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Environmental fate of phenanthrene in lysimeter planted with wheat and rice in rotation

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ABSTRACT

An outdoor lysimeter experiment was conducted to investigate the fate of ^{14}C-labeled phenanthrene in the soil planted with wheat and rice in rotation. Results showed that applied ^{14}C-activity in the soil decreased mainly through gaseous losses; 67.5% of it evaporated as $^{14}CO_2$. After the rice harvest, the surface soil retained 21.7% of applied ^{14}C-activity, of which 92.4% remained in nonextractable soil residues. The ^{14}C-activities found in deeper layers of the soil column indicated vertical migration of phenanthrene or metabolites. Furthermore, the ^{14}C-activities detected in five organs of mature wheat or rice decreased in the order: roots > leaves > shells > stems > grains. The vertical migration and its accumulation by grains suggest that PAHs in field have adverse effects on the security of groundwater and food.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of concern due to their ubiquitous distribution in the environment and potential toxicity to organisms. The contamination of PAHs in soil has been a hot topic in environmental studies. Recently, increased concentrations of PAHs are often detected in various environmental media; particularly, more than 90% of PAH environmental burden has been found in surface soil [1]. In the latest 100–150 years, concentrations of PAHs in soil have increased in wide-ranging latitude of the world, especially in urban areas [2–5].

PAHs can be taken up by crops grown in PAHs-contaminated soils [6,7]. Thus, food chain contamination is an important pathway through which these toxic pollutants enter the human body: 88–98% of human exposure to PAHs is connected with food [8]. On the other hand, organic materials and preferential flow can enhance the transport of organic pollutants to the deeper soil layers. If the upland soil is frequently irrigated or saturated with water for a significant part of a year, there is an increased likelihood of PAHs leaching from the zone of contaminated sites to the deeper layers to endanger the groundwater quality [9]. PAHs can be retained in soils and subjected to many processes and reactions, including adsorption and desorption, volatilization, degradation, plant uptake, and leaching [10–13]. Consequently, the fate of PAHs in soil has attracted the attention of the scientific community. Laboratory and field studies of PAHs have been carried out; however, they both have practical limitations. Although the laboratory studies are useful for evaluation of the influence of single parameters (e.g., soil type, vegetation, contaminants, temperature, or moisture content) on the fate of PAHs, laboratory conditions are quite different from field conditions [14]. Equally, to better understand the fate of PAHs using field samples is complicated by the number of variables that have to be taken into account for samples from different locations to be comparable (e.g., soil type, vegetation, or cocontaminants) [11].

Employing an outdoor lysimeter to study ^{14}C-labeled PAHs may overcome the difficulties mentioned above. It has been demonstrated that the outdoor lysimeter with undisturbed soil monoliths reflects field conditions [15–20]. In addition, the use of radio-labeled compounds has facilitated the research on PAHs, significantly increasing the sensitivity and accuracy of determining their fate and behavior by establishing a mass balance [21]. Thus, a large number of outdoor lysimeter experiments have been carried out by using ^{14}C-labeled chemicals to investigate their fate in agroecosystems for about 30 years, mainly in Europe [22]. Doick et

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al. [11] utilized two outdoor lysimeters to evaluate the behavior of two PAHs – fluoranthene and benzo[a]pyrene – and two polychlorinated biphenyls (PCBs) – congeners 28 and 52 – in soil; the results indicate that the use of outdoor lysimeters is effective in quantifying ^{14}C-labeled organic compounds in field conditions. However, these studies investigated only part of the environmental behavior of PAHs (volatilization, degradation, plant uptake, or distribution) in soil. Few studies comprehensively explored their loss processes, and the research in their leaching process is especially rare.

This study employed ^{14}C tracer and a lysimeter to investigate the fate of phenanthrene in an agricultural soil that had undisturbed soil profiles established in 2000. The aims of this study were as follows: (i) to quantify the gaseous losses of phenanthrene and the effect of plants on the gaseous losses, (ii) to quantify the leaching loss and movement of phenanthrene residues through the soil column, (iii) to quantify the transport and distribution of phenanthrene residues in crops, and (iv) to achieve a mass balance of the applied ^{14}C-phenanthrene, on the basis of the results of the first three aims. This study may provide very important information about the adverse effects of the PAHs-contaminated soil on the environment and food.

