

# Adsorption, persistence and bioavailability of napropamide in soil

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**Abstract:** Soil adsorption is generally recognized as a key to controlling the fate and transports of a pesticide in environment, and it also affects the persistence and bioavailability of pesticide. The present study was conducted to investigate the adsorption, persistence and bioavailability of the herbicide napropamide in soils with different properties using high-performance liquid chromatography (HPLC). Soil adsorption of napropamide was determined using the batch equilibration technique described by a Freundlich isotherm equation with correlation coefficients ( $r$ ) > 0.99. Regression of adsorption coefficient ( $K_f$ ) against selected soil indicates that organic matter (OM) content was the most influential factor governing adsorption of napropamide ( $P < 0.01$ ) followed by clay content ( $P < 0.1$ ). Napropamide had relatively longer persistence in soil, and its degradation in soil followed the first-order kinetics with the half-lives ( $t_{50}$ ) varying from 61.3 to 97.6 d, which appeared to decrease with soil OM content. The persistence of napropamide in sterilized soil was 2.09-3.65 times longer than that in the corresponding unsterilized soil, which indicated that microorganisms were the predominant contributors for the dissipation of napropamide in soil. Uptake and bioaccumulation of napropamide in soil by earthworm *Eisenia foetida* also mainly depended upon soil properties, especially the level of OM content ( $P < 0.05$ ). The  $K_f$  values of napropamide were negatively correlated with  $t_{50}$  ( $r = -0.885$ ,  $P < 0.05$ ) and the bioaccumulation factor ( $r = -0.796$ ,  $P < 0.05$ ). The corresponding linear regression equation was  $t_{50} = 94.210 - 3.535 K_f$  and  $BAF = 0.264 - 0.014 K_f$ , respectively. The results here revealed the potential of using the adsorption coefficient  $K_f$  as the model to evaluate the persistence and bioavailability of napropamide in soil.

**Keywords:** napropamide; soil; adsorption; degradation; bioavailability

## 敌草胺在土壤中的吸附及其与持久性和生物有效性之间的关系

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**摘要:** 土壤吸附是农药在环境中归趋的关键支配因素, 也是支配农药在环境中的持久性和生物有效性的重要因素之一。该文采用高效液相色谱法研究了除草剂敌草胺在不同性质土壤中的吸附、持久性和生物有效性以及吸附与土壤持久性、蚯蚓生物有效性之间的关系。结果表明, 在

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供试浓度范围内, 采用批量平衡技术测定的敌草胺土壤吸附等温线可用Freundlich模型表征 ( $r > 0.99$ ), 土壤有机质含量 ( $P < 0.01$ ) 是影响敌草胺在土壤中吸附的主要因素, 其次为黏粒含量 ( $P < 0.1$ )。敌草胺在土壤中的持久性较长, 其降解过程符合一级动力学特征, 降解速率随土壤有机质含量的升高而加快, 半衰期 ( $t_{50}$ ) 在 61.3-97.6 d 之间; 微生物对敌草胺在土壤中的持久性影响显著, 微生物降解是敌草胺在土壤环境中降解的主要途径, 灭菌处理后其在土壤中的半衰期延长了 2.09~3.65 倍。蚯蚓 *Eisenia foetida* 对敌草胺的吸收和生物积累也主要取决于土壤性质, 特别是土壤的有机质含量水平 ( $P < 0.05$ ); 敌草胺在土壤中的吸附系数与其半衰期 ( $r = -0.885, P < 0.05$ )、生物积累因子 (BAF) ( $r = -0.796, P < 0.05$ ) 之间均存在负相关关系, 相应回归方程分别为  $t_{50} = 94.210 - 3.535 K_f$  和  $BAF = 0.264 - 0.014 K_f$ , 表明吸附系数可用作模型参数来评价敌草胺在土壤中的持久性和生物有效性。

**关键词:** 敌草胺; 土壤; 吸附; 持久性; 生物有效性

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Herbicides are generally considered as the most economical and effective method for controlling noxious weeds. However, increasing use of herbicides has resulted in potential water pollution and other ecological problems<sup>[1]</sup>. The behavior and fate of herbicides entering into the soil are influenced by several processes, including adsorption, mobility, degradation, and bioavailability. Adsorption is often considered as a key process for regulating the concentration of a contaminant in soil, which also affects degradation and bioavailability. However, evidence indicates that the effect of adsorption on degradation and bioavailability of a chemical is much more complicated and depends on the complex interactions of numerous abiotic and biotic factors, such as chemical characteristics, soil properties, partitioning of chemicals, and biological characteristics of the organisms<sup>[2-6]</sup>. Completely opposite impacts or relationship were observed for pesticides with different degradation routes and mechanisms<sup>[7-8]</sup> and different bioavailabilities<sup>[9]</sup>. Thus, it is important to characterize adsorption, degradation and bioavailability of a certain herbicide in soil and their relationship, so as to increase the safety of the herbicide use and to minimize the negative impact on environmental quality.

