Field Crops Research 137 (2012) 163–169

Contents lists available at SciVerse ScienceDirect

Field Crops Research

journal homepage: www.elsevier.com/locate/fcr

The transfer of fluorine in the soil–wheat system and the principal source of fluorine in wheat under actual field conditions

Cheng Wang[a], Zhongfang Yang[b], Lingxiao Chen[a], Xuyin Yuan[c], Qilin Liao[d], Junfeng Ji[a,*]

[a] Key Laboratory of Surficial Geochemistry, Ministry of Education, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, China
[b] School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China
[c] College of Environment and Engineering, Hohai University, Nanjing 210098, China
[d] Geological Survey of Jiangsu Province, Nanjing 210018, China

ARTICLE INFO

Article history:
Received 15 April 2012
Received in revised form 28 July 2012
Accepted 1 August 2012

Keywords:
Fluorine
Transfer
Wheat tissues
Soil
Atmosphere

ABSTRACT

Very few studies of F in soil and wheat grain, straw and root under actual field conditions have been reported. In order to study F concentration (contamination) in wheat and its relationship to soil F and other elements, the present study collected and analyzed 150 pairs of topsoil and wheat samples (root, straw and grain) from the Yangtze River delta region, China. Compared with the Chinese maximum permissible concentration in wheat grain for F, 36.7% of wheat grain samples in the present study area are contaminated with F. The concentrations of F in different wheat tissues generally decreased in the order of root > straw > grain. Fluorine in wheat tissues showed significant correlations with Fe, S, P and heavy metals. The soil total F and water soluble F concentrations in the present study area range from 0.29 to 0.79 $g\,kg^{-1}$ and 2.28 to 30.11 $\mu g\,g^{-1}$, respectively. The soil total F and water soluble F exhibits no significant correlations with wheat root F or grain F. It is inferred that the major source of F in wheat is not from the soil, whereas F in wheat grain may mainly derive from the atmosphere.

1. Introduction

Fluorine shows a relatively narrow range between intakes associated with beneficial effects and exposures causing adverse effects compared with other elements (Malinowska et al., 2008). Human populations in many regions such as China, India, Iran, and others suffer from the fluorosis resulted from the excess intake of F. Although many researchers believe the principal sources of F that cause fluorosis in human are drinking water, the food materials, especially the staple food such as wheat grain should also be examined carefully. In addition, uptake F in excess is also toxic to the plants (Singh et al., 1979).

However, our knowledge of F transfer from soil to wheat and other plants is limited compared to that of heavy metals. The previous investigations have found that wheat F content exhibits no significant correlation with soil total F or water soluble F, and certain publications have reported that in the soil, only water soluble F (WS-F) can be taken up by the plants (Brewer, 1965; Larsen and Widdowson, 1971). Some researchers considered that F in the plants mainly derived from the WS-F in the soil (Chavoshi et al., 2011; Singh et al., 1979), and most of the researches focused on the effect of soil properties on soil WS-F (Barrow and Ellis, 1986; Jha et al., 2011). Although certain publications have reported the relationship between wheat F with soil WS-F, most of them were performed under the special experimental conditions with considerable dose of F added to the soil (Arnesen, 1997; Façanha and Okorokova-Façanha, 2002; Nayak et al., 2009). For example, Singh et al. (1979) reported that wheat straw F concentration increases with increasing soil WS-F through an experiment by adding NaF, and the soil WS-F concentrations (15–52 $\mu g\,g^{-1}$) that are much higher than the normal level of agricultural soil. Few publications have reported the relationship between wheat F with soil WS-F under actual field conditions, especially including wheat root, straw and grain at the same time.

The uptake of F by the plant is an issue of concern and complexity to agricultural scientists. Some researchers believe that F in the wheat mainly come from atmosphere, and the soil has little influence on F accumulation in the plants (Chen, 2002; Mcclure, 1949; Tang et al., 1999). Gritsan (1992) reported that the accumulation rate of F in wheat straw is linear to atmospheric F content under experimental conditions. In China, some publications also reported that wheat F concentration exhibits significant correlation with airborne F concentration and no significant correlation with soil total F or WS-F (Li et al., 1991; Sun et al., 1998; Tang et al.,

Abbreviations: WS-F, soil water soluble F; Av-Fe, soil bio-available Fe; Av-P, soil bio-available P; Av-Mo, soil bio-available Mo; TOC, soil total organic carbon.