2. Experimental

2.1. Experimental site

The study was carried out in Changshu Agroecological Experimental Station, the Chinese Academy of Sciences (Changshu, Jiangsu, China) (31°32′45″N, 120°41′57″E). The research site had a humid subtropical monsoon climate. Its annual mean air temperature was about 15.5 °C, mean annual precipitation was 1038 mm, and the annual length of the non-frost period was approximately 242 days. A rice-wheat rotation system prevailed in this region. The field was used for agronomic management before, without any pre-contamination with PAHs. The soil was classified as gleysols with a pH of 7.36. The sand, silt and clay contents of the upper soil (0–15 cm) were 32.6%, 44.7% and 22.7%, respectively. Organic carbon concentrations were 4.6% in the upper 0–15 cm layer, 2.5–1.9% in 15–40 cm layer, and 1.5% in the 40–70 cm.

2.2. Lysimeter

The lysimeter used was set up in 2000. It was constructed by transforming a 1-cm-thick PVC plate into a column (100 cm in height and 80 cm in inner diameter). A carefully chiseled, undisturbed soil monolith (81 cm in length) was tailored to the lysimeter. Next, a layer (4 cm in thickness) of silicon sand, which had been washed with 5% (v/v) HCl and filtered with a 70-mesh sieve, was placed below the monolith. The bottom of the lysimeter was closed with a circular PVC plate, and a percolating outlet was drilled in its center.

On November 10, 2007, the plowed layer of soil (0–15 cm in depth, ~90 kg) was removed from the monolith, air-dried, crushed, and mixed thoroughly with phenanthrene-[9-^{14}C] (Hartmann Analytic GmbH, Braunschweig, Germany; 99% purity) (^{14}C radioactivity 1.61×10^9 DPM in all), whose final concentration in soil reached 126.32 mg/kg soil. Finally, the polluted soil was added back into the lysimeter. Since the plowed layer was originally poorly structured, presumably, spiking did not adversely alter its structure.

Field management of plants followed agricultural practices of the local farmers. On November 15, 2007, wheat was sowed in hills at a density of 10 seeds per hill. There were 7 hills in the lysimeter, and wheat was harvested on May 29, 2008. Nitrogen fertilizer was provided during tillering stage as urea (150 kg h^{-1}). There was no artificial irrigation in wheat season. Rice was planted on June 20, 2008, and harvested on November 4, 2008. The rice seedlings were manually transplanted at a density of 3 seedlings per hill, and the lysimeter consisted of 7 hills. Base fertilizer, tillering stage fertilizer and head fertilizer were also provided as urea (150 kg h^{-1}) separately. In rice season, the soil was kept submerged. Rainfall was abundant in this season. There were 43 times recorded with precipitation ranging from 0.1 mm to 32.4 mm and about 417 mm in total amount. Irrigation was carried out daily according to a fixed level of submersion (6 cm above the soil surface) except for rain and the period restraining the inefficacious tillering (August 13–19, and 23–26).

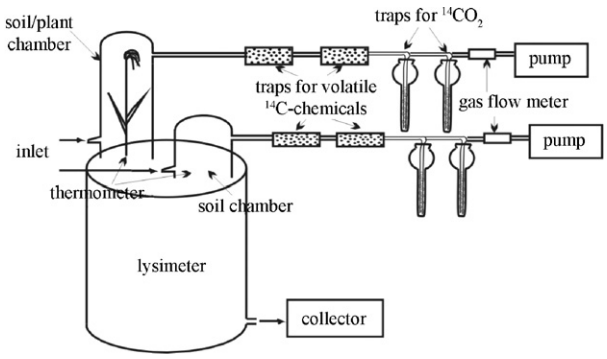

Fig. 1. A two-chamber system to quantify the mineralization and volatilization of ^{14}C-labeled chemicals from soil surfaces with plant and without plant separately.

