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Effect of linear alkyl benzene sulfonates (LAS) on the fate of phenanthrene in a model ecosystem (water-lava-plant-air)

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Abstract: Advanced closed chamber system was used to study the fate of phenanthrene (3-rings PAHs) in the presence of linear alkylbenzene sulphonates (LAS). The results showed mineralization and metabolism of phenanthrene are fast in the "culture solution-lava-plant-air" model ecological system. The distribution proportions of applied ^{14}C-activity in this simulative ecological system were 41%—45%, 14% to 10% and 1% in plant, lava and culture solution respectively, and 18% to 29%, 11% to 8% recovered in the forms of VOCs and CO_2. Main parts of the applied ^{14}C-activity exist in two forms, one is polar metabolites(25%) which mainly distribute in the root(23%), the other is unextractable part(23%) which have been constructed into plant root(8.98%), shoot(0.53%) or bonded to lava(13.2%). The main metabolites of phenanthrene were polar compounds(25% of applied ^{14}C-activity), and small portion of ^{14}C-activity was identified as non-polar metabolites(6% of applied ^{14}C-activity) and apparent phenanthrene(1.91% of applied ^{14}C-activity). Phenanthrene and its metabolites can be taken up through plant roots and translocated to plant shoots. The presence of LAS significantly increased the the concentration of ^{14}C-activity in the plant and production of VOCs, at the same time it decreased the phenanthrene level in the plant and the production of CO_2 at the concentration of 200 mg/L.

Keywords: phenanthrene; LAS; plant; closed chamber systems

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are by-products from the incomplete combustion or pyrolysis of organic materials. These aromatic compounds are ubiquities and can be found in plant and animal tissues, surface waters, sediments, soils, and air(Edwards, 1983). Phenanthrene is one of the mostly distributed PAH compound in the environment, contains three fused benzene rings. It has often been used as a model compound for studying the fate of PAHs.

Linear alkyl benzene sulfonates (LAS) is a group of anionic surfactants. It is one of the major ingredient of synthetic surfactants and is used worldwide for both domestic and industrial applications. The annual worldwide consumption of LAS is approximately 2×10^6 ton per year(de Wolfe, 1998).

The coexistence of LAS and phenanthrene in the environment is a common fact. It is important to have more information on the interaction of LAS and phenanthrene in the environment. The experiments described in this study have been conducted using two closed cultivation chamber systems. The advantages of these "closed chambers" compared with field experiments are: (1) climatic conditions such as temperature, humidity, light, wind velocity, can be controlled facilitating the reproducibility of experiments; (2) gas phase can be controlled by filters which are designed to prohibit undesired input of airborne pollutants; (3) ^{14}C-labeled test substances can be applied to explain the degradation and transfer processes of test substances within the system and to make mass balance possible and to monitor the occurrence of volatile test substances, their volatile metabolites and the degradation end-product CO_2 in the gas phase. All these information are useful to evaluate the fate of organic chemicals by means of quantitative balances.

1 Materials and methods

1.1 Chemicals and reagents

Water and solvents: Water used was generated by a millipore water purifying system (Milli-RO plus + Mill-Q plus). All solvents were GC or HPLC grade and used as received. Methanol, cyclohexane, chloroform, and ethylene glycol monomethyl ether (EMME) were purchased from MERCK (Darmstadt, Germany). Acetone and dichloromethane were obtained from Riedel-deHaën (Seelze, Germany).

Phenanthrene: The 9-^{14}C-labeled phenanthrene was purchased from Biotrend Chemical (Köln, Germany) with a purity of more than 99% and specific activity of 55mCi·mmol^{-1}. Before use, the purity of the ^{14}C-phenanthrene was

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checked by thin layer chromatography (TLC). Unlabeled phenanthrene with a purity of 99.5% from Aldrich-Chemie was used additionally.

Surfactant (LAS): Anionic surfactant LAS (linear alkybenzene sulphonate) was obtained from Sigma-Aldrich Chemie(Steiheim, Germany) and used as received.

