supply was not significant and interactions were not often observed; however, fruits harvested on plants grown with the lowest nitrogen supply tend to have the highest phenolic content [37]. Nitrogen deprivation was also able to increase flavonol accumulation in mature vegetative tissue of tomato plants [38]. In the case of artichokes, a balanced NPK fertilization involves a higher polyphenols content with respect to an excessive fertilization [39].

For tartary and normal buckwheat [40] aerial parts, no significant effect on the concentration of flavonoids between low and high levels of nitrogen could be detected. In winter grain [41], total phenolic content decreases with respect to the absence of nitrogen fertilization: When N-fertilization is applied, increasing nitrogen amount involved increased polyphenols content.

As concerns anthocyanins content, a decrease in their content or a non-correlation along with nitrogen supply was found. Specifically in the case of berries, there was no significant interaction between sampling date and N-treatment or N-fertilization effect on the total anthocyanins and anthocyanidin levels of bilberries (*Vaccinium myrtillus*) in any of the 3 years considered. A significant decrease along with N-fertilization was observed only in the case of cyaniding-3-glucoside, while for petunidin, delphinidin, malvidin and peonidin-3-glucosides, no differences were pointed out [42]. For grapevine berries [31, 43, 44] and black chokeberry [45], anthocyanins content decreased as the amount of nitrogen was increased. For vine berries, N supply decreases the anthocyanin content, changes the anthocyanin composition and favors the degradation of anthocyanins in berry skin [44]. In the molecular regulation of the anthocyanins biosynthesis, both positive (MYB transcription factor) and negative (LBD proteins) are involved [43]. The low-bush blueberry anthocyanins content was examined along 2 years with a fertilization mainly based on nitrogen, phosphorous and potassium. Lime was also added to the three levels of fertilizer. In year 2005, no significant differences were pointed out with the three fertilizers with or without lime, while in the year 2004 the fertilizer with the lowest nitrogen amount in the presence of lime gave the highest anthocyanins amount [46]. Blackberries [47] exhibited the highest anthocyanins content with high nitrogen and low potassium (66.4 kg ha^{-1}) levels. Purple-blue potatoes showed the highest anthocyanins content with the highest nitrogen fertilization (120 kg N ha^{-1}) and the lack of phosphorus and potassium fertilization [48].

Table 1 reports fertilization mode, polyphenols kinds (anthocyanins and flavonoids) and analysis methods.

Other inorganic fertilizer

The simultaneous applications of nitrogen, phosphorus and potassium increased total polyphenols content of bush tea (*Athrixia phylicoides*) only in a peculiar N, P and K combination; in all other combinations reported, no effect on polyphenols content was pointed out [49]. With commercial fertilizer containing typical macro and micronutrients, the lowest fertilization level increased the contents of flavonols and ellagic acid in strawberry (*Fragaria* × *ananassa* Duch.) [50], while P and K fertilization had little effect on red cabbage anthocyanins, and heavy fertilization negatively affects their content [51]. The same trend was reported for total phenolic content of potatoes which tends to decrease at higher mineral fertilization [52, 53]. Elemental agricultural sulfur was added to soil in order to increase the amount of glucosinolate compounds in *Brassica rapa* [54]; sulfur fertilization increased the amount of total phenols while total flavonols content was reduced by

Table 1 Fertilization characteristics and kind of polyphenols and anthocyanins analysis