2.3. Analysis of gaseous losses

A two-chamber system was set up to quantify the gaseous losses of ^{14}C-labeled chemicals from soil surfaces with plant (soil/plant chamber) and from surfaces without plant (soil chamber), separately. The system was constructed according to that used by Schroll et al. [22] but with some modifications to facilitate the long time practice in field (Fig. 1). Both the soil chamber and the soil/plant chamber were made of glass, 15 cm in diameter. At the low part of the chambers, there were tightly joint stainless steel metal frame, which were pressed completely into the soil to avoid the transfer of air containing ^{14}C-chemicals from the around soil surface into the chambers. Soil without plants was covered by the soil chamber. Soil with a hill of wheat plants was covered by the soil/plant chamber. The height of the soil/plant chamber was increased from 15 cm to 100 cm with growth of wheat.

Small thermometers were placed in the middle and the outside of the chambers to compare the inside soil microclimate with the outside one. The flow rate of the air was controlled by two flowmeters in accordance with the temperature indicated by the thermometer. The air in the chamber was changed more than once per minute (with the flow rate at about 3 L/min) to reduce the difference between the inside and the outside temperatures.

More than 10 m away from the lysimeter, the air which was free of ^{14}C-labled chemicals was pumped into the chambers. The air was filtered through a specially designed trapping-system consisting of two resin adsorption columns (3 cm in diameter and 20 cm in height) and two CO_2 absorption bottles (5 cm in diameter and 50 cm in height). The columns were filled with resin NDA-150 provided by Aimin Li from Nanjing University, China [23] to trap ^{14}C-labeled volatile organic compounds (VOCs). Each of the CO_2 absorption bottles contained 1 L of 2 M NaOH to trap $^{14}CO_2$. The resin and NaOH solution in the trapping system were changed and collected weekly; the trapped components were extracted and analyzed for radioactivity. The sampling system wall was made of glass or Teflon to minimize adsorption effects.

The experiment of determining gaseous losses started on November 10, 2007 and ended on May 23, 2008. The ^{14}C-labled VOCs trapped in the resin were extracted with a mixture of acetone and n-hexane (1:1 v/v) for 24 h [24], and aliquots of the resulting extracts were mixed with equal volumes of a scintillation cocktail (Lumasafe Plus, Lumac LSC BV, Groningen, The Netherlands). The total volume of NaOH solution with trapped $^{14}CO_2$ was measured and aliquots of the solution were directly mixed with the scintillation cocktail (Lumasafe Plus, Lumac LSC BV, Groningen, The Netherlands; 1:3 v/v). ^{14}C-acitivity in each aliquot was quantified by a liquid scintillation counter (LS6500, Beckman Coulter TM, USA).

In the lysimeter, the total amount of ^{14}C emitted by soil with plant surfaces was calculated from the amount of ^{14}C emitted by one hill of plants in soil/plant chamber with an area of 176.71 cm^2 multiplied by the total number of hills (n = 7) of plants in the lysimeter. The total amount of ^{14}C emitted from soil without plant material was calculated from the surface of the lysimeter (5026.55 cm^2) minus the total surface of soil with plants (surface covered by one soil/plant chamber multiplied with 7; 176.71 cm^2 × 7 = 1236.97 cm^2).

2.4. Plant analysis

Wheat plants were sampled at five growth stages: seedling (February 28, 2008), tillering (March 21, 2008), heading (May 5, 2008), booting (May 16, 2008), and grain maturity (June 10, 2008) stages. Rice plants were sampled at four growth stages: tillering (August 4, 2008), heading (August 22, 2008), booting (September 10, 2008), and grain maturity (October 24, 2008) stages. At grain maturity, the plants of wheat or rice were harvested and divided into five parts (leaves, stems, shells, grains, and roots).

Plant samples were lyophilized and intensively homogenized. Aliquots of the homogenized samples were extracted and ^{14}C-activity in the resulting extract was quantified according to the method for analyzing ^{14}C-labled VOCs in resin as described in Section 2.3.