Reagents and cocktails for measurement of ^{14}C-activity: PERMABLEND® Ⅲ (PPO 91% + bis-MSB 9%) was obtained from PACKARD Instruments (Meriden, USA). PERMAFLUOR® E$^+$, CARBO-SORB® E (3-metho-xypropylamine), and ULTIMA GOLD™ (XR) were products of PACKARD BioScience B. V. (Gröningen, The Netherlands).

Cocktail-I for measuring ^{14}C-VOCs (volatile organic compounds) consisted of 11 g of PERMABLEND® Ⅲ dissolved in 1 liter toluene. Cocktail-Ⅱ for absorption and measurement of $^{14}CO_2$ was a mixture of CARBO-SORB® E and PERMAFLUOR® E$^+$ in a ratio of 2:3 (v/v).

Characteristics of the "closed chambers", a laboratory ecosystem: Dimensions of two identical "closed chambers" are: 1.2 × 1.0 × 0.6(height × length × width) = 0.72 m^3, built with UV-permeable glass and stainless steel frames. Upper part of the chambers can be opened with the help of a lifting. Each of the glass tanks is mounted on movable racks. Wind velocity with average speed is variable in the range of 4 m/s—8 m/s. The high wind velocity prohibits re-assimilation of $^{14}CO_2$ from the degradation of test substances into plants.

Light regime consists of a combination of UV light, regular light bulbs and special plant growth lights, which providing 21 W/m at 0.5 m height for the spectrum of 350—770 nm. Temperature is variable between 15℃ and 30℃, regardless of outdoor weather conditions. Relative humidity can be varied from 40% to 80%.

Controlled air supply consists of two separate parts of cultivation container and adsorption devices for trapping volatile organic chemicals(VOCs), metabolites, and for the end degradation product $^{14}CO_2$ formed by the mineralization of the test chemical. The system is shown in Fig.1.

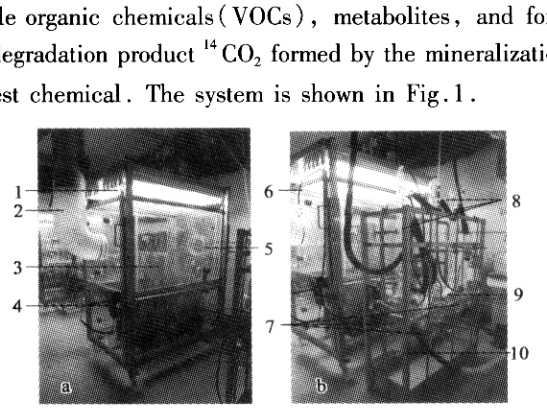

Fig.1 Closed chamber system(a) and its adsorption devices(b)
1. light regime; 2. air outlet; 3. plant(Juncus effuses); 4. hygrometer; 5. air inlet; 6. Teflon pipe for branch air out; 7. adsorption glass bottle; 8. upper system; 9. lower cooler system; 10. holes for sampling

The inlet air is filtered by two different filters, which remove small particles and volatile organic pollutants. Before the chambers are used, required temperature, air humidity are regulated accordingly to experimental require. Volatile organic components of the test substance and organic metabolites, and metabolite CO_2 are adsorbed from the exhaust air on branch glass plug mounted in the air outlet holes in the chamber as well as in the main exhaust air pipe that conducts away all the air leaving the chamber. In order to quantitative determine, these components in the exhaust air were achieved by means of separating out part of the airflow from the overall airflow through a controlled valve with mass flowmeter (Gossen, model 5876) for the purpose of analysis. After the air has passed through the glass plug, three large cooled absorption traps connected with glass plug through Teflon pipe are used to quantitatively bind the volatile organic compounds and the carbon dioxide (inactive and radioactive) from the analytical airflow (Fig.1b). The precisely defined and controlled split ratio permits the total amount of ^{14}C-VOCs and $^{14}CO_2$ leaving the system to be calculated. The outlet air is filtered by charcoal in order to trap the residual $^{14}CO_2$.

1.2 Experimental procedure

Preparation of lava: Lava material(normal diameter 2—8 mm) was used as a supporting culture media for plant growth. It contains low organic matter (< 0.2%) and therefore shows weak adsorption capacity for PAHs (He, 1996). It was used after drying at 105℃ to stabilize its weight.

