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An exploration into the relationship between mineral elements (nitrogen and phosphorus) and nutritional quality in soil-watermelon (*Citrullus lanatus*) system

Shan He[1], Yuyan Zhao[1,3], Chuanpeng Liu[2], Zhenghe Li[1], Zeyu Zhang[1], Bing Li[1,3] and Xiaodan Tang[1,3*]

Abstract

To fundamentally explore the correlation between crop nutritional quality and mineral elements, specific tests and accurate analysis were carried out on all organs and root soil of watermelon (*Citrullus lanatus*). The results showed that the distribution patterns of nitrogen and phosphorus at watermelon maturity were similar, and the average nitrogen and phosphorus contents were in the orders of leaf and seed > stem, peel, root > pulp > root soil, and peel > seed > root, stem, leaf > root soil > pulp, respectively. From the perspective of element geochemistry, biophile and lithophile elements had the strongest correlation with nitrogen and phosphorus, and watermelon did not antagonize soil nitrogen and phosphorus uptake. The prediction model of nitrogen translocation factor in watermelon organs to total acid was established by partial least squares with $R^2 = 0.81$. Significantly, when the isometric log-ratio of nitrogen to phosphorus in watermelon leaves was 1.97 to 2.19, the watermelon pulp showed better quality with total acid > 0.5%, total sugar > 5% and soluble solids > 10%. Therefore, the characterization of nitrogen and phosphorus in watermelon leaves can serve as a non-destructive analysis to predict watermelon fruit quality.

Keywords: Nitrogen, Phosphorus, Soil, Watermelon, Migration and accumulation, Geochemical classification of elements, Fruit quality

Introduction

In recent decades, nitrogen (N) emissions have increased sharply with the continuous intensification of human activities such as fossil fuel combustion, chemical fertilizer application and automobile exhaust emission, which has made more and more active N compounds accumulate in the atmosphere and sink into terrestrial and aquatic ecosystems (Bai et al. 2010). Human activity has also altered the global phosphorus (P) cycle. This anthropogenic eutrophication not only increases the primary productivity of ecosystems, but also alters the relative importance of nutrients in limiting productivity (Fourqurean and Zieman 2002). The research on mineral nutrition has become the main theme in ecology, agronomy and genetics (Tsige et al. 2022). N and P are the two most needed mineral nutrients in terrestrial ecosystem, which are closely related to the growth and physiological metabolism of plants (Nie et al. 2018; Dong et al. 2020). N is a component element of protein and nucleic acid in plant cells and participates in the synthesis of chlorophyll in chloroplast (Grzyb et al. 2021). P is an important component of nucleic acids and enzymes in plant cells and plays a key role in cell division, proliferation, genetic variation and other life activities (Richardson et al. 2009).

Plant growth and distribution patterns are determined by both external and internal resources. Water and nutrients in the soil and sunlight constitute external resources,

*Correspondence: tangxiaodan@jlu.edu.cn

[1] College of Geo-Exploration Science and Technology, Jilin University, Changchun 130026, China
Full list of author information is available at the end of the article

while the preferential distribution, migration and transformation of elements in different organs of plants constitute internal resources. In the process of exploring external resources, there is no doubt that soil and its components have become the key factors affecting the life process of plants. The bioconcentration factor (BCF) can be applied to reflect the ability of plants to absorb elements from the soil. Most modern soils were formed in the Quaternary period, and the Quaternary geological processes also controlled the distribution of elements in the earth's surface system (Pan 2000). Soil-forming parent material is one of the five natural factors (parent material, climate, biology, topography and time) for soil formation. Its inherent mineralogical properties and physicochemical properties have great influence on soil characteristics and fertility. As early as the mid-nineteenth century, the concept of agricultural geology was put forward to explain the relationship between rock weathering and soil formation. In natural soil, soil fertility comes from natural fertility, which depends on the chemical composition of rocks and minerals to some extent, and is released gradually through weathering. Therefore, the content of mineral elements in soil affects the abundance and deficiency of elements in the parent material-cultivated soil–plant system and improves or limits the quality of crops (Ludvik and Schernthaner 2012). In order to improve the quality and yield of crops, scholars have done a lot of research on N and P fertilizer, but rarely explored the source of N and P in natural soil.

Previous studies have mostly focused on the source, migration and transformation of heavy metals rather than mineral nutrients in rock–soil–plant system (Rastegari Mehr et al. 2020; Zhao et al. 2021; Sun et al. 2022). A comprehensive understanding of mineral nutrients is helpful for agronomy, botany and ecology to set up plant varieties and manage fertilization measures according to local conditions. The migration and transformation of mineral nutrients in soil–plant system are also an indispensable part of the internal resources of plant life activities.

With the gradual improvement of agricultural cultivation techniques and daily living standards, people's requirements for fruit quality are also constantly improving. Therefore, fruits are studied not only in quantity, but also in quality. Fruit nutritional quality is one of the most concerned problems in life, and its detection and evaluation have become a meaningful research topic. Meanwhile, watermelon, as a cash crop, is more and more favored by people. Because of its social importance, a variety of research on its fruit quality have been carried out (Ali et al. 2017). Shuanghou watermelon, well-known in China, has sweet flesh with little seeds and thin peel. It is a typical representative of watermelon varieties. During the watermelon quality analysis, the translocation factor (TF), one of the commonly used evaluation indexes, represents the mineral element enrichment ability of aboveground organs and reflects their internal vitality (Colle et al. 2009). The isometric log-ratio (ILR) method based on ion balance can not only explain nutrient concentration and balance, but also well correct the concentration deviation caused by plant physiological interaction (Geikloue et al. 2019).