2.5. Soil analysis

In the wheat season, surface soils (0–15 cm in depth) were collected at its seedling, tillering, heading, and booting stages. In the rice season, surface soils were sampled at its tillering, heading, and booting stages. Soil cores (2 cm in diameter and 80 cm in depth) were sampled after the wheat harvest on June 20, 2008 and the rice harvest on November 4, 2008, respectively. The soil cores were sampled using an earth boring auger (2 cm in diameter). Samples were taken layer by layer, at 10-cm-deep intervals. Each soil layer was thoroughly mixed, and a tiny amount of soil samples was taken from each layer for determination of ^{14}C-activity. Soil cores in the same size were also taken from the control field, and the same amounts of soil were sampled from the corresponding layers. Soil from lysimeter left after sampling and soil samples from control field were mixed layer by layer. The holes in the lysimeter were then carefully restocked with the mixed soil of related layer and compacted.

Soil samples were lyophilized and intensively homogenized. The homogenized soil samples were extracted and the extractable ^{14}C-activity was quantified according to the method for analyzing ^{14}C-labled VOCs in resin as described in Section 2.3. To determine the total ^{14}C-activity of soil, 1.0 g of soil was combusted at 800–900 °C in a combustion unit (Ox500 Biological Oxidizer, Zinsser Analytic, Germany) and then mixed with a scintillation cocktail (Oxysolve C-400, Zinsser Analytic, Germany). The ^{14}C-activity in nonextractable soil residues (nonextractable ^{14}C-activity) was calculated by subtracting the extractable ^{14}C-activity from the total ^{14}C-activity of soil.

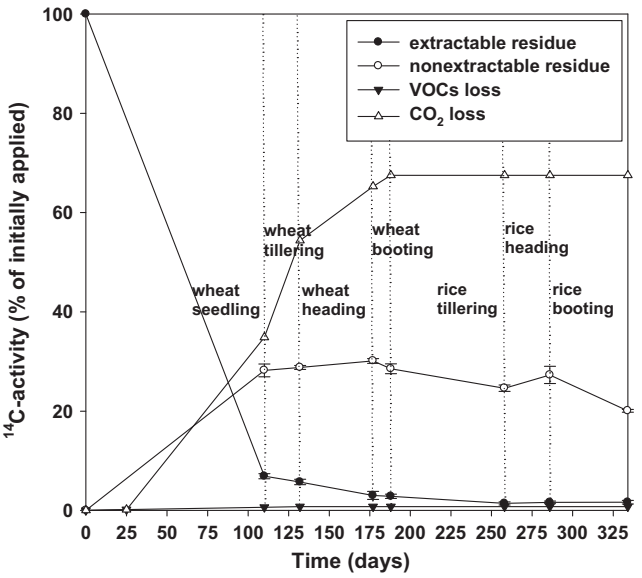

Fig. 2. Temporal changes in ^{14}C-chemical concentration in the surface soil (0–20 cm) and gaseous losses from the surface of the lysimeter. Four curves show changes in extractable ^{14}C-activity, nonextractable ^{14}C activity in soil, $^{14}CO_2$ loss and ^{14}VOCs loss, respectively. ^{14}VOCs were not detectable after 132 days, and $^{14}CO_2$ were not detectable after 188 days. ^{14}VOCs loss after 132 days and $^{14}CO_2$ loss after 188 days were not changed. ^{14}C-radioactivity applied = 100%.

2.6. Leachate analysis

In the wheat season, due to the dry climate, only two leachate samples were collected: 10.7 L obtained on January 23, 2008 and 11.5 L on February 2, 2008, caused by a heavy rainfall and a heavy snow, separately. In the rice season between June 20, 2008 and October 6, 2008, which was a local rainy season, 2.5 L (calculated from the leaching rate of the soil) of leachate was collected daily when the lysimeter was in submersion condition.

Leachate samples were analyzed immediately for radioactivity or stored at 4 °C for the analysis in 3 days. Aliquots of the leachate were directly mixed with the scintillation cocktail (Lumasafe Plus, Lumac LSC BV, Groningen, Netherlands; 1:3 v/v), and quantified for ^{14}C-activity.