Plants(hydrophytes): The plants(Juncus effusus) used for this study were bought from Renatur, Germany, and kept under controlled conditions in phytothrone at 19℃, 60% humidity and the 16:8 light cycle on/off. After the arrival of the pre-cultivated plants, the roots were cleaned off soil particles carefully with water and were placed in the glass tanks (40 cm × 25 cm × 30 cm) which containing 5 kg lava and 5.5 L nutrient solution. After an adaptation time of six weeks, they were transported to the closed chambers and allowed to acclimate for 8 d in the "closed chambers" prior to dosing the nutrient solution with ^{14}C-phenanthrene. 250 ml mixture of distilled water and nutrient solution (V : V = 70 : 30) was added daily into the glass tank to compensate the losses due to the evapotranspiration.

Preparation of phenanthrene column: In order to obtain high concentrated aqueous stock solution of phenanthrene, so called "phenanthrene column" was prepared using sterile millipore water(SMW) as follows: A glass tube (1.5 cm i.d. × 25 cm length) with stopper and a small piece of glass wool was packed with glass beads (ca. 2 mm) to a length of ca. 20 cm and rinsed with acetone(50 ml), dichloromethane (50 ml) and cyclohexane(50 ml) successively. In order to obtain an application concentration of 75 μCi per closed chamber and final phenanthrene concentration of 500 μg/L in feeding nutrient solution, the ^{14}C-labeled phenanthrene was mixed with the unlabeled inactive phenanthrene. Therefore,

5 ml of 500 mg/L unlabeled phenanthrene solved in dichloromethane and 406 μl ^{14}C-phenanthrene(55 mCi/mmol) in methanol were slowly applied to the glass column while nitrogen gas was blowing from the bottom through the column to evaporate the solvent. After the solvent had been completely evaporated, the column was prepared for adding ^{14}C-phenanthrene into glass tank with the aid of apparatus shown as Fig.2.

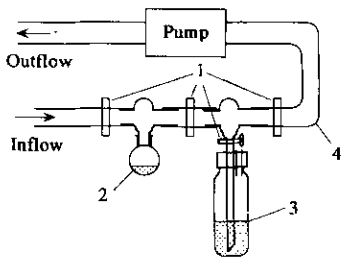

Fig.2 The apparatus for nutrient solution addition and its samples collection
1. control volve; 2. glass bottle for samples collection; 3. glass bottle for nutrient solution; 4. Teflon pipe

Culture and measurement of degradation: This test was studied with two same closed cultivation chamber systems, applied with "phenanthrene" and "LAS plus phenanthrene" respectively. Glass tanks with the test plants were put into the closed chambers and the system was assembled as illustrated in Fig.1.

After 8 d adaptation for the plant, the first trap(Fig. 1b) was filled with a 100 ml EMME to absorb VOCs, the second and third traps were filled with 100 ml 1 mol NaOH to absorb active and inactive CO_2. 100 ml LAS stock solution (11000 mg/L) was added into one of closed chamber systems. The phenanthrene columns were connected to both of closed chambers and rinsed by the circulation of the culture solution with the aid of pump. The pump ran at 90 L/min for first 2 h, 30—60 L/min for another 22 h except sample collection at the beginning of the experiment. Then pump ran at 90 L/min for 30 min before collecting nutrient solution sample. The phenanthrene columns were disconnect from the system 2 d later and dried with nitrogen air. Then they were rinsed with 100 ml EMME and measured on Liquid Scintillation Analyzer (LSA, Parkard Tri-carb). At 23 d later, 2.06 mg mixture of active and inactive phenanthrene (at the same radio as above) was compensated by the same method into both closed chamber systems. After 46 d exposure, nutrient solution, lava and plants were extracted and analyzed for residual ^{14}C-activity and metabolites.

Experimental sampling: Culture solution in glass tank was collected every 2 h at the first 24 h after addition of test chemicals in order to ensure that phenanthrene could be dissolved in the nutrient solution totally, then collected once a day. Replicate 5 ml culture solution were removed from sample glass bottle(Fig.3) and mixed with 15 ml ULTIMA GOLD™(XR) in 20-ml LSA vials and counted on LSA for ^{14}C-activity.