To deeply investigate the relationship between nutritional quality and mineral elements in soil-watermelon system, this article analyzed the N and P concentrations in different organs and root soil of watermelon, explored the migration and enrichment modes of N and P during watermelon maturity, and elaborated the influence of rock-forming elements on N and P contents from the perspective of geochemistry.

Materials and methods

Plant and soil sample preparation

Plant and soil samples were collected from plantation of watermelon, located in Yinan, Shandong, China (35°28′ N, 118°14′ E). The watermelon variety was "Shuanghou Watermelon" also known as "Sesame Grain Tight-skinned Watermelon". The area of Shuanghou watermelon plantation was about 10 km^2, and about one watermelon was planted per m^2 at creeping cultivation. In 2021, seedling was planted in mid to late April, and fruit was harvested in late June. Based on the principles of representativeness, typicality and timeliness, typical samples were collected from representative fields. A total of 30 watermelon samples and 30 soil samples were collected, and these samples were collected by five-point sampling method from 30 representative fields almost evenly distributed in Shuanghou watermelon plantation. Marginal effects and special individuals are avoided in sampling. Plant samples were collected from whole plants at maturity, and soil samples were collected from the top layer of soil 0–20 cm near the roots of the plants. The plant was fresh and intact, free from pests, diseases and mechanical damage. The soil was all sandy loam.

The watermelon samples were washed, and their organs were separated. The organs (except pulps) were dried at 105 ℃ for 30 min and then at 60 ℃ for 24 h, cooled to room temperature (25 ℃), crushed with plant crushing machine (200 T, Huangdai, China), filtered through a 74-μm sieve, and sealed for use. Watermelon pulps were pressed into juice after removing seeds. The root–soil samples were air dried, ground with an agate mortar, screened through a 74-μm sieve, and sealed for use.

Main reagent and equipment

Sulfuric acid (H_2SO_4), nitric acid (HNO_3), perchloric acid ($HClO_4$), hydrochloric acid (HCl) and hydrofluoric acid (HF) were in guaranteed reagent grade. Copper sulfate, sodium hydroxide (NaOH), boric acid, methyl red, bromocresol green, 95% ethanol, hydrogen peroxide (H_2O_2), phenolphthalein and phenol were of analytical grade. They were all purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China. The water needed for the experiment is ultrapure deionized water with a resistivity of 18.2 MΩ·cm at 25 ℃. The national standard solution of P (GSB04-1741-2004) was 1000 μg/mL and obtained from National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials. Its required concentration gradient was obtained by stepwise dilution. The certified reference materials (CRMs) (GBW07403 and GBW10012) were acquired from the Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences (Langfang, China) and applied to verify the accuracy and precision of the experimental methods.

Determination of watermelon pulp pH

The pH of watermelon juice was measured by a calibrated pH meter (PHBJ-260, Leici, China).

Determination of N content in plant organs and soil

1 g of sample, 5 g of copper sulfate and 10 mL of H_2SO_4 were accurately added into the digestion tube, digested in a graphite furnace (KDNX-20, Leici, China) at 480 °C for 1 h, cooled to room temperature and then distilled with 400 g/L NaOH in Kjeldahl analyzer (KDN-08C, lichen, China). The distilled liquid was absorbed with 20.00 mL 20 g/L boric acid and 3 drops of mixed indicator (0.1 g methyl red and 0.5 g bromocresol green dissolved in 100 mL 95% ethanol) and titrated with 0.1 mol/L HCl to obtain the N content.

Determination of P content in plant organs and soil

0.5 g of plant (except pulp) and soil samples, a few drops of ultrapure deionized water, 5 mL H_2SO_4 and 2 mL H_2O_2 were added into digestion tubes in sequence, digested at 340 °C for 1 h, cooled, added with 10 drops of H_2O_2, simmered for 5 min, and repeated until the solution was colorless or clear.

0.5 g of pulp samples, 10 mL HNO_3, 1 mL $HClO_4$ and 2 mL H_2SO_4 were accurately added into conical flasks and digested on the electric heating plate (SB-1.8–4, Shanghai Shiyan, China) at medium temperature until the digestion solution was colorless or yellowish. After cooling, the digestion solution was added with 20 mL ultrapure deionized water and driven out acid at high temperature until its volume was about 10 mL.

The resulting solutions were used for the P content test in flow injection analyzer (FIA-6000+, Jitian, China).

Determination of total acid in watermelon pulp

25 g of watermelon pulp was accurately weighed into the conical flask, added with 40 mL ultrapure deionized water and 0.2 mL 1% phenolphthalein indicator, and titrated with 0.1 mol/L NaOH to obtain the total acid content.