3. Results and discussion

3.1. Gaseous losses of phenanthrene

As shown in Fig. 2, during the wheat season, volatilization and mineralization of ^{14}C-labeled phenanthrene occurred immediately after it was applied to soil. ^{14}C-labeled VOCs were detectable up to 18 weeks after the application, but not after the tillering stage. The process of producing $^{14}CO_2$ began with a slow phase (about 25 days), followed by a faster one and then a gradually decelerating one. Total gaseous losses of ^{14}C-phenanthrene accounted for 68.3% of its applied amount. Compared to VOCs, CO_2 was the main transformation product of phenanthrene, for 67.5% of initially applied ^{14}C evaporated from soil as $^{14}CO_2$.

In Table 1, we compared the gaseous losses from both "surface of the soil" and "surface of the soil/plant chamber" based on an identical surface area of 176.71 cm^2. At all growth stages of the wheat season, except for the seedling period, the presence of wheat plants in soil resulted in reductions of the gaseous losses of phenanthrene from soil surfaces. This is mainly due to that VOCs and CO_2 emitted

Table 1
Effect of wheat plants on gaseous losses of phenanthrene[a].

^{14}C-activity (% of applied radioactivity)	Seedling stage		Tillering stage		Heading stage		Booting stage	
	Soil/plants[b]	Soil[c]	Soil/plants	Soil	Soil/plants	Soil	Soil/plants	Soil
VOCs	0.009	0.019	0.004	0.005	ND[d]	ND	ND	ND
CO_2	1.422	1.225	0.187	0.830	0.300	0.414	0.064	0.087
Total	1.431	1.244	0.191	0.835	0.300	0.414	0.064	0.087

[a] Values represent ^{14}C emitted from a chamber area (176.71 cm^2).
[b] Soil surface covered with plants.
[c] Soil surface without plants.
[d] Not detected.

from the soil could be taken up by plant surfaces in the soil/plant chamber. VOCs like lipophilic chemicals can be easily taken up or adsorbed by lipophilic plant surfaces, and CO_2 as well as $^{14}CO_2$ could be taken up by plant as well to form ^{14}C-biomass. These are important routes for the uptake of ^{14}C into plants [25].

3.2. Movement of phenanthrene through the soil column

As shown in Fig. 2, after ^{14}C-labeled phenanthrene was applied to the soil, the total ^{14}C-activity in the surface soil (0–20 cm) decreased rapidly at the earlier growth stages of wheat, which was consistent with the pattern of the gaseous losses of phenanthrene; it then declined slowly at the later growth stages of wheat and finally kept relatively steady in the rice season. After a winter season of aging, most of ^{14}C-activity remained in nonextractable soil residues.

Fig. 3 shows vertical distributions of ^{14}C-activities in two soil cores after the wheat harvest and the rice harvest, respectively. For each core, the ^{14}C-activity in its 0–10 cm soil layer was the highest. This result agreed with the documented finding that topsoil contained more PAHs than subsoil [10,26–28]. Besides, the vertical distribution patterns of ^{14}C-activities in the two soil cores displayed some dissimilarity. In the rice season when the soil was flooded, probably due to the wash effect of the leaching of ^{14}C-labeled chemicals, ^{14}C-activities in the 0–10 cm layer of the soil core sampled were lower than their counterparts in the wheat season; in contrast, the extractable ^{14}C-activity in the 10–20 cm and 20–30 cm layers of the soil core sampled in the rice season was higher than its counterpart in the wheat season. Most likely, the pollutant applied into the soil as extractable ^{14}C-phenanthrene initially was subject to aging process. Accordingly, ^{14}C-activities in 30–80 cm layers were detected only as extractable ^{14}C-activities in the wheat season, while they were detected mostly as nonextractable ^{14}C-activities in the rice season.

In this study, the groundwater level of the research site was about 20 cm deep in the rainy season and depressed to a depth of 100–120 cm in the dry season. The result that ^{14}C-activity was detected in every layer of the soil column implies that vertical migration of PAHs can result in serious contamination of groundwater.