Sample under investigation	Nitrogen fertilization	Polyphenols	Anthocyanins	References
Apple tree leaves	From 3.6 to 13 g N per tree and year	Separated and quantified by HPLC		33
Artichoke heads	200 and 500 kg N ha^{-1}	Folin–Ciocalteu and HPLC analysis		39
Basil	From 0.1 to 5 mM NH_4NO_3	Folin–Ciocalteu method	Spectrophotometer analysis	30
Bilberry	NH_4NO_3 from 12.5 to 50.0 kg ha^{-1} $year^{-1}$		Separated and quantified by HPLC	42
Black chokeberry	25–30 kg N ha^{-1}		TLC and spectrophotometer analysis	45
Blackberry	60 and 100 kg N ha^{-1}	Folin–Ciocalteu method	Separated and quantified by HPLC	47
Blueberry	From 0.8 to 5.6 g N, 7.2 to 8.4 g P, 0.4 to 7.2 g K per m^2		Spectrophotometer analysis	46
Broccoli	From 105 to 225 kg N ha^{-1}	UV absorption of leaf epidermis		35
Buckwheat aerial parts	From 0.30 to 160 kg N ha^{-1}	Separated and quantified by HPLC		40
Bush tea	From 300 to 400 kg N ha^{-1}	Folin–Ciocalteu method		48
Grapes	From 15 to 60 kg N ha^{-1}	Spectrophotometer analysis	Spectrophotometer analysis	31
Grapes	From 0 to 120 kg N (as NH_4NO) ha^{-1}		Separated and quantified by HPLC	43
Grapes	From 1.4 to 7.2 mM N		Spectrophotometer analysis and HPLC	44
Grapes	From 0 to 250 g N per vine and from 0 to 250 g K_2O per vine	Folin–Ciocalteu		32
Potato	From 0 to 120 kg N ha^{-1}		Separated and quantified by UPLC	48
Sugar maple leaves	Weekly spray with 0.02 M NH_4NO_3 solution	Separated and quantified by HPLC		34
Tomato	From 4 to 12 mM NO_3^- solution	Separated and quantified by HPLC		37
Tomato	From 0 to 60 mM N	Separated and quantified by HPLC		38
Wheat grain	From 0 to 300 kg ha^{-1} urea	Colorimetric and HPLC		41

sulfur fertilization on two ecotypes; phenolic acid content was significantly increased only in the case of the *Lingua di cane* ecotype. In red radish (*Raphanus sativus* L. Mantanghon) the sulfur addition involved an increase in total phenolic and a decrease in anthocyanins contents [55].

Effect of management

The effect of management (conventional, sustainable, organic or biodynamic) is not easily predictable, and the explanation of the different behaviors is not univocal or understandable on the basis of a biochemical pathway. In the comparison of management systems, a great importance should be devoted to the different yields and the experimental growing conditions. In fact, environmental conditions affect polyphenols amount and therefore when vegetables or fruits, obtained from local market and organic farms, are compared, the results should be carefully taken into account and the differences not ascribed to the only farming method [56]. Table 2 summarizes the data of fruits polyphenols content.

As concerns apple fruits [57–59], the differences between organic and conventional management, if present, do not concern all varieties and all sampling years under study; these are of minor importance with respect to differences in sampling year and in variety.

Yellow plums [60] exhibited a lower polyphenols amount in organic with respect to conventional practice, especially concerning flavonols content. In the case of Sirah grapes, higher anthocyanins content was found in the peel of conventional managed vineyards with respect to organic ones; this result was ascribed to the extraordinary hot and dry 2002 summer climate, which caused a chemical stress of conventional production over biotic stress of

Table 2 Fruits, analyzed tissue, growing location and results in the determination of polyphenols

Sample	Tissue	Growing location	Results achieved	References
Apple	Pulp mixed with skin	Neighboring organic and conventional farms	Generally higher polyphenol content in organic production	57
Apple	Flesh and skin	Different farms	No differences	58
Apple	Leaves, pulp and skin	Neighboring organic and integrated farms	Higher in organic leaves and dependent on cultivar in fruits	59
Black currant	Fruit	Different farms in a climatically similar area	No differences	69
Blueberry	Fruit	Different farms in a surrounding area	Higher in organic than in conventional	68
Grapes	Skin	Neighboring parcels	Higher in conventional than in organic	61
Grapes	Berry	Different farms	No differences among organic biodynamic and conventional	62
Marionberry	Fruit	Same farm	Higher in organic and sustainable than in conventional production	65
Orange	Fruit, edible part	Different farms	Higher in organic than in conventional	63
Orange	Fruit, juice	Different farms	Higher in conventional than in organic	64
Peach	Cortex and peel	Same orchard	Higher in organic than in conventional	67
Strawberry	Fruit	Same farm	Higher in organic and sustainable than conventional production	65
Strawberry	Fruit	Same pedoclimatic area	Higher in biodynamic than in conventional production	66
Yellow plums	Fruit	Same farm	Higher in conventional than in organic production	60

organic production [61]. Sangiovese and Pignoletto grapes, sampled in different farms, showed no differences in the polyphenols content among conventional, organic and biodynamic practice [62]. Organic red oranges [63] exhibited higher anthocyanin and polyphenol contents with respect to integrated samples; Tunisian red oranges showed no differences in total phenolic compounds, while total flavonoids were higher in conventional juices [64].