Trap solution samples were collected once a day for measuring ^{14}C-VOCs and ^{14}C-CO_2. Triplicate of EMME(10 ml) from the first trap were mixed with 10 ml Cocktail-Ⅰ and measured in LSA. Solution samples from the second and third traps had to be transferred into ^{14}C-CO_2 before measured on LSA. Transferring system is shown in Fig.3.

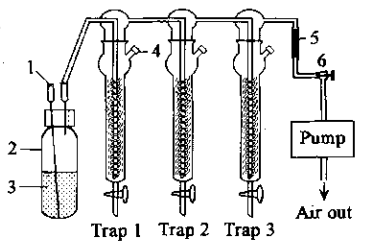

Fig.3 The transformed equipment for CO_2
1. air and HCl inlet; 2. sample bottle; 3. sample solution from the second and third trap in the closed chamber system; 4. glass cap; 5. glass tube with active charcoal; 6. control valve

After the sample bottles were connected with the system (Fig.3), 32% HCl (20 ml) was dropped into bottles filled with solution from the second and third traps slowly by pippet. During this period, the pump was running continuously. Procreant CO_2 was absorbed by a serious of trap systems, which were filled with 15 ml Cocktail-Ⅱ. After HCl addition, pump still ran for another two hours for adequate uptake of CO_2. Then, the trap solution and 5 ml Cocktail-Ⅱ used to rinse the trap system were collected and counted on LSA.

Plants were harvested after 46 d exposure. The plants got from the "phenanthrene" and "LAS plus phenanthrene" treated systems were both cleaned with the 100 ml mixture of acetone and distilled water(V : V = 50 : 50) to remove ^{14}C-compounds absorbed on their surface three times. The radioactivity in the washing solution was measured on LSA by adding cocktail ULTIMA GOLD™. Then the plants were separated into stems and roots and cut into small pieces. Plant samples were freeze-dried. Twelve replicate samples (0.1 g) of each plant part from different treatments were oxidized with a Packard Tricarb oxidizer, and levels of radioactivity were determined by LSA to be the total radioactivity in the shoot or root. The remaining samples were stored at −80℃ for later extraction.

Lava samples were freeze-dried and milled into fine powder. Twelve samples (1 g) were oxidized, and levels of radioactivity were determined by LSA to be total radioactivity in the lava. The remaining samples were stored at −80℃ for later extraction.

Extraction and analysis of culture solution after termination of culture: Nutrient solution was extracted three times with 40, 30 and 20 ml cyclohexane, respectively. The combined organic phase and the extracted aqueous phase were counted on LSA for ^{14}C-activity representing the total non-

polar and polar metabolites derived from ^{14}C-phenanthrene, respectively.

The organic extract was dehydrated by filtrating through 30 g anhydrous sodium sulfate held in a funnel plugged with glass wool. It was then evaporated to 0.1 ml on a rotary evaporator at water bath temperature of 35℃, cooling temperature of 4℃ and vacuums of 150 mPa and dried to dryness with nitrogen flow and reconditioned in 1ml methanol. 100 μl extract was then cochromatographed with known amounts of ^{14}C-phenanthrene standards by thin-layer chromotography (TLC, 0.25mm Silica, 60F254, Laboratorium BERTHOLD, Wildbad, Germany). The TLC eluant was mixture of chloroform, acetic acid and methanol (V∶V∶V = 90∶5∶5). After developed and air-dried, the plate was placed under UV light and ^{14}C-phenanthrene was identified by comparison with the standard phenanthrene. Spots of phenanthrene and its metabolites were scraped under dim light into LSA vials, respectively. 15 ml ULTIMA GOLD™ was added and ^{14}C-activity was counted on LSA.

Extraction and analysis of lava after termination of culture: 10 g dried lava power was extracted with 20 ml dichloromethane (DCM) using ultrasonic for 1 h, and the extract was allowed to settle down overnight. One part of the supernatant was counted for ^{14}C-activity on LSA, which depicted the total extractable ^{14}C-compounds associated with lava. The remained extract of known volume was dried on a rotary evaporator and reconditioned with 1 ml methanol. To separate phenanthrene and its metabolites, the certain volume of the methanol extract was applied to a TLC plate and developed with cyclohexane. After identified under UV-light, spots of phenanthrene (with R_f value of about 0.5 to 0.6) and its metabolites were scraped into separate LSA vials under dim light. ^{14}C-activity was measured on LSA using the same cocktail that used for nutrient solution. Compound having R_f values higher and lower than that of phenanthrene were defined as non-polar and polar metabolites, respectively. After extracted with DCM, residual lava was combusted and counted for ^{14}C-activity representing un-extractable ^{14}C-compounds in lava.

