Accelerated Phosphorus Accumulation and Acidification of Soils Under Plastic Greenhouse Condition in Four Representative Organic Vegetable Cultivation Sites

Yanling Wang[a,b,c*], Hailin Zhang[d], Jianwu Tang[c], Jiangbing Xu[a,b], Taiji Kou[e], Hongmei Huang[f]

[a] International Center for Ecology, Meteorology & Environment, School of Applied Meteorology, Nanjing University of Information Science and Technology, Nanjing 210044, China

[b] State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Science, Nanjing 210008, China

[c] Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA 02543, USA

[d] Dept. of Plant and Soil Sciences, Oklahoma State University, Stillwater, OK 74078, USA

[e] College of Agriculture, Henan University of Science and Technology, Luoyang, 471003, China

[f] Crop Cultivation Guidance Station, Lishui County, Nanjing 211200, China

[*]**Corresponding author:** Yanling Wang, International Center for Ecology, Meteorology & Environment, School of Applied Meteorology, Nanjing University of Information Science and Technology, Nanjing 210044, China. Email: wangyl2117@hotmail.com; Phone number: +86 25 5873 1543 (O), 13512513723(M)

ABASTACT

Organic vegetable cultivation under plastic greenhouse conditions is expanding rapidly in the suburb of big cities in China due to the increasing demand for organic, out-of-season green vegetables and the sustainable development of agriculture. Phosphorus (P) is not only an important plant nutrient, but also a major contaminant in the water environment. However, information on the accumulation and distribution of P in organic vegetable soils under plastic greenhouse conditions is limited, relative to the open cultivation systems. Therefore, twenty-six plastic greenhouse vegetable soils (PGVS) were selected randomly from four representative organic vegetable cultivation sites located in the suburb of Nanjing, China. For comparison, 15 open vegetable soils (OVS) near the PGVS with similar soil and cultivation practices were selected. Soil pH, organic matter (OM) and the various P accumulation characteristics were investigated. We found that soil pH in PGVS were significantly decreased by 0.57~1.17 unit with obvious signs of acidification, compared with that in OVS. Soil OM was different for different sampling locations, but in general it was higher in PGVS than OVS. Soil total P (TP), inorganic P (P_i) and Olsen-P of PGVS were higher than those in the OVS. Olsen-P of all soil samples were far above the recommended optimum value of 20 mg kg^{-1} for field crops, and over 60% soil samples were considered excessive (>150 mg kg^{-1}) in the PGVS and OVS. There were significant correlations between total P, available P and soil pH in those vegetable soils. Al-P/Fe-P ratio was also significantly correlated with vegetable soil pH ($Y_{pH} = 7.44 - 1.32 X_{Al-P/Fe-P}$, r = - 0.705, $p < 0.01$). Soil total P_i was negatively correlated with soil pH in vegetable soils (r = -0.328, $p < 0.05$), but the interactive effect of soil various P_i and soil pH need to be further investigated through a series of controlled tests. Our results suggest that the rapid P accumulation and acidification make the current plastic greenhouse vegetable production in the study area unsustainable and better organic manure management practices need to be implemented to sustain crop yields while minimizing the impact of vegetable production on the environment.

Key words: Phosphorus accumulation, soil acidification, organic farming, vegetable soils, plastic greenhouse

1. Introduction

With the rapid urbanization, greenhouse vegetable cultivation systems in the suburban area of big cities have been expanding rapidly in order to meet the demand of increased vegetable consumption (Chang et al., 2013). Two types of vegetable production systems are typically used:

one is to utilize cover (glass or plastic sheet) to extend growing season and the other is the ordinary open field system. Unlike the open field vegetable production systems, greenhouse vegetable cultivation systems have special climate conditions and management practices, such as higher temperature in cooler seasons, higher fertilizer inputs, and higher vegetable yields and cropping indexes (Chang et al., 2011; Yang et al., 2011). Therefore, negative outcomes such as soil acidification, accumulation of nutrients, salts and heavy metals in soils, and even declined production in greenhouses are widespread. In addition, groundwater pollution by nitrate and surface water entrophication as the result of this intensive greenhouse cultivation practice has been widely reported (e.g. Hu et al., 2012). Mineral fertilizers, especially phosphate fertilizers, or organic P, such as that from animal wastes or compost, are often excessively applied to greenhouse vegetable soils due to lack of phosphorus (P) information in many parts of the world, resulting in about 70-90% of P in soils that are transformed into fixed forms unavailable to plants (Wang et al., 2011). Typically, the crop only uses 10-25% of the applied P in the year of application, and P accumulation occurs in the soil as the production continues (Miao et al., 2011). The non-point source contribution to water quality degradation has worsened due to the buildup of soil P after long-term over application or inefficient use of P from mineral fertilizers and/or animal manures (McDowell et al., 2000; Yan et al., 2013; Sims et al., 2013). Meanwhile, water-soluble or particulate P can be lost through runoff and erosion. As a result, most vegetable fields and other croplands in China are high or excessive in soil test P (Miao et al., 2011), which may become a source of water contamination if better management strategies are not implemented.