Determination of total sugar in watermelon pulp

1 g of watermelon juice, 25 mL water and 10 mL HCl were added into a conical flask, shaken well, hydrolyzed in boiling water bath for 1 h, cooled to room temperature and filtered through a 0.45 μm membrane. The resulting solution was added with 1 mL phenol solution and 5 mL H_2SO_4, left for 10 min, shaken well, and cooled to determine the total sugar content by ultraviolet–visible spectrometer (T6, Persee, China).

Determination of soluble solid in watermelon pulp

The soluble solid of watermelon juice was measured by a calibrated Abbe refractometer (SW-32D, Suwei, China).

Determination of major and trace element content in soil

4 g of soil sample was made into round cake under the pressure of 30 MPa for the determination of Al/Ca/Fe/K/Mg/Na/Si/Sr/Ti content by X-ray fluorescence spectrometer (EDX6000B, Skyray, China).

0.25 g of soil sample, 10 mL aqua regia (V_{HCl}: V_{HNO3} = 3: 1) and 2.5 mL HF were accurately added into the Teflon digestion tube, shaken well, heated to 125 °C for 2 h, cooled, fixed volume to 50 mL with ultrapure deionized water, and left overnight for the B content test by inductively coupled plasma mass spectrometry (NexION350D, PerkinElmer, America).

0.2 g of soil sample and 2 g of NaOH were accurately weighed into a nickel crucible, covered, heated to 570 °C for 20 min, cooled, dissolved with boiling hot water, transferred into a 100 mL volumetric flask, slowly added 5 mL 50% HCl, diluted with ultrapure deionized water to the mark, shaken well, and left for the F content test by the ion meter (PXSJ-216F, Leici, China).

Bioconcentration factor (BCF)

BCF (Kelsey et al. 2006) refers to the ratio of element content in plants to the corresponding content in growing soil, and it is one of the specific manifestations of the element enrichment ability in plants. The formula is as follows:

$$\mathrm{BCF} = C_{\mathrm{R}}/C_{\mathrm{S}} \quad (1)$$

where C_R and C_S are the contents of an element in root and root soil, respectively.

Translocation factor (TF)

TF (Kumar et al. 2018) refers to the ability of the above-ground parts of plants to accumulate elements, which can be served for evaluating the capacity of plant organs such as stems and leaves to absorb and transfer elements through roots. The formula is as follows:

$$\mathrm{TF} = C_{\mathrm{AP}}/C_{\mathrm{R}} \quad (2)$$

where C_{AP} and C_R are separately the contents of an element in the above-ground part (stem, leaf, peel, seed or pulp) and root of the plants.

Isometric log-ratio (ILR)

ILR (Parent 2011), an analysis method based on ionic equilibrium, fully considers the interaction between mineral ions since the interactions among plant ions are projected into a Euclidean space (Parent et al. 2013). It is accepted to be the most suitable description way for plant ionomics data at present. The ILR was computed as follows:

$$\mathrm{ILR}_{[\mathrm{N}|\mathrm{P}]} = \left(\frac{1}{2}\right)^{\frac{1}{2}} \mathrm{Ln}\frac{g(C_{\mathrm{N}})}{g(C_{\mathrm{P}})} \quad (3)$$

where $g(C_N)$ and $g(C_P)$, respectively, represent the content of N and P.

Statistical analysis

The experimental data were analyzed and plotted by analysis of variance and regression using Excel and Origin. The clustering and correlation analysis and the partial least squares regression prediction were achieved by MATLAB. The coefficient of variation was mostly less than 1%. If the variation of element content exceeded 5%, an identical run would be undertaken, and closer data points were used. All mean values are the averages of three independent samples. It should be noted that both N and P contents obtained from the tests in this article were total N and total P contents, respectively. Blank and parallel controls were set in experiment.

Results and discussion

Validation of analytical methods

According to the requirements of the geological and mineral industry standard DZ/T0011-2015 of the People's Republic of China, the CRMs GBW07403 and GBW10012 were analyzed five times, and the logarithmic deviation (ΔlgC) and relative standard deviation (RSD) values between the measured mean value and the standard value of each element were computed and the results are listed in Additional file 1: Table S1. The ΔlgC and RSD values of the two CRMs were all smaller than the standard monitoring limits (ΔlgC and RSD $\leq$7%), and the detection limits (DLs), estimated as three times standard deviation of the blank solution, were, respectively, 0.067 and 0.006 mg/g for N and P. These indicated that the accuracy, precision and detection abilities of above experimental methods could satisfy the requirement of analysis test.

Accumulation of N *and* P *in crop organs*

The N and P contents in root soils and various organs of watermelon were measured and are shown in Additional file 1: Table S2. The N and P contents were not significantly different between the 30 samples, indicating that there were no exceptional samples.

In different growth stages of crop, the accumulation of N varied greatly (Zhao et al. 2012). The N enrichment in different crop organs at maturity was also significantly different (Ookawa et al. 2003). The comparison result of N content in various organs of watermelon at mature stage is shown in Fig. 1a. Among watermelon organs, the N enrichment in seed was the highest, which was 30.35 ± 2.64 mg/g (mean $\pm$ standard deviation, the same below) and the lowest in pulp was 13.70 ± 4.54 mg/g. The order of average N accumulation was leaf and seed > stem, peel and root > pulp > root soil.