Napropamide (*N*, *N*-dimethyl- $\alpha$ -phenylbenzeneacetamide), an acetanilide herbicide, is widely used for pre-emergence control of annual grasses and some broad-leaved weeds in a wide range of crop

field since its introduction to China. The fate of napropamide has aroused increasing concern because of the relatively high water solubility, the relatively long persistence in the field (from 60 to 70 days), and the significant toxicological properties<sup>[10]</sup>. For regulatory purposes, there is a requirement to estimate its behavior and fate in soil ecosystems. Most research to date concerning the environmental behavior and the fate of napropamide has focused on the description of its respective adsorption and degradation in soil environment<sup>[10-12]</sup>. Data in the open literature about the bioavailability of napropamide in soil are limited. A few studies were conducted to investigate the bioavailability of napropamide to crops<sup>[13-14]</sup>. Little work, however, has been done to describe the correlation between the adsorption with the degradation and the bioavailability of napropamide, especially the latter.

The aims of this work were (i) to characterize the adsorption and the persistence of napropamide in five soil samples with the different properties, and its bioavailability to earthworm *Eisenia foetida* that is widely used as bioindicators of soil health and models in the toxicology testing for chemicals, (ii) to elucidate the main parameters of the soil that influence the adsorption, persistence and bioavailability of napropamide using correlation analysis, and (iii) to evaluate the correlation between the adsorption of the herbicide involved and its persistence and bioavailability.

## 1 Materials and methods

### 1.1 Materials

**1.1.1 Herbicide** Analytical-grade napropamide (99.5% purity) was obtained from Dima Technology Inc., USA. This herbicide has a relative molecular mass of 271.36 g/mol and a solubility of 73.0  $\mu\text{g/mL}$  in water at 25 °C. Its octanol/water partition coefficient is 3.36 ( $\log K_{ow}$ ).

**1.1.2 Soil** Five surface soil (0-20 cm) samples

were collected randomly from the plow horizon of agricultural lands in southwest China, including Guiyang city (A), Zunyi city (B), Bijie city (C), Kaili city (D) and Qiannan state (E). The soils were air-dried at room temperature and passed through a 2 mm sieve. All samples were stored at 20 °C in the dark before use. The main parameters of the soils were determined using methodology outlined by Bao<sup>[15]</sup>. The results are given in Table 1.

**Table 1 Selected characteristics of the five soil samples used in this study**

Soil	OM/%	Clay/%	Sand/%	Silt/%	CEC/(cmol/kg)	pH
A	3.94 ± 0.23 a	26.23 ± 0.73 a	53.26 ± 0.89 a	20.51 ± 0.78 d	22.31 ± 0.72 a	6.32 ± 0.04 b
B	2.72 ± 0.20 b	18.41 ± 0.70 b	25.75 ± 0.78 d	55.84 ± 0.92 a	18.25 ± 0.65 b	5.15 ± 0.03 d
C	2.08 ± 0.22 c	19.32 ± 0.81 b	47.49 ± 0.91 b	33.19 ± 0.84 c	12.16 ± 0.60 c	6.62 ± 0.04 b
D	1.22 ± 0.16 d	17.46 ± 0.69 b	50.35 ± 0.94 ab	32.19 ± 0.79 c	16.02 ± 0.68 b	5.96 ± 0.04 c
E	0.84 ± 0.14 e	16.24 ± 0.63 c	44.59 ± 0.93 c	39.17 ± 0.89 b	15.45 ± 0.62 b	7.14 ± 0.05 a

Note: Values in columns followed by the same letter are not statistically different ( $P < 0.05$ ).

**1.1.3 Earthworm** The earthworm *E. foetida* was obtained from the Wandong flower-bird market, Guiyang city, Guizhou province, China. On average, the mass of the earthworm was 0.35 g (wet weight). All earthworms were allowed to acclimatize to the laboratory conditions for 14 days before the test.