In recent years, organic cultivation systems and green-organic vegetables have been developed and become more popular among consumers concerned with the potential impact of modern agriculture on environmental quality and human health. It is generally accepted that organic production is more environmentally-friendly than conventional practices if managed properly, because organic agriculture is considered as “a holistic production management system which promotes and enhances agro-ecosystem health, including biodiversity, biological cycles, and soil biological activity (Knight and Newman, 2013)”. While the origins of modern organic agriculture can be traced to an environmentally oriented social movement, the recent growth in the market share can be best explained by the rising consumer demand for products perceived as being healthier and tastier (Hughner et al., 2007; Lotter 2003). However, large quantities of farmyard manure or compost have been generally used as a main nutrient source as a complete substitute for chemical fertilizers in most of so-called organic vegetable production systems. Long-term repeated applications of manure based on vegetable N requirement can lead to build-up of P and other nutrients in vegetable soils with high crop indexes and therefore result in high risk of P losses to the environment (Zhao et al., 2013; Yan et al., 2013). Generally, farmyard manure is applied as a soil amendment without taking into account crop nutrient requirement based on yield goals and soil residual nutrients in most vegetable cultivation systems in China, which has resulted in low nutrient use efficiencies but high N and P losses (Zhang et al., 2005). According to a nation-wide analysis, only 18% of the P applied to soils could be captured in food for consumption in the year of application (Wang et al., 2011). Meanwhile, the vegetable soils have become one of the major sources of water pollution due to the buildup of N, P and heavy metals in soils (Yan et al., 2013). Therefore, accumulation of P in organic vegetable soils, especially under plastic greenhouse cultivation conditions, along with other negative effects due to the excessive use of farmyard manures in organic vegetable cultivation systems should be concerned and further evaluated.

In this study, 41 topsoil samples were collected from the plastic greenhouse vegetable soils (PGVS) and open vegetable soils (OVS) in four representative organic vegetable cultivation bases with similar fertilizer application history. The objectives were to investigate (1) the accumulation characteristics of soil total P (STP), various inorganic P (P_i) fractions and Olsen-P in PGVS, compared with those in OVS; (2) the differences of soil pH and organic matter (OM) changes in PGVS and OVS; and (3) the relationship between soil pH, N level and P accumulation in all vegetable soils.

2. Materials and methods

2.1 Brief introduction of the organic vegetable cultivation sites

Twenty-six plastic greenhouse vegetable soils (PGVS) were selected randomly from four organic vegetable cultivation sites located in the suburb of Nanjing, China. For comparison, 15 open vegetable soils (OVS) were also selected in similar soils near the PGVS studied. The soil of the selected sites was classified as Yellow Horse Liver soil developed from the Xia-shu loess. The study area has the north subtropical monsoon climate with an annual mean temperature and precipitation of 15.7℃ and 1072.9 mm, respectively. The four sites mainly produced leafy vegetables, such as spinach (*Spinacia oleracea*), lettuce (*var. crispa*), celtuce (*var. angustana*), cabbage (*Brassica oleracea var. capitata*), Chinese celery (*Apium graveolens*), rape (*Brassica campestris* L.), etc. Brief descriptions of the four organic vegetable cultivation sites (Site 1 to 4) are as below:

Site 1 (S1) was established in 2006 and located at Bamboo Town, Liuhe District (N32°27'32.8", E118°34'31.6"). This site is a typical modern circular agricultural production base, and it has about 150 hectares of organic vegetable cultivation area. Composted pig, sheep and chicken manures were the main source of nutrients to fertilize the vegetable crops. Three samples from the open vegetable soils (OVS) and five samples from the plastic greenhouse vegetable soils (PGVS) with 3 cropping years were collected for the study. Composted pig manure (about 20,000 kg ha^{-1}) was uniformly broadcasted and incorporated into the topsoils before rape (*Brassica campestris* L.) cultivation every year.

Site 2 (S2) was located at Honglan Town, Lishui District (N31°38'01.7", E119°11'00.7"). This site has about 320 hectares organic vegetable planting area, and uses organic fertilizers according to the national standards of organic or green vegetable production systems. Three OVS and 10 PGVS with 3 cropping years were collected for analyses. About 7,000~9,500 kg ha^{-1} composted animal manure were uniformly broadcasted and mixed with the topsoil annually.

Site 3 (S3) was located at the source of Qinhuai River (N31°35'28.5", E119°04'01.9"), LiShui District. It has about 67 hectares of organic vegetable cropping area, and it strictly uses animal manure and biological fertilizer. Three OVS and five PGVS with 5 cropping years and three OVS and three PGVS with 8 cropping years were collected for the study. About 2,000~3,500 kg ha^{-1} composted animal manure was applied annually.

Site 4 (S4) was located at Honglan Town (N31°33'32.8"，E118°59'17.2"), Lishui District. It has about 200 hectares of organic vegetable production area, and uses only manure and biological fertilizer. Three OVS and five PGVS with 10 cropping years were collected for the study. About 15,000 kg ha^{-1} composted poultry manure was applied annually.