In general, the N accumulation in the watermelon leaf and seed was almost twice as much as that in the pulp. N is the main constituent of protein and chlorophyll (Hikosaka 2016). In order to meet the needs of photosynthesis, leaves contain a large amount of chlorophyll and protein, and therefore, the N content in leaves is relatively high (Evans and Clarke 2019). During the different developmental stages of watermelon, the growth of organs is uneven. The growth center is the organ that develops first and has the greatest demand for organic material at different stages of watermelon development. Watermelon seeds are reproductive organs with high protein content and the growth center after fruit maturity, thus leading to a large accumulation of N in the seeds. In addition, watermelon peel contains high levels of protein amino acid, citrulline and minerals, which makes its N content relatively high as well. The low N accumulation in the pulp is mainly due to the degradation of protein after maturity, and N is transferred to the seed for storage (Bancal 2009). However, it should be noted that N redistribution occurs in crops at any time, which is usually related to the growth center of crop (Millard and Grelet 2010; Sanchez-Bragado et al. 2017).

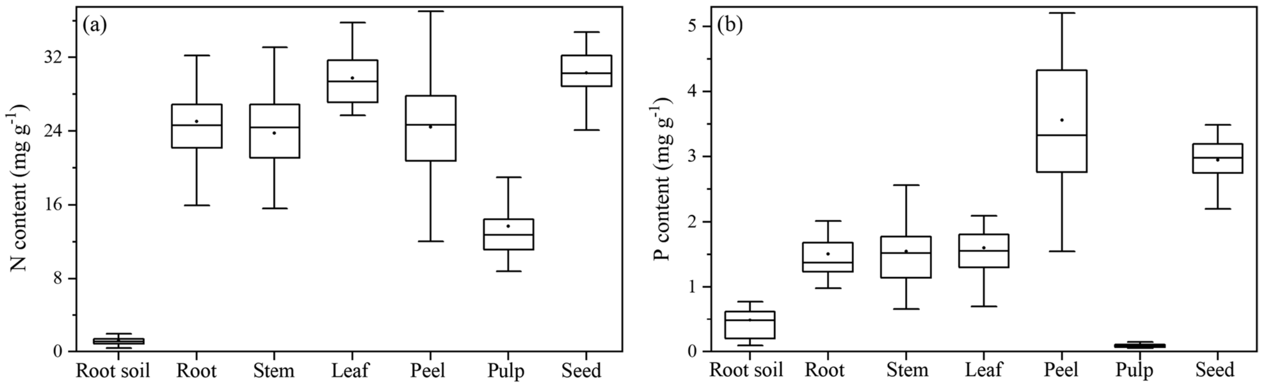

Fig. 1 Comparison of N **a** and P **b** accumulation in root soil and various organs of watermelon

Similarly, at mature stage, in different organs, the P enrichment varied greatly. The comparison result of P accumulation in various organs of watermelon at mature stage is presented in Fig. 1b. In watermelon, the highest accumulation of P was 3.56 ± 1.17 mg/g in the peel, and the lowest one was 0.09 ± 0.02 mg/g in the pulp. The order of average P accumulation was peel > seed > root, stem, leaf > root soil > pulp.

The P enrichment in the watermelon pulp was the lowest, but that in peel was the highest. Peel plays an important role in plant stress tolerance, and P has a positive impact on this function (Rajsz et al. 2016; Chen et al. 2018); hence, P was relatively enriched in the peel. The low P accumulation in pulp was still due to the transfer of P from pulp to seed after ripening to meet the seed's demand for mineral elements. The P enrichment of each organ varies due to the different growth centers of plants at each developmental stage. When mineral nutrients migrate in organs, they follow the law of preferential distribution (Ding et al. 2020). Generally, before maturity, stems, leaves and the other organs are the growth center with high P accumulation. After maturity, some of the P in various vegetative organs will migrate to seeds. On the whole, the P enrichment in leaves is higher than that in pulp, which is consistent with the analysis results of various litters (Zhang et al. 2018).

Geochemical analysis of N and P elements in soil

In plants, the migration patterns of N and P in mature crops are similar, while the demand for N and P in plant growth is obtained from the soil through the root of plants. The BCF of watermelon is the direct expression of N and P enrichment ability of the root to soil. The BCF values of N and P were calculated by Eq. (1) and are listed in Additional file 1: Table S3. The means of BCF for N and P were 24.92% and 4.82%, respectively. Therefore,

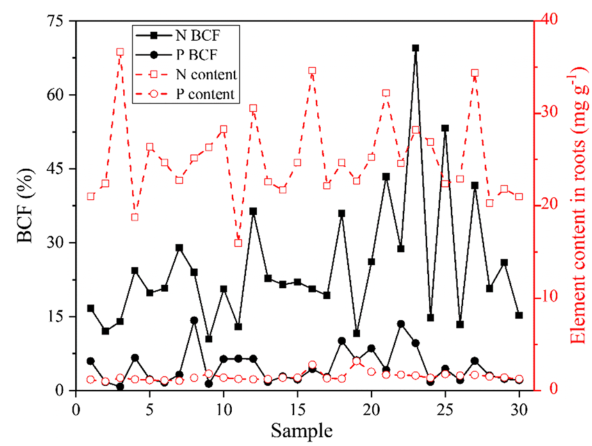

Fig. 2 Trends of bioconcentration factor (BCF) and element content in roots

the enrichment capacity of N in watermelon root was stronger than that of P.