* Corresponding author at: School of Earth Sciences and Engineering, Nanjing University, 22 Hankou Road, Nanjing 210093, China. Tel.: +86 25 83595795; fax: +86 25 83595795.
E-mail address: jijunfeng@nju.edu.cn (J. Ji).

0378-4290/$ – see front matter
http://dx.doi.org/10.1016/j.fcr.2012.08.001

1999). However, these studies were conducted either in the regions with the atmosphere strongly polluted by F or under special experimental conditions. The investigation on the relationship between wheat F and soil F under actual field conditions should be done to find out the principal source of F in wheat and the geochemical characteristic of F in the agricultural system.

China is one of countries in the world that suffer from the fluorosis relatively seriously. The Yangtze River region is a very important agricultural and industrial area in China, and also is one of the most famous alluvial deltas in the world. Wheat (*Triticum aestivum* L.) has been a prominent crop here. Therefore, a regional scale survey was performed to study (1) F transfer in a soil–wheat system, (2) the principal source of F in wheat grain, and (3) the relationship between F with other physical–chemical parameters under actual field conditions.

2. Materials and methods

2.1. Study area and sampling

The study area is located at 30°00′N–33°20′N and 119°10′E–121°40′E in East China, covering an area of 109.65 km^2 with a warm and humid subtropical climate. The annual mean temperature and rainfall are approximately 15 °C and 1000 mm, respectively. According to the soil classification in the world reference base for soil resources, anthrosol is the major soil order in this area. The winter wheat (*T. aestivum* L.) is a dominant crop here, and is usually sowed in October and harvested in May.

A total of 150 pairs of topsoil and wheat (*T. aestivum* L.) samples (66 pairs of root and straw samples) were collected randomly with the aid of a Global Positioning System from the study area shortly before harvesting in 2009 (Fig. 1). At each site, five topsoil (depth: 0–20 cm) sub-samples were collected in a 400 m^2 area using a stainless steel trowel, and mixed in a cloth bag. At the same time, five corresponding wheat plant sub-samples with the sampling area of 1-m^2 quadrant were collected by hand and combined into a single composite sample, then separated into root, straw and grain samples. The wheat grains were generally fully filled and normally developed. The soil samples were air-dried and sieved through a 2-mm polyethylene sieve to remove larger debris, stones and pebbles. After the pH was measured, the soil samples were ground to fine particles (<0.15 mm) for chemical analysis. The plant samples were carefully rinsed with deionized water, initially air-dried at room temperature, and ground into fine particles (<0.15 mm). The powdered samples of plant tissues were oven-dried at 60 °C for 48 h before chemical analysis.

2.2. Chemical analysis

Soil pH was determined in a paste with a ratio of 1:2.5 of unground soil to water using a pH meter (Model PHS-3C, Shanghai Precision and Scientific Instrument Co. Ltd., China) (Soil Science Society of China, 1983). The total concentrations of Ca, Mg, K, Al, Fe, S and P in soil samples were determined by a powder X-ray fluorescence (XRF, ZSX primus II, Rigaku Japan, Osaka, Japan). To determine concentrations of trace elements, the soil samples were first digested by HCl–HNO_3–$HClO_4$–HF. The Mn concentrations were determined with an inductively coupled plasma-optical emission spectrometer (ICP-OES, Thermo Element iCAP6000 (Radial), Cambridge, BZ, UK). Cadmium and Mo concentrations were determined with an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Element X Series 2, Bremen, Germany). Total organic carbon (TOC) was determined by dichromate oxidation using a modified Tyurin method (Nelson and Sommers, 1996). The determination of total C in soil sample was achieved with a high frequency IR-absorption spectrometry (HIR-944B, Wuxi Analytical Ultra Scientific Instrument Co. Ltd., China) (Shi et al., 2001). Total soil F was obtained by the NaOH fusion method per as McQuaker and Gurney (1977), and the concentration was measured using the F-ion selective electrode method.