2.2 Soil sampling

At each location, composite soil samples consisted of 15 random subsamples (0-15 cm) were taken from each selected plastic covered greenhouse (PGVS) with an area of 60 m^{2} (6×10 m). While, 3 open vegetable field (OVS) were randomly chosen for comparison, which had similar history of cultivation and organic amendment application at each site. The composite soil sample was air-dried at room temperature (25±1℃) and ground to pass a 2 mm sieve, and used for chemical analysis in the lab.

2.3 Fractionation of soil inorganic P

For all soil samples, five sequential P fractions were determined according to Chang and Jackson (1957). This fractionation technique uses a series of extractants to identify inorganic phosphates with different solubility. In brief, soil samples were sequentially extracted by each of the following extractants: 1.0 mol L^{-1} NH_4Cl for the loosely bound phosphate (NH_4Cl-P), 0.5 mol L^{-1} NH_4F (pH 8.2) for aluminum phosphate (Al-P), 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} Na_2CO_3 for iron phosphate (Fe-P), 0.3 mol L^{-1} $Na_3C_6H_5O_7 \cdot 2H_2O$ for the occluded phosphate (Oc-P), and 0.5 mol L^{-1} H_2SO_4 for calcium phosphate (Ca-P). The concentrations of P_i in the extracts were immediately determined by the phosphomolybdate colorimetric method of Murphy and Riley (1962) as described by Kuo (1996), using a UNICO (China) UV-2100 spectrophotometer.

2.4 Plant available soil P (Olsen-P)

Soil available P (Olsen-P) was determined by the Olsen method (Olsen et al., 1954). Olsen-P is the official method for assessing soil plant available P in China (Lu, 1999). Briefly, 2.5 grams of air-dried soil sample (< 2 mm) and 50 mL $NaHCO_3$ (0.5 mol L^{-1}, pH 8.5) were placed into a 250 mL extraction bottle; and the bottles were shaken mechanically for 30 min at room temperature (25±1℃). The suspension was filtered through a Whatman No. 42 P free filter paper. The P concentration in the filtrate was determined by the phosphomolybdate colorimetric method.

2.5 Chemical properties of vegetable soils

Soil pH was measured using a combination glass electrode in a 1:2.5 soil/water suspension. Soil organic matter (OM) was determined by the dichromate wet oxidation method. Total N (TN) in the soil was determined using the Kjeldahl method. Total P (TP) was determined after digestion with 70% $HClO_4$, phosphorus in the digests and extracts was determined colorimetrically with the molybdate-ascorbic acid procedure (Kuo, 1996). Total K (TK) and available K were determined by a flame photometer; available N was determined by the alkaline hydrolysis diffusion method. All procedures used were documented in Lu (1999) except noted otherwise.

2.6 Statistical analyses

Data processing and regression analyses were performed using SPSS program, version 18.5. Software ORIGIN 8.5 (Northhampton, MA) was used to draw the figures.

3. Results

3.1 Soil pH and organic matter (OM)

The pH of all open vegetable soils (OVS) and plastic greenhouse vegetable soils (PGVS) varied from 5.5 to 7.5 and 4.7 to 7.3 with the average of 6.7 and 5.7, respectively. The majority (63.4%) of samples had pH lower than 6.5. Compared with OVS, soil pH of PGVS was decreased by an average of 0.57, 1.1, 1.12 in S1, S2 and S3 (Table 1) under similar fertilization practice, respectively.

Soil organic matter (OM) of all OVS and PGVS varied between 11.4~34.3 g kg^{-1} and 11.9~56.3 g kg^{-1}, with the average of 19.0 g kg^{-1} and 23.2 g kg^{-1}**,** respectively (Table 1). By comparison, OM contents of PGVS were increased by 55.4%, 92.2%, and 34.2% in S2, S3 (5 yr) and S3 (8yr) ($p<0.05$), respectively, but no significant changes were observed in S1 and S4 sites when compared with the adjacent OVS. Generally, PGVS has lower OM than that in OVS because of higher temperature in the greenhouse, but we observed the opposite results in S2 and S3 because the total application amounts of organic manure and the cropping index both were higher in PGVS than in OVS. OVS can only produce vegetables from spring to early autumn each year, while PGVS can produce vegetables for the entire year. Therefore, the OM contents had a significant difference in S2 and S3. As a whole, OM contents of PGVS were higher than that of OVS.

Table 1 Soil pH, organic matter (OM) and cation exchange capacity (CEC) in the open vegetable soils (OVS) and plastic greenhouse vegetable soils (PGVS) collected from different organic vegetable production sites