In Fig. 2, the trends of BCF values for N and P were displayed together with those of N and P contents in roots. It was found that the BCF trend of N and P in samples was similar, in spite of the evident distinction of N and P contents in root. This suggested that the ability of each plant to obtain various mineral elements was similar and would not be significantly different due to the diversity of mineral element contents in soil or root. The similar enrichment degree of N and P in the plants revealed that the absorption of N and P in watermelon plants did not repel each other. In other words, there was no antagonistic in roots on the assimilation of N and P.

It is an indisputable fact that the elemental composition of soil is inherited from parent material and is largely influenced by it (Chaplot 2013). In addition to human activities, N and P in soil are also affected by rocks and minerals. Thus, the contents of rock-forming elements

Table 1 Pearson correlation between N, P and rock-forming elements in root soil ($n=30$)

Element	Al	Ca	Fe	K	Mg	Na	Si	Sr	Ti	B	F
N	0.26	0.16	0.06	0.24	0.03	0.36*	0.25	0.26	0.17	0.74**	0.34
P	0.47**	0.48**	0.45*	0.45*	0.30	0.58**	0.35	0.35	0.48**	0.86**	0.53**

*Significant correlation at 0.05 level (both sides)

**Significant correlation at 0.01 level (both sides)

Table 2 Geochemical classification results of elements

Classification	N	P	Al	Ca	Fe	K	Na	Ti	B	F
Siderophile		√			√					
Lithophile		√	√	√		√	√	√	√	√
Sulfophilic				√	√					
Atmophile	√									
Biophile	√	√	√	√	√	√	√		√	√

in root–soil samples were tested and are shown in Additional file 1: Table S4. Correlation test was conducted on N, P and rock-forming elements in watermelon root soil and is listed in Table 1.

Pearson correlation result showed that in root soil, there was correlation between Na, B and N, and between Al, Ca, Fe, K, Na, Ti, B, F and P. In the geochemical system, the elemental affinities are subject to the minimum energy law of the system. Under endogenous conditions, the elements with correlation are classified in Table 2, according to Goldschmidt's element geochemical classification.

N is an atmophile element. P is a siderophile and lithophile element. The elemental geochemical classification can reflect the distribution pattern of chemical elements in nature, and the characteristics of symbiotic combination of elements with each other. Ideally, elements with strong correlation with N should also belong to atmophile and biophile elements, and similarly, elements with strong correlation with P belong to siderophile, lithophile and biophile elements. In Table 2, most of the elements belonged to biophile elements, while no other elements except N belonged to atmophile; other elements related to P, such as Al, Ca, and K, belonged to lithophile elements, thus theoretically explaining that there were fewer elements related to N and more elements related to P. N and P in soil were partially derived from mineral decomposition. The soil-forming minerals were mainly gneiss, granite, diorite, quartz, feldspar, biotite, pyroxene, hornblende, kaolinite, limonite, calcite and dolomite in the study area. The mineral sources of N and P in root soil were remarkably different. There was almost no nitrogen in the above minerals, except for a small amount of fixed N (ammonium ions entering silicate minerals in isomorphism), while granite, gneiss, diorite, kaolinite, limonite, etc., all contained P, hence supporting again the correlation of N and P with other elements from a practical point. This may also provide some explanation for the correlation between elements under supergene condition. Since the mineral (biotite, kaolinite, quartz, feldspar, etc.) decomposition was also one of the main sources of B in soil, N in root soil was significantly correlated with B, and P was also highly correlated with B. In the endogenic products, the existing states of B, N and P have obvious specificity, they belong to the elements of salt acid radical, and this affinity is easy to appear in the state of salt mineral. Adding N (Kaundal et al. 2014) and P (Muhlbachova et al. 2017) fertilizer to the soil will reduce its B content, but the B content of soil itself largely depended on the physical and chemical properties of soil (Tkaczyk et al. 2017). Soil physical and chemical properties can be divided into two categories: nutrient indexes (related to N, P and K) and environmental indexes (related to pH, bulk density and cation exchange capacity). Therefore, there was a certain degree of correlation between N, P and B in soil-watermelon system. It was worth noting that P content also had a significant correlation with Ti content in the Pearson correlation of Table 1. Although Ti is not an essential element for crop growth, it is a beneficial element and plays an important role in growth and metabolism. Zahra et al. (2017) proved through experiments that the application of nano-TiO_2 in soil had a significant effect on P, that is, it could qualitatively increase P contents in crop roots, stems, and seeds.