Extraction and analysis of plant tissue after termination of culture: The procedure for extraction and analysis of shoots and roots was the same as that for lava. The dried plant tissue (1 g) was put into a 100 ml-glass extraction bottle containing 25 ml methanol. The sample was homogenized for 5 min by using a homogenizer (Type: Ultra Turrax T25; Company: Janke & Kunkel, Germany) and then extracted by using ultrasonic for 1 h. In order to prevent the loss due to evaporation, the extraction bottle was placed in ice-water to keep the solution cool during the process of homogenization and ultrasonic extraction. The homogenate was filtered through pre-weighed glass filter paper with the aid of vacuum. Residues on the filter paper were washed with two aliquots of 5 ml methanol, which was also collected and combined into the filtrate. The extract was then evaporated to small volume, dried to the dryness with nitrogen flow and reconditioned in 2 ml methanol. After separated on TLC plate and collected into LSA 5vials containing cocktail, ^{14}C-activity of the phenanthrene and its metabolites was determined in the same way as lava. The methanol-washed residues on the filter was combusted on oxidizer after air-dried and counted on LSA for ^{14}C-activity, which represented the un-extractable compounds in plant tissue.

2 Results and discussion

2.1 ^{14}C budget at harvest in test system

Mass balances of ^{14}C-activity within the closed chambers were examined by measuring ^{14}C-activity in all components of the system. Results, expressed as percentage of ^{14}C-activity recoveries, are presented in Fig. 4. The total recoveries of ^{14}C-activity were 87% and 95% of the applied ^{14}C-activity in the absence and presence of LAS, respectively. At the end of experiment, 38% to 42% of the total ^{14}C-activity applied was found in the plant roots, about 2% in the plant shoots, 1% in culture solution and 10% to 14% in lava. 17% to 29% and 8% to 11% of the total applied ^{14}C-activity volatized in forms of VOCs and CO_2, respectively. Only small amount of ^{14}C-activity (less than 0.55 % of the total ^{14}C-activity) was adsorbed on the surface of apparatus. The presence of LAS alters the total recovery in the test system.

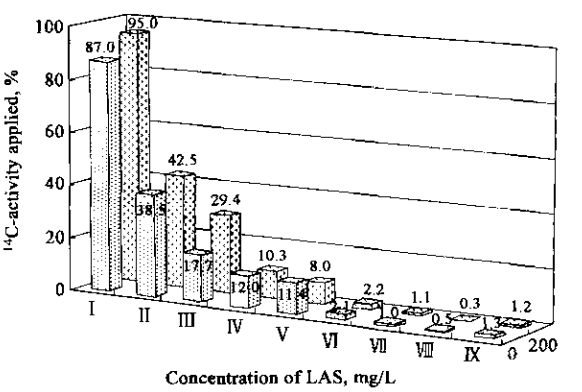

Fig.4 Mass balance and influence of LAS on the distribution of ^{14}C-activity in the test system at the end of experiment
I. total; II. root; III. VOCs; IV. CO_2; V. lava; VI. shoot; VII. culture solution; VIII. apparatus; IX. rinsing solution

2.2 Influence of LAS on the kinetics of volatilization and degradation of ^{14}C-phenanthrene

Fig. 5 presents the kinetics of the emission of VOCs and CO_2 and the decrease of ^{14}C-activity in culture solution during the culture period.