Site	Farming types	Soil sample code	Cultivated year	Cultivated vegetables	Sample size	pH	OM	CEC
							g kg^{-1}	cmol kg^{-1}
S1	OVS [†]	1-O-3	3	Rape	3	$7.00\pm0.38^{d\dagger}$	12.5 ± 0.69^{a}	31.4 ± 1.41^{e}
S1	PGVS [‡]	1-P-3	3	Rape	5	6.43 ± 0.87^{c}	14.0 ± 2.88^{a}	30.7 ± 2.89^{e}
S2	OVS	2-O-3	3	Lettuce	3	6.26 ± 0.34^{bc}	12.1 ± 0.66^{a}	18.9 ± 0.85^{a}
S2	PGVS	2-P-3	3	Lettuce	10	5.17 ± 0.39^{a}	18.8 ± 1.94^{b}	21.6 ± 2.26^{b}
S3	OVS	3-O-5	5	Spinach	3	7.11 ± 0.39^{d}	15.3 ± 0.84^{a}	25.4 ± 1.14^{cd}
S3	PGVS	3-P-5	5	Spinach	5	5.94 ± 0.75^{b}	29.4 ± 5.13^{d}	27.3 ± 1.47^{d}
S3	OVS	3-O-8	8	Spinach	3	7.05 ± 0.39^{d}	32.5 ± 1.79^{e}	24.0 ± 1.08^{c}
S3	PGVS	3-P-8	8	Spinach	3	5.93 ± 0.28^{b}	43.6 ± 11.0^{f}	17.7 ± 2.53^{a}
S4	OVS	4-O-10	10	Celtuce	3	5.86 ± 0.32^{b}	22.7 ± 1.25^{c}	25.7 ± 1.15^{cd}
S4	PGVS	4-P-10	10	Celtuce	3	5.87 ± 0.33^{b}	22.5 ± 1.75^{c}	19.8 ± 5.95^{ab}

[†] OVS, open vegetable soils; [‡] PGVS, plastic greenhouse vegetable soils.

[†] Means and standard deviation within one column followed by the same lowercase letters are not significantly different at $P < 0.05$.

3.2 Soil total and available N, P, and K

Soil total nitrogen (TN) varied between 0.48 g kg^{-1} and 1.48 g kg^{-1} among all samples. Soil TN contents of PGVS were increased by 38.3%, 58.4% and 20.0% over those of OVS in S2, S3 and S4 ($p<0.05$), respectively (Table 2). Soil total P (TP) of OVS and PGVS varied in 0.55~1.16 g kg^{-1} and 0.67~1.89 g kg^{-1}, with the average of 0.91 g kg^{-1} and 1.23 g kg^{-1}**,** respectively. Compared with OVS, soil TP contents of PGVS were increased by 37.5%, 77.2% and 55.1% in S2, S3 and S4, respectively (Table 2). Soil total potassium (TK) in all vegetable soils was in the ranges of 3.93 ~ 6.50 g kg^{-1}, and the only significant difference between OVS and PGVS occurred in S2 and S3 (Table 2). Both soil available N (29.6~256.4 mg kg^{-1}), and available K (75.6~645.5 mg kg^{-1}) were higher in the PGVS than OVS in S1, S2 and S3 (Table 2). By comparison, soil available P of PGVS was increased by 12.9%, 15.9% , 283.6%,124.8% and 97.3% over OVS in corresponding S1, S2, S3 (5 yr), S3(8 yr), and S4, respectively (Table 2). Soil plant available P in OVS (39.1 mg kg^{-1}) was lower than recommended for optimum vegetable production (60 mg kg^{-1}) by Zhang et al.(2009) at the site of 3-O-5. However, it was only cultivated with spinach for one season before sampling and before the carrot (*Daucus L.*) was planted. Moreover, the amount of organic manure applied in the carrot season was lower than in the spinach-season. No vegetable yields were collected before sampling, so we cannot give the exact reason of the low available P content at the site of 3-O-5 (Table 2).

Table 2 Soil nitrogen (N), phosphorus (P) and Potassium (K) contents in the open vegetable soils (OVS) and plastic greenhouse vegetable soils (PGVS) collected from different organic vegetable production sites

Site	Soil sample code	Total N	Total P	Total K	Available N	Available P	Available K
			$g\ kg^{-1}$			$mg\ kg^{-1}$	
S1	1-O-3	$0.59 \pm 0.03^{ab\dagger}$	1.08 ± 0.05^{cd}	5.41 ± 0.24^{ef}	35.4 ± 1.59^{a}	171 ± 7.67^{cd}	194 ± 8.73^{bc}
S1	1-P-3	0.59 ± 0.12^{ab}	0.95 ± 0.20^{bc}	5.78 ± 0.50^{g}	40.4 ± 8.82^{ab}	193 ± 70.0^{d}	234 ± 64.3^{bc}
S2	2-O-3	0.60 ± 0.03^{ab}	0.88 ± 0.04^{b}	4.28 ± 0.19^{a}	72.0 ± 3.23^{de}	296 ± 13.3^{e}	344 ± 15.5^{d}
S2	2-P-3	0.83 ± 0.18^{c}	1.21 ± 0.23^{e}	4.67 ± 0.61^{bc}	91.0 ± 63.5^{ef}	343 ± 99.3^{f}	444 ± 195^{e}
S3	3-O-5	0.51 ± 0.02^{a}	0.58 ± 0.03^{a}	4.54 ± 0.20^{ab}	46.3 ± 2.08^{abc}	39.1 ± 1.76^{a}	163 ± 7.33^{ab}
S3	3-P-5	0.85 ± 0.06^{c}	1.16 ± 0.11^{de}	4.83 ± 0.27^{bc}	63.6 ± 7.98^{cd}	150 ± 35.1^{c}	547 ± 98.4^{f}
S3	3-O-8	0.88 ± 0.04^{c}	1.10 ± 0.05^{de}	5.50 ± 0.05^{fg}	67.9 ± 3.05^{cd}	86.3 ± 3.88^{b}	266 ± 11.9^{cd}
S3	3-P-8	1.32 ± 0.22^{d}	1.70 ± 0.21^{g}	5.15 ± 0.12^{de}	100.8 ± 28.4^{f}	194 ± 50.7^{d}	218 ± 180^{bc}
S4	4-O-10	0.55 ± 0.02^{a}	0.89 ± 0.04^{b}	5.15 ± 0.23^{de}	59.6 ± 2.68^{bcd}	80.6 ± 3.62^{b}	99.5 ± 4.47^{a}
S4	4-P-10	0.66 ± 0.03^{b}	1.38 ± 0.13^{f}	4.95 ± 0.32^{cd}	56.3 ± 3.79^{abcd}	159 ± 1.82^{cd}	104 ± 12.2^{a}