### 1.2 Methods

**1.2.1 Adsorption experiment** Adsorption of napropamide was measured using the batch equilibration technique using the method previously described by Yu *et al.*<sup>[9]</sup>. Briefly, 2 g soil sample was weighed into a 25 mL polyethylene centrifuge tube, and 1.00 mol/L  $\text{CaCl}_2$  solution containing analytical grade napropamide of known concentrations (0, 5, 10, 15, 20 and 25  $\mu\text{g/mL}$ ) was added to each tube. The tube was closed with a Teflon-lined cap, shaken automatically for 24 h and centrifuged at 5 000 r/min for 15 min (20 °C). Triplicate samples were prepared for each concentration. The supernatant of 2 mL was taken, passed through a 0.45  $\mu\text{m}$  membrane filter and analyzed using the high-performance liquid chromatography (HPLC). The adsorbed concentration was calculated from the difference between the initial and equilibrium concentrations of napropamide. The adsorbed and equilibrium concentrations for each soil

were fitted to the Freundlich equation:

$$\lg C_s = \lg K_f + (1/n) \lg C_e \quad (1)$$

Where,  $C_s$  is the concentration of napropamide sorbed by soil ( $\mu\text{g/g}$ ),  $C_e$  is the concentration of napropamide in the solution at equilibrium ( $\mu\text{g/mL}$ ), and  $K_f$  ( $\mu\text{g}^{1-n} \text{mL}^n/\text{g}$ ) and  $1/n$  represent the intercept and the slope of the isotherm, respectively.

**1.2.2 Persistence experiment** Laboratory incubation experiments were conducted to investigate the persistence of napropamide under sterilized versus unsterilized conditions using the method previously described by Guo *et al.*<sup>[12]</sup>. Briefly, 10 g soil sample was placed in a 50 mL flask and were spiked aseptically with 1 mL of napropamide stock standard solution in methanol to attain the initial concentration of 6  $\mu\text{g/g}$ . The napropamide-spiked soil samples were agitated on a reciprocating shaker for 24 h at room temperature in the dark to allow the methanol to evaporate. Sterile distilled water was added to keep about 60% of the water holding capacity (WHC). The soil samples were incubated for 0, 15, 30, 60 and 90 days in the dark at 20 °C. Soil moisture contents were measured each week, and the sterile distilled water was added to maintain constant weight. The remaining levels of napropamide in soils were determined

by extracting samples at each sampling time point after application. The triplicate soil samples were mixed with 30 mL  $V(\text{acetone}) : V(\text{water}) = 25 : 5$ , shaken for 2 h on a reciprocating shaker and ultrasonically extracted for 20 min at 20 °C, respectively. After filtration, acetone within the filtrate was allowed to evaporate on a vacuum rotary evaporator. 2 mL solution was taken and passed through a 0.45  $\mu\text{m}$  membrane filter prior to analysis by HPLC.

To evaluate the effect of microorganisms on the persistence of napropamide in soils, the degradation was also performed under sterilized conditions. These tests were undertaken only in soil A and E with the highest and lowest OM content, respectively. Sterilization was achieved by autoclaving twice at 121 °C for 60 min. The degradation data in the nonsterile and sterilized soils were fitted to the first-order reaction kinetics model:

$$C_t = C_0 \times e^{-kt} \quad (2)$$

Where,  $C_0$  is the herbicide concentration in the soil at the application time ( $\mu\text{g/g}$ ),  $t$  is the time (d),  $C_t$  is the herbicide concentration detected in the soil at time  $t$  ( $\mu\text{g/g}$ ), and  $k$  is the first-order rate coefficient ( $\text{d}^{-1}$ ). The degradation data were summarized by calculating the degradation half-life time ( $t_{50}$ , d) from  $k$  with the following equation:

$$t_{50} = \ln 2/k \quad (3)$$

**1.2.3 Bioavailability experiment** Bioavailability of napropamide in soil to *E. foetida* was evaluated using the method by previously described Yu *et al.*<sup>[16]</sup>. Briefly, 100 g soil sample was placed in a 250 mL flask and sterilized twice using autoclave at 121 °C for 60 min. Addition of napropamide (6  $\mu\text{g/g}$ ) and adjustment of the feasible moisture level for each soil was conducted using the same procedures as described above for the degradation. Prior to exposure, mature (clitellate) earthworms were allowed to depurate their gut contents on the damp filter paper for two days. After ten worms were added to the soil surface, the flasks were covered with aluminum foil (ten small holes were cut in the foil for aeration) and incubated for 7 days in the dark at 20 °C. Four