The pedigree diagrams of N, P and rock-forming elements in watermelon root soil by cluster analysis (within groups, Euclidean distance) are shown in Fig. 3. When $d=20$, the clustering analysis was divided into three

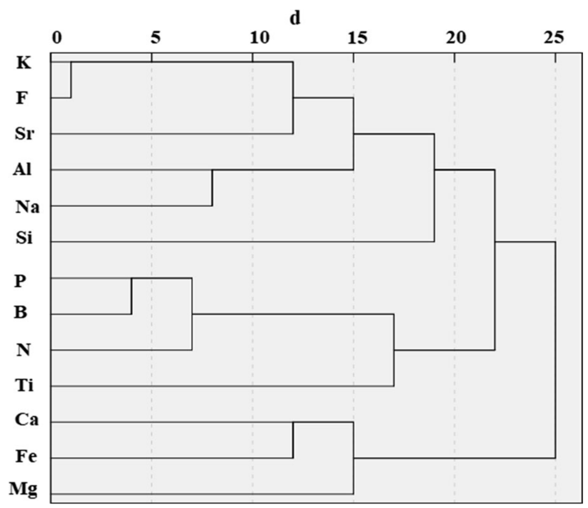

Fig. 3 Cluster analysis pedigree diagram of N, P and rock-forming elements in watermelon root soil

categories, ① K, F, Sr, Al, Na, Si; ② N, P, B, Ti; ③ Ca, Fe, Mg. With reference to the basic geological survey results, the bedrock types in the study area were mainly acidic rocks such as Cenozoic granitic gneiss, Mesozoic granite and diorite, whose rock-forming minerals are mainly quartz SiO_2, feldspar $(K,Ca,Na)[AlSi_3O_8]$, biotite $K(Mg,Fe)_3[Si_3AlO_{10}](OH,F)_2$, pyroxene $(Ca,Na)(Mg,Fe,Al,Ti)_2[(Si,Al)_2O_6]$ and hornblende $(Ca,Na)_{2-3}(Mg,Fe,Al)_5[Si_6(Si,Al)_2O_{22}](OH,F)_2$. After the weathering of these primary minerals, secondary minerals such as kaolinite $Al_4(Si_4O_{10})(OH)_8$, limonite $FeO(OH)\cdot nH_2O$, calcite $CaCO_3$ and dolomite $CaMg(CO_3)_2$ were formed. All of the above primary and secondary minerals were retained in the soil and formed soil minerals. Therefore, the three types representing the light mineral rock-forming elements, N and P nutrient elements, and dark mineral rock-forming elements obtained by cluster analysis corresponded well with the geological conditions of the study area. When $d = 25$, watermelon soils were divided into two groups. N, P and light-colored mineral elements were consolidated into one group. According to the chemical formula of these minerals, primary mineral orthoclase, albite, muscovite and quartz do not contain dark mineral-forming elements. During the magmatic activity under the endogenous conditions, these four minerals can exist in the granite at the same time. While in supergene environment, Na, K, Si and Al in the light-colored mineral-forming elements are alkali metal elements, which are the most abundant in shale and argillaceous rock and the least abundant in carbonate rock. Ca, Mg, and Sr in the dark mineral-forming elements are alkaline earth metal elements, with the highest content in carbonate and the lowest content in sandstone.

In the cluster analysis, N and P were classified into the same category with the light mineral rock-forming elements, which suggested that there was a certain relationship between N, P and rock-forming elements. Since the soils in different areas had experienced their own soil-forming process, the category of N and P might also be caused by the soil-forming process in different areas. Therefore, the classification of mineral nutrient elements could explain the source of soil parent material.

Influence of mineral elements on nutritional quality

N and P are essential mineral nutrients in plants. They can increase crop yield, improve the quality of agricultural products, and increase sugar content in crops. Thus, the effects of N and P on fruit quality parameters should be further explored after finding out the accumulation of N and P in various organs of crops at maturity. Two methods including correlation and regression analysis were used to study the connection of them.

Fruit quality parameters include external quality (such as color and size) and internal quality (such as soluble solid, total sugar and total acid) (Ali et al. 2017). The internal quality parameters concerned in watermelon are shown in Additional file 1: Table S5. In order to explore the internal relationship between nutritional quality and N and P accumulation in each organ of watermelon, the correlation test was conducted on, and no significant correlation was found. However, there was a certain correlation between TF (Additional file 1: Table S6) and total acid, and their Pearson correlation results are listed in Table 3.

The total acid in watermelon had a certain correlation with the TF of N, but had no significant correlation with

Table 3 Pearson correlation between total acid and watermelon organs' translocation factor ($n = 30$)

Watermelon	TF (root-stem)		TF (root-leaf)		TF (root-peel)		TF (root-seed)		TF (root-pulp)	
	N	P	N	P	N	P	N	P	N	P
Total acid	0.09	− 0.25	0.39*	0.20	0.41*	0.08	0.35	0.01	0.51**	0.06

*Significant correlation at 0.05 level (both sides)

** Significant correlation at 0.01 level (both sides)

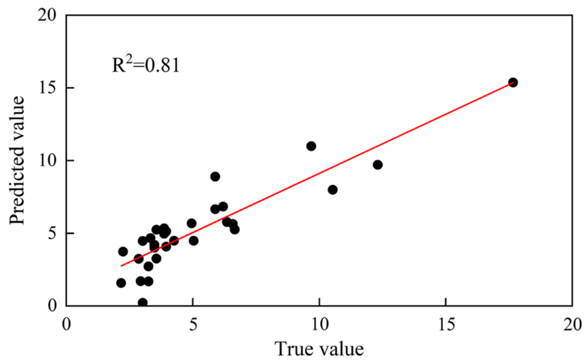

Fig. 4 Partial least squares regression prediction results for total acid

that of P. Especially, it was significantly correlated with the TF of N from root to leaf, peel and pulp. Since each stage of plant development has its own nutritional and environmental requirements, growth and nutrient allocation occur in individual genetic variations throughout the plant life cycle. In the mature stage of watermelon, the seed is the growth center, so the N compounds in stems, leaves, peels and pulps will be partially decomposed and transferred to the seeds. At the same time, due to the preferential distribution under regulation, the mineral nutrients absorbed by each organ from the root will also migrate during the mature stage. Therefore, Pearson correlation results in Table 3 suggested that N migration from root to leaf, peel and pulp might cause the change of total acid quality in watermelon.