[†] Means and standard deviation within one column followed by the same lowercase letters are not significantly different at $P < 0.05$.

3.3 Soil inorganic P fractions

Soil total P_i (T-P_i) ranged between 669.4~1884.6 mg kg^{-1} and 548.0~1163.9 mg kg^{-1} in PGVS and OVS, which accounted for 65.6~96.7% and 78.9~92.0% of TP, respectively (Table 3). By comparison, the amount of T-P_i in PGVS was significantly higher than that of OVS in S2, S3 and S4 (Table 3).

Soil T-P_i was fractionated into five fractions. The loosely bound P (NH_4Cl-P) is generally low or undetectable in most natural soils, but it was high in the vegetable soils of this study. As shown in Table 3, the average amount of NH_4Cl-P in PGVS was 126.6 mg kg^{-1}, which is about 2.75 times as much as OVS (46.0 mg kg^{-1}). Compared with OVS, the amount of Al-P in PGVS was increased by 13.8% in S1, 54.7% in S2, 262.3~124.3% in S3, and 57.9% in S4. But the amount of Fe-P in

PGVS was decreased by 29.1% in S1, no significant difference in S2, but significantly increased by 59.9% in S3(5 yr), 11.2% in S3(8 yr) and 57.9% in S4. Oc-P was increased by 13.0~68.7% and 14.4% in PGVS than those in S3 and S4, respectively. Ca-P was also significantly increased in PGVS over OVS, except for the vegetable soils with 8 years' cultivation (Table 3). Generally, those results clearly show that long-term application of farmyard manure in PGVS significantly increased soil total P_i and various P_i fractions, compared with OVS (Table 3).

Table 3 Contents and proportions of various inorganic phosphorus (P_i) in the open vegetable soils (OVS) and plastic greenhouse vegetable soils (PGVS) collected from different organic vegetable production sites

Site	Soil sample code	Contents					
		NH_4Cl-P	Al-P	Fe-P	Oc-P	Ca-P	T-P_i
		mg kg^{-1}					
S1	1-O-3	$58.2 \pm 2.61^{b\,\dagger}$	198 ± 8.89^{cd}	255 ± 11.5^{cd}	111 ± 5.00^{a}	248 ± 11.1^{e}	870.5 ± 39.1^{b}
S1	1-P-3	127 ± 72.3^{cd}	225 ± 57.5^{de}	181 ± 19.4^{b}	126 ± 28.9^{a}	125 ± 62.8^{d}	784.5 ± 165^{b}
S2	2-O-3	102 ± 4.57^{c}	240 ± 10.8^{e}	236 ± 10.6^{c}	136 ± 6.10^{a}	98.1 ± 4.40^{cd}	812.3 ± 36.5^{b}
S2	2-P-3	163 ± 67.3^{e}	372 ± 45.0^{g}	247 ± 54.5^{c}	147 ± 46.5^{a}	121 ± 36.9^{d}	1048 ± 203^{c}
S3	3-O-5	15.9 ± 0.71^{a}	45.9 ± 2.06^{a}	118 ± 5.30^{a}	292 ± 13.1^{bc}	37.6 ± 1.70^{a}	509.2 ± 22.9^{a}
S3	3-P-5	96.0 ± 20.5^{c}	166 ± 29.5^{bc}	188 ± 36.5^{b}	330 ± 41.2^{c}	76.5 ± 16.0^{bc}	857.2 ± 97.7^{b}
S3	3-O-8	41.7 ± 1.87^{ab}	150 ± 6.74^{b}	244 ± 10.9^{c}	316 ± 14.2^{bc}	119 ± 5.30^{d}	870.4 ± 39.1^{b}
S3	3-P-8	135 ± 37.2^{de}	337 ± 84.6^{f}	271 ± 4.90^{d}	533 ± 85.3^{d}	123 ± 51.2^{d}	1399 ± 247^{d}
S4	4-O-10	12.6 ± 0.56^{a}	166 ± 7.44^{bc}	249 ± 11.2^{c}	284 ± 12.8^{b}	54.5 ± 2.40^{ab}	765.5 ± 34.4^{b}
S4	4-P-10	49.2 ± 12.1^{b}	262 ± 38.0^{e}	312 ± 16.2^{e}	325 ± 60.8^{c}	80.3 ± 31.0^{bc}	1028 ± 51.5^{c}