Integrated and organic marionberry (frozen, freeze-dried, air-dried) and frozen strawberry [65] exhibited the same behavior. Fresh strawberry fruits had higher pelargonidin-3-glucoside, cyaniding-3-glucoside, quercetin, kaempferol and ellagic acid contents in biodynamic with respect to conventional management. The differences were ascribed both to compost utilization in the biodynamic growing system and to the use in conventional agriculture of herbicides blocking the shikimate pathway and thus reducing the synthesis of aromatic amino acids, the starting point of the of phenolic compounds pathway [66]. Organically grown peach [67] so as organically grown blueberry [68] contained higher amounts of total polyphenols than conventionally grown fruits, while for organically grown pear [67], only two of three samples followed the same behavior; an enrichment in plant defense mechanisms against infestations, through an increase in endogenous polyphenols, could explain such behavior. The cultivation technique of black current [69] sampled in several organic and conventional farms did not affect total phenolic content.

Table 3 lists the vegetables, which were studied comparing their phenolic content under different agronomic managements. From a quick glimpse at Table 3, the large number of articles concerning tomatoes immediately comes out. Tomato polyphenols have been extensively regarded in connection with the kind of farming. A review on variations of antioxidants also in relation to the kind of cultivation [36] does not report any article on the specific issue of polyphenols variation. Total average phenolic content was slightly higher in organic agriculture in a 3-year study (1 and 7% for the two investigated cultivars) [70]. In a 2-year study, on two cultivars, no differences were pointed out [71] and on four cultivars for 3 years no differences were found apart from the behavior of one cultivar along 2 years (one case higher under organic cultivation and in the second higher under conventional cultivation) [72]. Individual phenolic compounds of the four cultivars were analyzed using HPLC–DAD–MS/MS, and 30 polyphenols were identified and quantified; the cultivation method had generally minor impact on the content of phenolic compounds with respect to growing year and cultivar. Organic tomatoes of the Redondo cultivar were richer in total phenolics and flavonoids [73]. When individual polyphenols are considered, a more complex situation is pointed out. Only rutin and naringenin contents are higher under organic management, while the content of chlorogenic acid, the most abundant component, is higher under conventional management [74]. For two cultivars along 3 years [70], quercetin

Table 3 Vegetables, analyzed tissue, growing location and results in the determination of polyphenols

Sample	Tissue	Growing location	Results achieved	References
Broccoli	Florets	Same field	No differences between organic and conventional	89
Cabbage	Internal leaves	Fields in the same location	Higher in organic than in conventional	85
Carrot	Edible part	Same farm	No differences between organic and conventional	87
Cauliflower	Edible part	Bordering fields	No differences between organic and conventional	88
Chicory	Leaves	Plots in the same field	No differences between biodynamic and conventional	90
Eggplant	Pulp	Different farms	No differences between organic and conventional	81
Eggplant	Pulp	Neighboring farms	Slight differences between organic and conventional	82
Lettuce	Leaves	Same field	Higher in biodynamic than in conventional	84
Oat	Grains	Same farm	No differences between organic and conventional	91
Onion	Edible part	Same farm	No differences between organic and conventional	87
Pepper	Fruit	Fields under same conditions	No differences between organic and conventional	70
Pepper	Green and red fruit	Different farms	No differences between organic, integrated and soilless	80
Pepper	Fruit	Near fields	Higher in organic than in conventional	78
Pepper	Fruit without seeds	Neighboring farms	Total phenolics higher in organic than in conventional	79
Potato	Edible part	Same farm	No differences between organic and conventional	87
Red beet	Roots	Blocks in the same experimental field	Higher in biodynamic than in conventional	83
Rice	Grain	Same area	No differences between organic and conventional	92
Spinach	Leaves	Different farms	Higher in organic than in conventional	86
Tomato	Fruit	Farms with similar environmental conditions	Small differences between organic and conventional	74
Tomato	Fruit	Fields under same conditions	Higher in organic than in conventional	70
Tomato	Fruits without seeds	Close farms	No differences between organic and conventional	71
Tomato	Fruit	Same farm	Dependent on year and compound	72
Tomato	Fruit	Plots in the same farm	Higher in organic than in conventional	76
Tomato	Fruit	Next greenhouses	No differences between organic and conventional	73
Tomato	Fruit, peel, pulp, seeds	Two near greenhouses	Higher in organic than in conventional	75