Because of absorption with the plant root, the wall of glass tank and lava, ^{14}C-activity in the culture solution decreased to 49% of the total dose during the first 37 h and tended to reach equivalent. The ^{14}C-activity level in the culture solution remained relative constant after 37 h for about 10 d. And then the ^{14}C-activity level decreased fast and

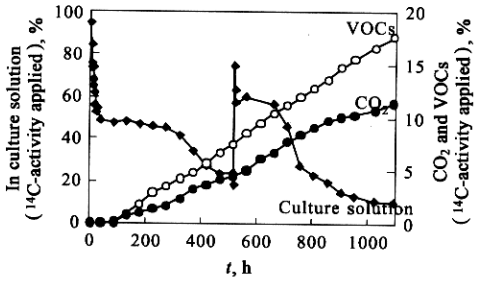

Fig.5 Kinetics of volatilization and degradation of ^{14}C-phenanthrene in the closed "culture solution-lava-plant-air" system without the presence of LAS

ranged from 45% to 25% of ^{14}C-activity applied before phenanthrene was applied once again. For the system with the presence of LAS, the situation was the same as shown as Fig.6.

Fig.6 presents the kinetics of the emission of VOCs and CO_2 and the degradation of ^{14}C-phenanthrene during the exposure period in "culture solution-lava-plant-air" system with absence and presence of LAS. With the presence of LAS, the accumulative production of ^{14}C-VOCs was much higher than without LAS. The possible reasons are due to two aspects: (1) phenanthrene was degraded and metabolized incompletely with the presence of LAS; (2) LAS decrease the interfacial tension, which is easier for VOCs to emit from the culture solution at the same conditions. From Fig. 6b, during the first 500 h, the accumulative production of CO_2 was similar with the absence and presence of LAS. Then the accumulative production of CO_2 was higher with absence of LAS than with presence of LAS. CO_2 was produced by two sources: (1) emission by degradation of microorganism; (2) emission by the respiration of plant which uptake the phenanthrene and its metabolites. It indicates that ^{14}C-phenanthrene can not be degraded completely with the presence of LAS by microbial in the culture solution, which increased the middle metabolites' production. Some of middle metabolites were volatile and carried out by wind, they can not be reused by the plant and microbial to produce the CO_2. All these reasons results the accumulative CO_2 production with the presence of LAS was much lower than with absence of LAS.

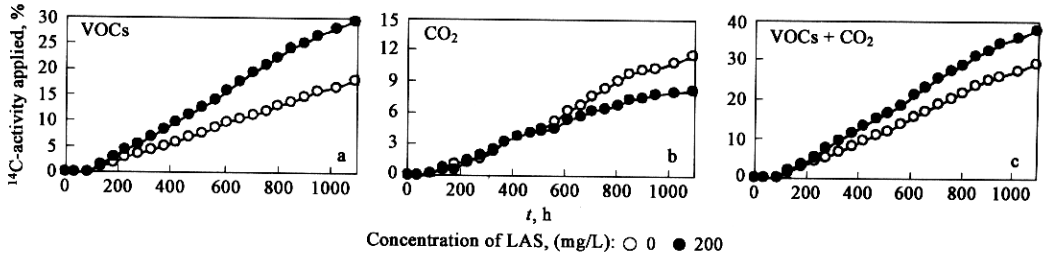

Fig.6 Influence of LAS on the degradation kinetics of ^{14}C-phenanthrene in culture solution-lava-plant-air system

2.3 Distribution of ^{14}C-phenanthrene metabolites among plant tissues and culture media in the absence of LAS

The highest ^{14}C-activity was still found in the root. After washing the roots with a 1:1 mixture of acetone and distilled water, 39% of ^{14}C-activity applied was left. Therefore, it was assumed that about 39% of the total ^{14}C-activity is incorporated with root tissues at harvest (Fig. 4). The percentage of ^{14}C-activity in the shoots was 2%. Lava accounted for 14% of ^{14}C-activity applied, which is higher than with the presence of LAS (10%). The difference between these two systems dues to two aspects: (1) in this experiment with the presence of LAS, LAS was applied into the system first, active hydrophobic adsorption sites on lava were occupied by LAS, which inhibit phenanthrene adsorption to these sites(Ou, 1995); (2) phenanthrene was desorbed from the lava with the present of LAS and dissolved into the LAS micelles. All of these results in adsorption decrease of phenanthrene on lava.