Site	Code	Proportion of T-P_i					T-P_i/TP
		NH_4Cl-P	Al-P	Fe-P	Oc-P	Ca-P	
		%					
S1	1-O-3	6.68 ± 0.15^{c}	22.7 ± 0.10^{de}	29.3 ± 0.20^{cd}	12.8 ± 0.10^{a}	28.5 ± 0.21^{e}	80.4 ± 0.45^{b}
S1	1-P-3	15.3 ± 5.81^{f}	29.0 ± 5.99^{f}	23.6 ± 2.83^{b}	16.1 ± 1.91^{b}	16.0 ± 7.07^{d}	83.0 ± 5.10^{bcd}
S2	2-O-3	12.5 ± 0.17^{f}	29.6 ± 0.12^{f}	29.1 ± 0.13^{cd}	16.7 ± 0.15^{b}	12.1 ± 0.11^{c}	92.0 ± 0.46^{e}
S2	2-P-3	15.1 ± 3.23^{e}	36.2 ± 5.51^{g}	23.5 ± 1.85^{b}	13.8 ± 2.97^{a}	$11.4 \pm 1.90b^{c}$	86.4 ± 6.53^{cd}
S3	3-O-5	3.13 ± 0.10^{ab}	9.01 ± 0.24^{a}	23.2 ± 0.11^{b}	57.3 ± 0.20^{f}	7.38 ± 0.21^{a}	87.8 ± 0.34^{de}
S3	3-P-5	11.2 ± 1.87^{de}	19.3 ± 2.25^{bc}	21.9 ± 2.80^{b}	38.6 ± 2.89^{e}	9.02 ± 1.97^{ab}	74.0 ± 9.66^{a}
S3	3-O-8	4.80 ± 0.10^{bc}	17.3 ± 0.16^{b}	28.0 ± 0.10^{c}	36.3 ± 0.10^{d}	13.7 ± 0.31^{c}	78.9 ± 0.36^{ab}
S3	3-P-8	9.50 ± 0.96^{d}	23.9 ± 2.97^{de}	19.8 ± 2.95^{a}	38.2 ± 2.04^{de}	8.55 ± 2.30^{a}	82.2 ± 10.72^{bc}
S4	4-O-10	1.64 ± 0.11^{a}	21.6 ± 0.20^{cd}	32.5 ± 0.08^{e}	37.1 ± 0.11^{de}	7.11 ± 0.20^{a}	86.1 ± 0.55^{cd}
S4	4-P-10	4.79 ± 1.19^{bc}	25.4 ± 3.21^{e}	30.4 ± 2.34^{d}	31.4 ± 4.58^{c}	7.93 ± 3.39^{a}	74.8 ± 4.40^{a}

†Means and standard deviation within one column followed by the same lowercase letters are not significantly different at P < 0.05.

3.4 Correlation between P accumulation and soil acidification

Long-term application of organic manure significantly increased P accumulation and reduced soil pH in PGVS compared with OVS (Table 1 and Table 2). Regression analysis showed that there are significant correlations between total P, available P and soil pH in vegetable soils (Figure 1, $p < 0.01$). Soil pH was decreased by 0.874 or 0.004 unit when the total P or available P increased by one mg kg^{-1}, respectively (Figure 1).

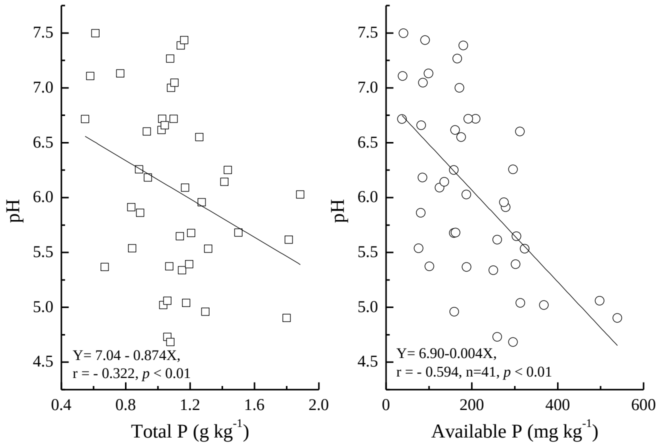

Figure 1 Correlation between total P, available P and pH in the vegetable soils (n=41)

4. Discussion

Organic vegetable production is perceived to be environmentally friendly, but P accumulation and acidification in the PGVS may lead to faster degradations of soil quality than in the OVS and may be an important cause of eutrophication in waterbodies. Generally, strategies for the application of animal manure compost have been based on meeting crop N needs to maximize plant growth and minimize nitrate loss by leaching, a potential groundwater contaminant (Kim et al., 2001). In most cases, this strategy has led to an increase in soil phosphorus levels in excess of crop requirements, due to the generally low N/P ratio of the added manure (Kim et al., 2001). Our study showed that long-term application of organic manure increased the soil total N and available N levels and the corresponding increase in soil total P and available P in vegetable soils (Figure 2). There was a significant correlation between soil N contents and soil P contents, and the correlation coefficients ranged between 0.333 and 0.844 (Figure 2).