3.3. ^{14}C-activity detected in leachate

For the wheat season, two leachate samples collected contained ^{14}C-labeled chemicals at concentrations (transferred to phenanthrene equivalent) of 2.36 mg/L and 0.41 mg/L, respectively. It is worth noticing that the radioactivity detected in the first leachate is higher than the solubility of phenanthrene (1.29 mg/L). This difference can be explained: (1) the detected radioactivity came from ^{14}C-labeled chemicals rather than only ^{14}C-phenanthrene, the parent compound; (2) some factors, such as dissolved organic carbon (DOC) and colloid-facilitated transport, might have affected the transport of phenanthrene in the lysimeter. It has been proved that movement of PAHs through the soil column is associated with leachate [29] or with movement of particles [2].

In rice season, ^{14}C-activity was detected in each leachate sample (Fig. 4), indicating that the pollutants leached into deeper soil layers under real field conditions, which was consistent with the documented finding that leaching was an important mechanism of vertical transmission of the contaminants [2,29]. In addition, ^{14}C-activities in leachates varied with sampling time over a range from 0.12 to 0.76 mg/L with average concentration of 0.51 mg/L, and the variation seemed to be irregular. In this experiment, this was very likely due to the concentrations of ^{14}C-labeled chemicals in soil fluctuating with time and flooded conditions resulting from

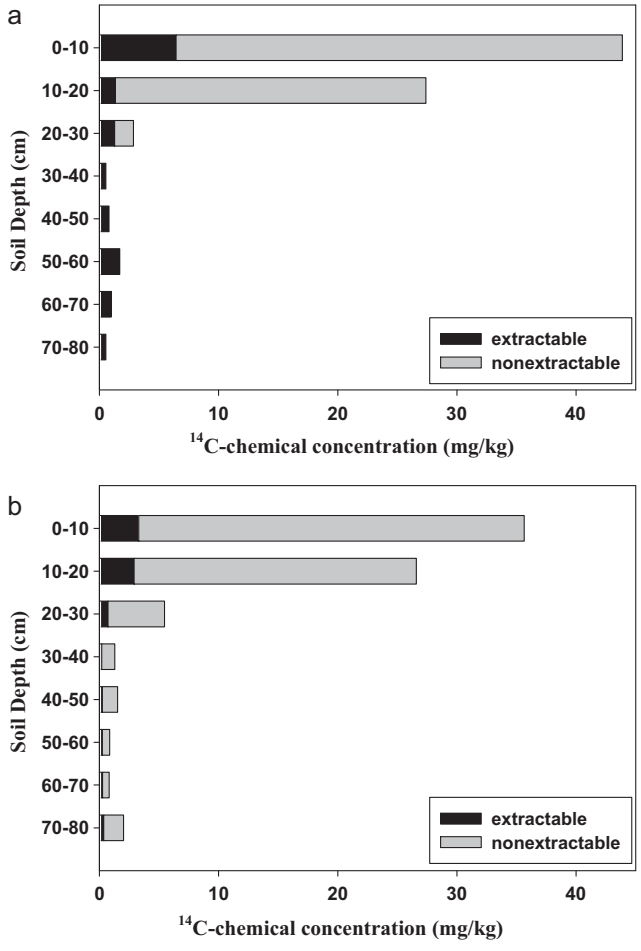

Fig. 3. Vertical distribution of ^{14}C-chemical (mg/kg dry soil as phenanthrene equivalent) in the soil column. Each bar represents extractable (black) and nonextractable (grey) ^{14}C-activity in a 10-cm-deep layer of the soil core sampled after the wheat harvest on June 20, 2008 (a) or the rice harvest on November 4, 2008 (b).

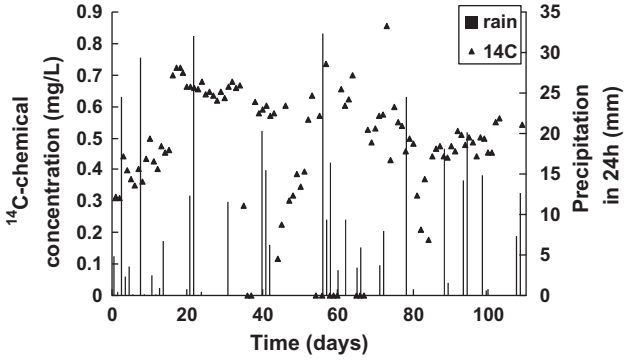

Fig. 4. Variation in ^{14}C-chemical concentration (mg/L as phenanthrene equivalent) in leachate over time (June 20, 2008 to October 6, 2008, 109 days in all) and rainfall (mm) during the period. Each spot represents ^{14}C-chemical concentration in the leachate sampled in a single day in the rice season. Each bar represents rainfall in 24 h.