As shown in Fig.7, most of ^{14}C-activity applied is found as polar metabolites (25.45%) and un-extractable part (22.70%). For polar metabolites, it mainly exists in the root for 90%(23.14% of applied ^{14}C-activity). Un-extractable part that could not be extracted with organic solvents such as methanol and dichloromethane had been constructed into plant tissues or bonded to organic or mineral components of lava. This part is mainly found in the lava for 58% (13.2% of applied ^{14}C-activity), and root for 39%

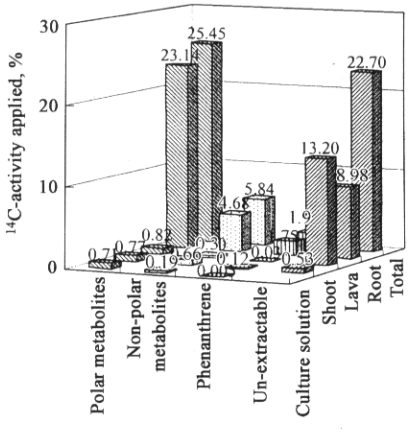

Fig.7 Distribution of ^{14}C-activity in plant tissues and culture media expressed as % of the applied ^{14}C-activity without the presence of LAS

(8.98% of applied ^{14}C-activity). Very small portions were identified as non-polar metabolites (5.84% of applied ^{14}C-activity) and parent phenanthrene (1.91% of applied ^{14}C-activity).

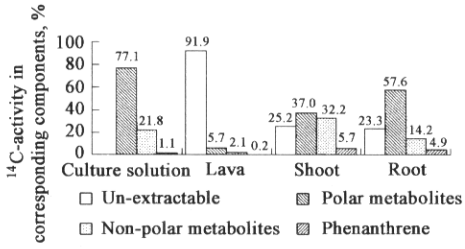

Fig.8 Distribution of ^{14}C-activity in plant tissues and culture media expressed as % of ^{14}C-activity in corresponding components without the presence of LAS

More information on the proportion of bonded, polar and non-polar metabolites and apparent phenanthrene in their corresponding components for culture solution, lava, plant root and shoot are shown in Fig. 8. Proportion of unextractable ^{14}C-activity found in the lava, root and shoot were 92%, 23% and 25% respectively, which indicate the absorbed ^{14}C-activity was more easier to bonded into lava or constructed into plant roots and shoot. The portions of polar metabolites were the highest among their corresponding components for culture solution (77%), plant root (58%) and shoot (37%) except for lava, the explanation for this phenomenon is that main degradation metabolites of phenanthrene was polar metabolites(Rehmann, 1996) by the microbial in the culture solution. The rest ^{14}C-activity existed in the forms of non-polar metabolites and phenanthrene.

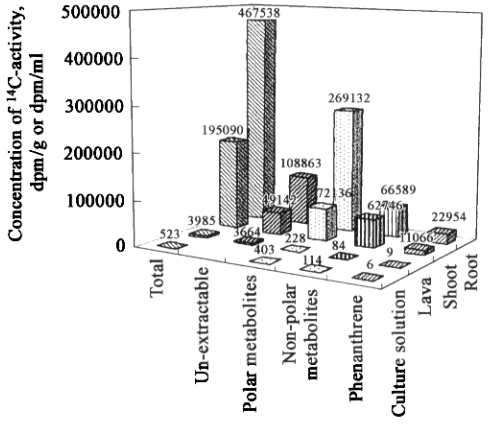

Fig.9 Concentration distribution of ^{14}C-activity in plant tissues and culture media without the presence of LAS

2.4 Influence of LAS on the concentrations of ^{14}C-activity among plant tissues and culture media

In order to explain the effect of LAS on the distribution of ^{14}C-activity and transformation of phenanthrene among plant tissues and culture media, concentrations of ^{14}C-activities in these components are shown in Fig. 9.