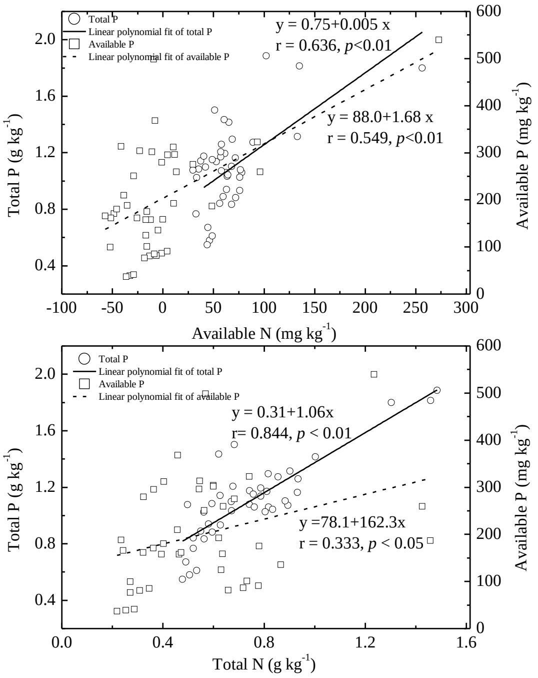

Figure 2 Correlation between soil total N, available N and total P, available P in vegetable soils (n=41)

Soil acidification is an important cause of soil degradation. Many researches showed that application of N fertilizers can lead to soil acidification (Tian and Niu, 2015; Guo et al., 2010). Guo et al. (2010) showed that severe soil acidification in China's croplands occurred, and attributed it to the combination of high-N fertilizer inputs, plant uptake and removal of base cations from soils, and acid deposition, with the dominant effect from the overuse of N fertilizer. Ju et al. (2007) showed that soil pH under vegetable systems was significantly dropped in greenhouse vegetable systems in the North China Plain, due to high application rates of N fertilizers. The main mechanism of soil acidification by N fertilization is the release of hydrogen ion (H^+) during nitrification of NH_4^+ and the leaching of NO_3^-.

Soil acidification is a slow process under natural conditions over hundreds to millions of years, because soils are strongly buffered by ion exchange reactions, the weathering of soil minerals and interactions with aluminum and iron in the acidic range (Chadwick and Chorover, 2001).

However, this process is accelerated by agricultural activities due to the disturbances in the N and C cycles (Randall et al., 2006). Likewise, year-round excessive application of N fertilizers or farmyard manure to vegetable soils in China has resulted in significant soil acidification, secondary salinization, soil nutrient imbalance (Guo et al. 2010; Han et al., 2015). In our study, soil surface acidification phenomenon occurred in most of PGVS compared with that in OVS (Table 1). Compared with OVS which only produced vegetables from the spring to the early autumn every year, PGVS had the relatively high cropping indexes because of cultivation of the all seasons as well as related high input of organic manure, special field microclimate in cold season in PGVS. Therefore, soil acidification and N, P accumulation was relatively faster in PGVS than OVS.

Soil is a mixture of acid/base systems, so there are many causes of soil acidification in addition to N-induced acidification. In this study, we attempt to discuss the relationship between P accumulation and soil pH in vegetable soils. Compared with the other major nutrients, P is by far the least mobile and available to plants in most soil conditions. In most soils, inorganic P occurs at fairly low concentrations in the soil solution whilst a large proportion of it was strongly bound by diverse soil minerals. Phosphate ions can indeed be absorbed onto positively charged minerals such as (hydro) iron-aluminum oxides and they can also form a range of minerals in combination with metals such as Ca, Fe and Al (Chang and Jackson, 1957). The type of minerals formed will depend on the soil pH in the first place as it governs the occurrence and abundance of those metal cations that are prone to precipitation with P ions in the soil solution, namely Ca, Fe and Al (Hinsinger, 2001). Fractionation of soil inorganic P showed that Al-P and Fe-P were the predominant fractions in vegetable soils, except for the Oc-P (Table 3). Correlation analysis showed that NH_4Cl-P and Al-P were both significantly correlated with soil pH in vegetable soils (Figure 3), but Fe-P, Oc-P and Ca-P had no significant correlation with soil pH. Under actual conditions, NH_4Cl-P in soils is short lived because it is readily transformed into Al-P, as time passes, or into Fe-P (Zhu et al., 1981). So Al-P and Fe-P are relatively stable in most soils. Further analysis showed that the ratio of Al-P/Fe-P was significantly correlated with soil pH ($Y_{pH} = 7.44 - 1.32 X_{Al\text{-}P/Fe\text{-}P}$,r = - 0.705, $p < 0.01$). Finally, soil total P_i was negatively correlated with soil pH in vegetable soils (Figure 3, $p < 0.05$). Soil pH was decreased by 1.09 unit when the soil total P_i was increased by 1 g kg^{-1} (Figure 3). Those results suggest that various P_i may affect or adjust soil pH. Conversely, soil pH also can impact soil P_i. Therefore, the interaction between various soil various P_i and soil pH need to be further investigated through a series of controlled tests in the future.