and kaempferol amounts are higher with organic farming than with conventional one with the exception of quercetin amount in 2005 (higher in conventional farming). For cultivar Perfectpeel [75], quercetin, in the first year of cultivation, was significantly higher in the conventional product compared to the organic one, while in the second year, an inverse trend was achieved. In the second year of cultivation, naringenin and rutin were found to be higher in organic product. A long-term study (10 years) of tomatoes in organic and conventional plots showed that quercetin, naringenin and kaempferol content was higher in tomatoes from organic plots and the differences increased along with the cultivation year. These differences were ascribed to the lesser amount of available nitrogen [76].

According to Szafirowska and Elkner [77], higher content of soluble phenols and total flavonoids in organic pepper as compared to conventional one was found. Organically grown sweet pepper showed significantly higher content of phenolics whatever the mature stage [78], and according to authors, this increase occurs as a response both to pathogenic pressure and to a lower nitrogen availability. Total phenolic content in organic hot peppers was higher than in conventional one [79]. In other cases [70, 80], no differences were pointed out.

Only one eggplant cultivar among three and in 1 year along 2 years exhibited a higher polyphenols content under organic management [81], while no differences were found from eggplant fruits harvested in different locations under conventional and organic farming [82]. Biodynamic cultivated red beets had a higher polyphenol content than conventional and integrated ones [83] so as biodynamic lettuce leaves which exhibited a higher polyphenols content than conventional and organic ones [84]. In the case of cabbage internal leaves with four samplings from November to January, only for one sampling date, conventional grown plants exhibited a higher polyphenols content, while in the three other dates the opposite occurred [85]. Of 17 flavonoids determined, the levels of 10 were higher in organic spinach compared to conventional one [86] and total flavonoids content was significantly higher in organic spinach, with the exception of only one cultivar out of the 27 examined.

For onions, potatoes and carrots, no differences were found along 2 years and three different cultivation methods (conventional and two organic systems) [87]. Only one cauliflower genotype out of 2 and one organic cultivation out of 3 exhibited a higher polyphenols content with respect to conventional management [88]. Flavonoids and polyphenols broccoli content was unaffected by production practices [89], and no differences were found between biodynamic and conventional farming systems in the case of chicory [90]. Oat [91] and rice [92] grains exhibited no differences in the polyphenols content between organic and conventional farming.

Total phenolic and flavonoid contents in peels (zucchini squash, banana, potato, eggplant, orange, lime, mango, passion fruit and radish), leaves (zucchini squash, broccoli, carrot, collard, cassava, radish and grape), stalks (broccoli, collard and spinach) and zucchini seeds were studied. The samples were achieved from local markets, and no data are reported on their actual growing conditions. In some cases (banana peel, carrot and grape leaves), higher flavonoid contents in organic than in conventionally grown vegetables were found [93].

Conclusions

The only cases in which the increase or decrease in polyphenol content may be foreseen are bound to nitrogen supply; in most cases, a decrease in polyphenols content is correlated to a higher nitrogen supply. Nitrogen supply may derive from inorganic and/or organic soil fertilization, and the decrease is theoretically predictable based on the biochemical pathway leading to polyphenols synthesis. As concerns the kind of agricultural management, the results achieved can not be univocally explained and foreseen. Polyphenols are stress metabolites. and in this connection, many factors should be taken into account in order to explain the results and no general role actually can be drawn. The research in this peculiar field seems important in the light of the production of functional and health food. Secondary metabolites, in particular polyphenols (flavonols and anthocyanosides), present in seeds, grains, cereals, nuts, fruits, vegetables, are nutraceutical ingredients that find application in dairy products, seafood and confectionery items, in non-alcoholic beverages such as energy drinks, juices, sports drinks and in food supplements.

Compliance with ethical standards

Conflict of interest None.

Compliance with ethics requirements This article does not contain any studies with human or animal subjects.

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