Soil bio-available Fe (Av-Fe) was extracted using the diethylenetriamine penta-acetic acid (DTPA) method (Lindsay and Norvell, 1978), and the concentration was determined with an ICP-OES. Soil bio-available P (Av-P) was extracted using NH_4F-HCl or $NaHCO_3$ (based on pH) (Shi et al., 2008), and the concentration was determined with an ICP-OES. The bio-available Mo (Av-Mo) was extracted with Tamm reagent (ammonium oxalate–oxalic acid at pH = 3.5) and was then determined by inductively coupled plasma-mass spectrometry (Kabata-Pendias, 1999). Soil water soluble F was extracted in 1:1 deionized water using the standard method (Brewer, 1965), and the concentration was measured using the F-ion selective electrode method.

To determine the concentrations of element in wheat tissues, samples were digested using HNO_3 and H_2O_2. The concentrations of Ni, Cr, Cd and Mo were measured with an ICP-MS, and the concentrations of S, P and Fe were measured with an ICP-OES. The C concentration was measured by the $K_2Cr_2O_7$–H_2SO_4 oxidation method (Soil Science Society of China, 1983).

Quality assurance and quality control (QA/QC) for metals in soil (wheat) samples were estimated by analyzing metal contents in blank and duplicate samples and Certified Reference Materials (GBW07402 and GBW07406 for soil, and GBW10011 and GBW10014 for wheat) approved by the General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China. The blank and duplicate samples and Certified Reference Materials were including for every 20 samples in the chemical analysis process. The elemental recoveries and relative standard deviation (RSDs) for Certified Reference Materials were 94–106% and <5.0% (<7.5% for F, P, C, S and TOC), respectively.

2.3. Statistical analysis

Data were statistically analyzed using SPSS version 18 (SPSS Inc., USA). Pearson correlation coefficients were calculated to determine the relationship among different parameters. The spatial map of sampling sites was performed with ESRI ArcGIS 9.3 program.

3. Results

3.1. Soil F concentration and soil properties

The soil F and soil properties in 150 soil samples are shown in Table 1. The total soil F concentrations ranged from 0.29 to 0.79 $g\,kg^{-1}$, and the average concentration was 0.55 $g\,kg^{-1}$. The soil WS-F concentrations ranged from 2.28 to 30.11 $\mu g\,g^{-1}$ with a mean value of 9.27 $\mu g\,g^{-1}$, which constituted 0.45–6.33% (average: 1.71%) of the total soil F.

Soil pH ranged from 4.80 to 8.28, i.e., strongly acidic to mildly alkaline. The variation ranges of element P, S, C, Fe, Ca, Mg, Al, K, Mn, Ni, Cr, Cd and Mo concentrations and TOC content were 0.43–2.17 $g\,kg^{-1}$, 0.17–0.76 $g\,kg^{-1}$, 0.65–4.06%, 1.01–4.50%, 0.16–4.01%, 0.18–1.43%, 3.18–9.14%, 0.64–2.43%, 0.15–1.05 $g\,kg^{-1}$, 10.2–55.2 $\mu g\,g^{-1}$, 36.4–93.5 $\mu g\,g^{-1}$, 0.08–1.25 $\mu g\,g^{-1}$, 0.29–4.00 $\mu g\,g^{-1}$, 0.46–3.66%, respectively; and the ranges of Av-Fe, Av-Mo and Av-P were 0.01–0.53 $g\,kg^{-1}$, 0.05–2.14 $\mu g\,g^{-1}$, 1.74–182.59 $\mu g\,g^{-1}$, respectively. The wide variation in soil pH and the concentrations of above mentioned elements are typical of most of the world agricultural cropland, therefore, the present study area is representative for studying the elements transfer from soil to wheat under actual field conditions.