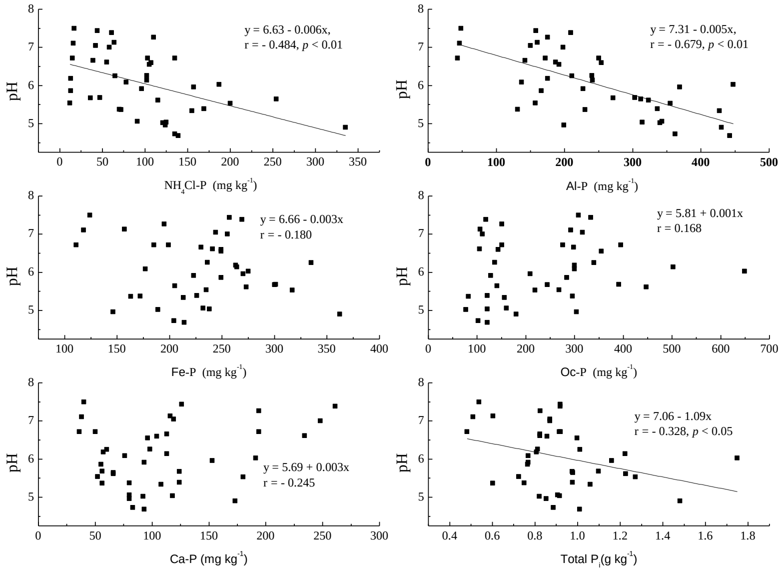

Figure 3 Correlation between various P_i and soil pH in vegetable soils (n=41)

Generally, the distribution of P among various species in solution is primarily determined by solution pH. Indeed, phosphate ions are derived from the dissociation of orthophosphoric acid which is characterized by three pK values (Lindsay, 1979). In addition to orthophosphate ions, P can occur as a range of negatively and positively charged or uncharged species in the soil solution, and the distribution of which is much dependent on the pH and on the concentrations of metal cations such as Ca, Fe and Al and organic and inorganic ligands (Hinsinger, 2001). Therefore, long-term application of organic manure can significantly decrease soil pH and increase P accumulation and P availability in vegetable soils (Table 2). Manure contains a large amount of organic P, which can be converted to P_i by mineralization (Turner and Leytem, 2004). Nearly 70% of total P in manure, therefore, is labile and P_i accounts for 50% to 90% (Dou et al., 2000). In this study, T-P_i was the dominant fraction with 78.9~92.0% and 65.6~96.7% of total P in OVS and PGVS, respectively, and the amounts of organic P were relatively low although large quantities of organic amendments were used (Table 3).

Furthermore, small molecular organic acids generation due to decomposition of large quantities of organic matter input could be another reason for the accelerated P accumulation and soil acidification. Many organic acids contain carboxyl and hydroxyl groups, and possess negative charge, which strongly compete for the adsorption sites with P_i (Shen et al., 2011). Manure can also change soil pH and thus alter soil P availability. Guo et al. (2010) pointed out that soil could be acidified by the excessive application of farmyard manure. But the mechanisms of manure-induced P transformation processes between various P_i and organic P in vegetable soils still need further investigation (Shen et al., 2011).

Generally, the N/P ratio of manure (2:1 to 6:1) is lower than that in crop uptake (7:1 to 11:1), so N-based manure management results in more P been added to the soil than the crop requires. Accelerated P accumulation and acidification could contribute to an increased risk of P transport from agricultural land to surface water (Gburek, et al., 2000). Lu (1980) found an Olsen-P of 20 mg kg^{-1} as the critical level for most crops. Plants would have little or no response to P fertilization when soil test P is above 20 mg kg^{-1}, and thus no P fertilizer is needed. However, Zhang et al. (2009) indicated that Olsen-P of 60~100 mg kg^{-1} was medium level for most vegetables, and 100 ~ 150 mg kg^{-1} was considered a high level. In this study, PGVS had higher contents of total P, various P_i and available P than those in OVS, in addition to higher organic matter contents. Alarmingly, all samples analyzed had a soil test P over the recommended optimum value of 20 mg kg^{-1} and 60% of soil samples were considered to be excessive in P according to Zhang et al. (2009), suggesting that vegetable crops will not respond to additional P input, but P loss risk will be high. This high soil P level due to intensive vegetable production is unsustainable and will lead to a real threat to water quality. Therefore, increasing P availability and reducing P loss from vegetable soils are essential to make vegetable production sustainable and environmentally friendly. Better management, therefore, should be implemented accordingly in preventing the further buildup of P in vegetable soils under plastic greenhouse cultivation condition and minimizing P loss to the environment. The relationship between soil acidification and P accumulation also need to be further investigated in the vegetable soils under long-term application of various organic amendments in future researches.

Acknowledgments

This work was supported by the National Natural Science Foundation, China (grant no. 41571286; 51479055); Open Research Fund Program of State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Science, Nanjing 210008, China (grant no.Y412201419); and the Fund of Jiangsu Overseas Research ＆ Training Program for University Prominent Young ＆ Middle-aged Teachers and Presidents.

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