In order to gain a clearer relationship between total acid and the TF of N, partial least squares method was applied to predict the total acid. The basic principle of this method was to extract the principal components (several comprehensive variables with the best explanatory power to both the independent variables TF values, pH and the dependent variable total acid) from the independent variable system consisting of pH and TF values of N from root to leaf, peel and pulp, establish the regression equation of total acid to the principal components and then restore the above equation to the partial least squares regression equation of total acid to pH and TF values of N from root to leaf, peel and pulp. In this article, the measured values of pH in Additional file 1: Table S5 and TF values of N from root to leaf, peel and pulp of watermelon in Additional file 1: Table S6 were set as predictive variables, the measured values of total acid (Additional file 1: Table S5) at corresponding points were set as response values, the calculation of partial least squares regression equation was realized by invoking "plsregress" function in MATLAB software, and the prediction results are shown in Fig. 4. The partial least squares regression equation of total acid and the TF of N from root to leaf, peel and pulp was as follows:

$$\text{Total acid} = 43.14 - 0.32 \times TF_{N(\text{root - leaf})} + 2.49 \times TF_{N(\text{root - peel})} + 2.64 \times TF_{N(\text{root - pulp})} - 7.36 \times \text{pH} \quad (4)$$

The coefficient of regression equation indicated the specific degree of each component's influence on the total acid. The order was as follows: pulp > peel > leaf. This was consistent with Pearson correlation results of Table 3.

In the diagnosis of crop nutrition problems, element ratio was a good calculation method and has been widely employed. The Ca to Mg ratio ([Ca|Mg]) reflects geographical location and soil minerals in agroecosystem, and the N to P ratio ([N|P]) reflects the balance between two basic life processes (synthesis of protein and r-RNA) (Loladze and Elser 2011). In other words, [Ca|Mg] is related to the external factors acting on plant growth, such as soil composition and geological characteristics, while [N|P] reflects the internal cause of nutrient balance in plants.

In view of the internal reason [N|P], many research directions have been carried out. The characteristics of N and P content in leaves are particularly important when exploring crop quality. Determination of the foliar [N|P] has been suggested as a method to assess the nutrient requirements for plant growth. Marchand et al. (2013) utilized the ILR to analyze the nutritional characteristics of crops in the study of cranberry and achieved remarkable effects; hence, the ILR was also used here to explore the crop nutritional quality. The $ILR_{[N|P]}$ of watermelon leaves computed by Eq. (3) was 2.08 ± 0.21 (ranged from 1.64 to 2.86), and its correlation with crop nutritional quality (total sugar, soluble solids and total acid) is presented in Fig. 5.

The correlation trends of $ILR_{[N|P]}$ in watermelon leaves to soluble solids and total sugars were the same because the soluble solids were related to sugar content. Particularly, 85% of the soluble solids in watermelon were total sugar (Macgillivray 1947). The soluble solid content was also related to the fruit viscosity. With the increase in soluble solid content, the fruit viscosity would also increase (Fukai and Matsuzawa 1999). Moreover, the soluble solid and total sugar contents of watermelon with pulp browning and softening disorder were lower than those of normal watermelon. The soluble solid content of most delicious fruits is more than 10% (Choudhary et al. 2012). In Fig. 5a, when the leaf $ILR_{[N|P]}$ was less than 2.19, the soluble solid content of watermelon was more than 10%. The higher the soluble solid content, the better the taste. If the total sugar was more than 5%, the taste will be

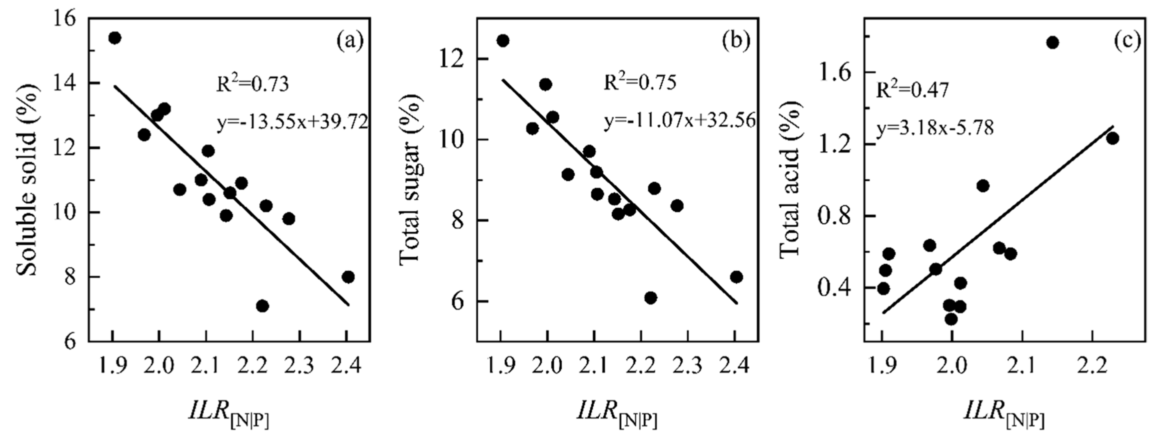

Fig. 5 Correlation between leaf isometric log-ratio of N to P ($ILR_{[N|P]}$) and soluble solid (**a**), total sugar (**b**), total acid (**c**) ($P < 0.05$)