watering and rainfall. Without runoff out of the lysimeter, the concentrations of ^{14}C-labeled chemicals changed mainly due to rainoff and evaporation in the lysimeter. Rain eluviation might induce the release of ^{14}C-labeled residues, increasing the concentration in leachate (Fig. 4).

3.4. Accumulation of ^{14}C-labeled chemicals by plants

Accumulation of ^{14}C-labeled chemicals by plants at different growth stages is shown in Fig. 5. The ^{14}C-activities in wheat at the seedling and tillering stages were greatly higher than those at the heading and shooting stages. The apparently lower ^{14}C-actvities at the two later stages might be due to the biomass of wheat increased by its growth, which did not exclude that the total amount of ^{14}C-chemicals in plant increased with the time. On the other side, the ^{14}C-activity in rice kept at a steady level over three tested growth stages. After ^{14}C-labeled chemicals experienced the earlier loss processes including gaseous losses and leaching, their residues remaining in soil tended to stabilize in the rice season.

As shown in Fig. 6, ^{14}C-labeled chemicals were accumulated by different organs of wheat or rice at grain maturity. For both wheat and rice, ^{14}C-actvities in five organs of the mature plants decreased in the following order: roots > leaves > shells > stems > grains. The documented studies also showed that PAHs were unevenly distributed in different organs of crops [30–33]. The result that ^{14}C-activity was detected in grains (Fig. 6) suggests that pollutants in soil can be incorporated into field-grown food, threatening its security.

3.5. Mass balance of applied ^{14}C

Table 2 shows distribution and mass balance of initially applied ^{14}C in the lysimeter after the harvests of rice. Considering the influence of the plant chamber on crop growth in the hot season as well as the data of volatilization in the later stages of the wheat season, the gaseous losses of applied ^{14}C were not determined in the rice season. The total residual ^{14}C in the soil column was calculated by adding up its concentration in each layer. Plant uptake was calculated as extractable ^{14}C-activity only, which would cause underestimation of the ^{14}C-recovery. However, due to the low biomass of plants, it had little influence on the recovery.

As shown in Table 2, 110.25% of the ^{14}C initially applied to the lysimeter was recovered after the harvests of rice. The overestimation of the ^{14}C-recovery could be the result of processes of sampling and analysis, especially in gaseous losses. In this study, the air change in the chambers was enhanced to reduce the temperature difference, which simultaneously increased the gaseous