Fig.9 shows the concentrations of ^{14}C-activity of each component (include plant root, shoot, lava and culture solution). According to the concentrations of ^{14}C-activity, Fig.9 describe the metabolism of phenanthrene in much more true and direct way. A descent order for ^{14}C-activity among the plant tissue and culture was plant root > plant shoot > lava > culture solution, which is different from according to the percentage of applied ^{14}C-activity. Almost the concentrations of all kinds of metabolites in root and shoot were much higher than in lava and culture solution, which indicated that most ^{14}C-activity was accumulative in the plant than in culture media. Higher concentration of ^{14}C-activity in roots than in shoots was due to that CO_2 and VOCs were carried out by wind and were not uptake by shoot, which also indicated the phenanthrene may be uptake, metabolized and translocated up to plant shoot. Same results has been reported by Edwards (Edwards, 1986), who could not prohibit the reusing of VOCs and CO_2 by plant with his equipment.

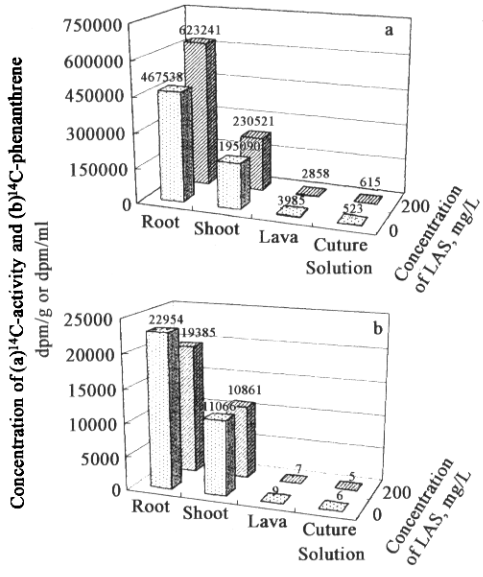

Fig.10 Influence of LAS on the concentrations of ^{14}C-activity in plant tissues and culture media

The presence of LAS has significantly influenced the concentrations of ^{14}C-activity among plant root, shoot, lava and culture solution(Fig.10a). Concentrations of ^{14}C-activity in the culture solution was higher, and in lava was lower in presence of LAS than in absence of LAS(615 to 523 dpm/ml for culture solution and 2858 to 3985 dpm/g for lava, respectively), which can be explained by the desorption of phenanthrene from the plant root and lava to the culture solution and increasement of ^{14}C-activity in the culture solution with the presence of LAS. Higher concentrations of ^{14}C-activity in the plant root, shoot were founded with the presence of LAS than absence of LAS (623241 to 467538 dpm/g for plant root and 230521 to 195090 dpm/g for plant shoot, respectively), which indicate the presence of LAS increased the uptake of the metabolites of phenanthrene into plant root and the translocation up to the shoot.

Contrary results were got about the concentrations of ^{14}C-

phenanthrene between plant root and culture media shown as Fig. 10b. The presence of LAS has significant influence on the concentrations of ^{14}C-phenanthrene in the root for much higher concentration than with the absence of LAS, but has no influence on the concentrations of phenanthrene in the plant shoot. These results indicated that the desorption of phenanthrene from plant root to culture solution decreased the uptake of phenanthrene by the plant root.

3 Conclusions

The mineralization and metabolism of phenanthrene are fast in a model ecosystem (culture solution-lava-plant-air).

Most of applied ^{14}C-activity was found in the plant (41%—45%), in which about 95% was associated or bonded with root and about 5% was with shoot. The ^{14}C-activity recovered in the forms of VOCs and CO_2 and in lava, culture solution was 18% to 29%, 11% to 8%, 14% to 10% and 1% respectively. Main parts of the applied ^{14}C-activity exist in two forms, one is polar metabolites (25%) which mainly distribute in the root (23%), the other is unextractable part (23%) which have been constructed into plant root (8.98%), shoot (0.53%) or bonded to lava (13.2%).

The main metabolites of phenanthrene were polar compounds (25% of applied ^{14}C-activity). Small portion of ^{14}C-activity was identified as non-polar metabolites (6% of applied ^{14}C-activity) and apparent phenanthrene (1.91% of applied ^{14}C-activity).

Phenanthrene and its metabolites were found in root and shoots, which indicated that they were taken up through plant roots and translocated to plant shoots.

The presence of LAS significantly increased the production of VOCs and decreased the production of CO_2 at concentration of 200 mg/L. LAS also reduced the phenanthrene level in the root and shoot, but significantly increased the concentration of ^{14}C-activity in the root and shoot.

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