more delicious. Based on Fig. 5b, when leaf $ILR_{[N|P]}$ was less than 2.48, the total sugar of watermelon was more than 5%. Total acids include inorganic acids and organic acids, organic acids have important nutritional value for the human body, malic acid with natural flavor is beneficial to the absorption of amino acids, while citric acid can increase appetite and promote the absorption of Ca and P. Usually, the total acid content above 0.5% makes the fruit taste better (Gao et al. 2018). In light of Fig. 5c, when leaf $ILR_{[N|P]}$ was greater than 1.97, the total acid of watermelon was more than 0.5%. In general, watermelons with a leaf $ILR_{[N|P]}$ of 1.97 to 2.19 have suitable acid and sweet flavor, just as 50% of Shuanghou watermelons in this experiment. The method of predicting fruit quality by leaf ILR characteristics was non-destructive to fruit. There are also other non-destructive techniques for watermelon quality assessment, such as dielectric spectroscopy, laser Doppler vibrometry and magnetic resonance imaging, but they have the disadvantages of complex mathematical modeling, cumbersome instrument adjustment and expensive equipment costs (Ali et al. 2017). While leaf ILR analysis is technically simple and low cost. Therefore, the internal quality prediction by leaf N and P data is believed to be another idea for future non-destructive analysis of watermelon quality.

Conclusions

In this study, the migration and enrichment characteristics of N and P in various organs of watermelon were clarified by testing the collected watermelon and its root–soil samples. The influence of rock-forming elements on N and P content was discussed by means of geochemistry. The internal correlation between fruit quality parameters and N, P of watermelon was quantified on the basis of N and P distribution.

The migration and accumulation patterns of N and P in mature watermelon were similar. The seed was the growth center of this period, so part of the mineral elements in each organ was transferred to seeds for storage. Since photosynthetic leaves required protein and chlorophyll which were synthesized by much N, there was abundant N accumulation in leaves. The special physiological function of P made it rich in the peel. The order of average N accumulation was leaf and seed > stem, peel and root > pulp > root soil, while that of average P accumulation was peel > seed > root, stem, leaf > root soil > pulp.

The BCF results demonstrated that there was no antagonistic but synergetic effect on the uptake of N and P by watermelon plants. From the geochemical point of view, biophile elements, lithophile elements and mineral elements were the most correlated.

N migration from roots to organs in watermelon would limit the total acid quality of pulp, and the TF of N from root to leaf, peel and pulp could predict the total acid content of pulp accurately together with the pulp's pH. Moreover, the contents of total acid, total sugar and soluble solid were the best when the $ILR_{[N|P]}$ of watermelon leaves was 1.97–2.19.

In conclusion, there was indeed an internal correlation between mineral elements and fruit nutritional quality. This study only took watermelon as an example to confirm the correlation between some nutritional quality parameters and the distribution of N and P accumulation in watermelon, and the indicating effect of mineral elements on the comprehensive nutritional quality of crops should be further investigated in future.

Abbreviations

N: Nitrogen; P: Phosphorus; BCF: Bioconcentration factor; TF: Translocation factor; ILR: Isometric log-ratio; H_2SO_4: Sulfuric acid; HNO_3: Nitric acid; $HClO_4$: Perchloric acid; HCl: Hydrochloric acid; CRMs: Certified reference materials; ΔlgC: Logarithmic deviation; RSD: Relative standard deviation; DLs: Detection limits.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40543-022-00357-y.

Additional file 1. Table S1 Measurement results of certified reference materials GBW07403 and GBW10012. **Table S2** Accumulation of N and P in root soils and various organs of watermelon. **Table S3** Bioconcentration factor (BCF) of N and P for watermelon. **Table S4** Content of rock-forming elements in watermelon root soil. **Table S5** Quality parameters of watermelon. **Table S6** Translocation factor (TF) of N and P from roots to organs in watermelon

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Not applicable.

Author contributions

TXD and ZYY designed the experiments. HS, LB and LZH performed the experiments. HS, LCP and ZZY carried out the collection, analysis, and interpretation of data. HS and ZYY wrote the manuscript. TXD helped to draft and revise the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets supporting the conclusions of this article are included within the article and its supplementary information files.

Declarations

Competing interests

The authors declare that they have no competing interests.

Author details

[1]College of Geo-Exploration Science and Technology, Jilin University, Changchun 130026, China. [2]The 7th Institute of Geology and Mineral Exploration of Shandong Province, Linyi 276006, China. [3]Institute for Black Soils, Jilin University, Changchun 130026, China.

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