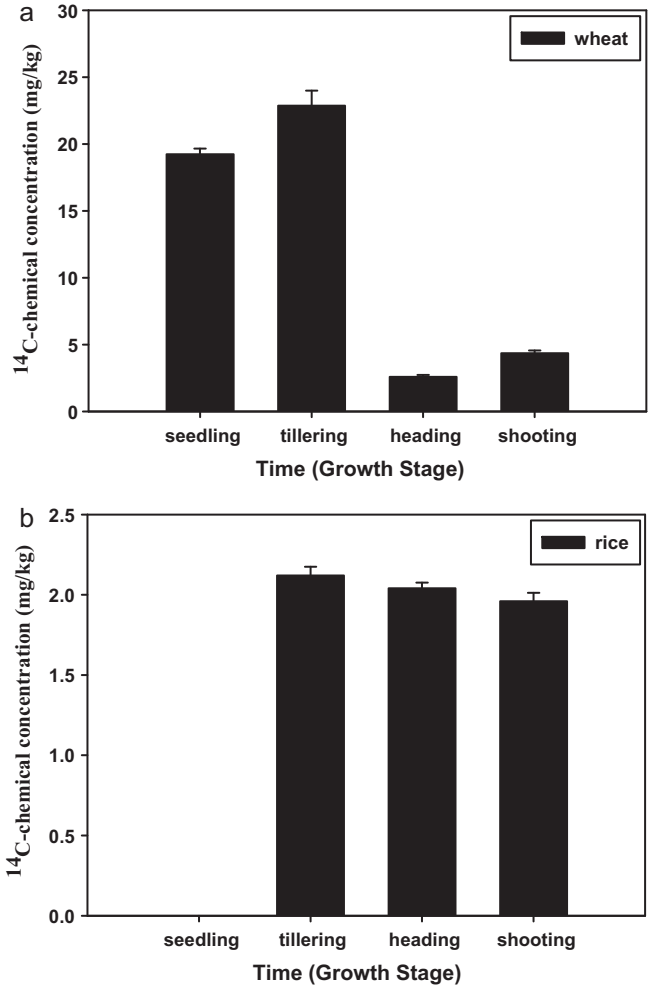

Fig. 5. Accumulation of extractable ^{14}C-labeled chemicals (mg/kg dry plant as phenanthrene equivalent) by the shoots of wheat (a) and rice (b) at different growth stages.

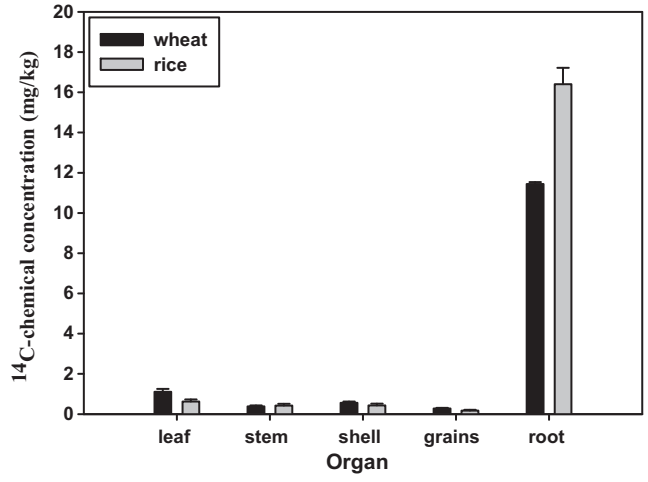

Fig. 6. Accumulation of extractable ^{14}C-labeled chemicals (mg/kg dry plant as phenanthrene equivalent) by five organs of mature wheat or rice. Each bar represents extractable ^{14}C-activity in a plant organ after the harvest of wheat on June 20, 2008 or rice on November 4, 2008.

Table 2
Distribution and mass balance of applied ^{14}C in the lysimeter after the harvests of rice.

^{14}C (% of applied radioactivity)	Gaseous losses	Residues in soil[a]	Plant uptake[b]		Leaching loss		Total
			Wheat	Rice	Wheat season	Rice season	
After the rice harvest	68.27	39.17	0.008	0.024	0.26	2.52	110.25

[a] Total residual ^{14}C in the soil (0–80 cm), calculated by adding up its concentration in each layer.
[b] Extractable ^{14}C in plants.

losses. Accordingly, gaseous losses from the lysimeter were overestimated. Nevertheless, the outdoor plant–soil–atmosphere system established in this study allows an overall evaluation of the behavior of ^{14}C-labeled phenanthrene in a terrestrial model ecosystem under real environmental conditions.

4. Conclusions

To investigate the fate of phenanthrene in agricultural soil, we employed ^{14}C tracer and lysimeter to increase the ease, sensitivity, and accuracy with which mass balance measurements can be conducted to determine the fate. The results from various aspects showed that using ^{14}C as a tracer was sufficient to estimate the fate of organic pollutants which were very difficult to degradation with long half-life in soil, such as higher molecular weight PAHs. For low molecular weight PAHs such as phenanthrene, ^{14}C-isotopic mass balance was not sufficient to describe the mass balance of target pollutants, and it needed to be supplemented with GC–MC to distinguish the parent compounds and metabolites. In addition, the study performed over a year in agricultural soil offered a good insight into the fate of the PAHs under environmentally realistic conditions. Sequentially, the residues in soil still need our follow-up investigation over years.

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