replicates were prepared for each soil. At the end of incubation period, worms were removed from the soil and allowed to purge the gut contents for 48 h. Worms were weighed and frozen at -10 °C for 24 h. Then the worms were ground with anhydrous  $\text{Na}_2\text{SO}_4$ , the homogenate were placed in the Soxhlet apparatus and extracted with 80 mL methanol for 12 h. The extracts were concentrated to about 1 mL and purified by a column containing 5 g of 5% deactivated florisil. After the columns were eluted with 10 mL hexane, the extracts were added into the columns and eluted with 50 mL  $V(\text{hexane}) : V(\text{ethyl acetate}) = 9 : 1$ . Before HPLC analysis, the elutes were concentrated to dryness and napropamide residues were recovered by rinsing the flask with 5 mL methanol and filtrated as described above.

After worms were removed from the soil, 10 g triplicate soil sample (wet weight) was mixed with 30 mL  $V(\text{acetone}) : V(\text{water}) = 25 : 5$  and the subsequent extraction and analysis processes were conducted as described above. Triplicate additional 10 g of each soil was weighed into the individual aluminum tins and placed in a 105 °C oven for 24 h for the determination of moisture level. Napropamide detected in soil and organism samples were expressed as  $\mu\text{g/g}$  on the basis of dry and wet weight, respectively. The bioaccumulation factor (BAF) was calculated as the ratio of the napropamide concentration in the worm tissues ( $C_w$ ) and the napropamide concentration in the soil.

**1.2.4 Analysis of napropamide** Analysis of napropamide was performed using Wasters 600E HPLC equipped with Waters 2487 ultraviolet absorbance detector and a reversed-phase  $\text{C}_{18}$  column (150 mm  $\times$  4.6 mm (i. d.), 5  $\mu\text{m}$ ). The eluting solvent was  $V(\text{acetonitrile}) : V(\text{water}) = 80 : 20$ . And the flow rate was 1.0 mL/min. The wavelength was set at 210 nm and the temperature was kept at 30 °C for the detection purpose. The injection volume was 5  $\mu\text{L}$ . Each sample was analyzed twice. The approximate retention time for napropamide was 6.6 min under these conditions.

The efficiency of the analysis procedure was

evaluated by spiking herbicide-free soil and worm samples at 0.05, 0.5 and 5  $\mu\text{g/g}$  level. Three replicates of each recovery assay and the corresponding blank sample were extracted and analyzed using the method described above. In all fortification levels, the recovery was higher than 85% for both soil and worm samples. The minimum detection limit of napropamide was 0.012  $\mu\text{g/g}$ . The specificity was demonstrated by the absence of interferences at the retention time of the analyte of interest.

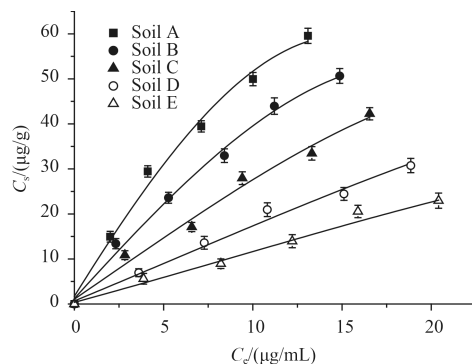
**1.2.5 Statistical analysis** The data were analyzed using SPSS 18.0 statistical software package and Microsoft Excel 2007. The statistical differences between means were assessed using One-way analysis of variance (ANOVA) followed by Least significant difference (LSD) test at  $P < 0.05$ . Pearson correlation coefficient test or Spearman correlation coefficient test, as appropriate, was used to further determine the extent of the linear relation between degradation, bioaccumulation and adsorption of napropamide. A two-tailed  $P$  value  $< 0.05$  was considered statistically significant.

## 2 Results and discussion

### 2.1 Adsorption of napropamide in soil

Adsorption isotherms of napropamide in five tested soils are shown in Fig. 1. Based on the classification of adsorption isotherms, the adsorption isotherm of napropamide for each of the tested soils was the  $L$ -type (Fig. 1), indicating a weak competition between solute and solvent molecules for the adsorbing sites of the surface. Adsorption of napropamide in soils was well described by the Freundlich equation over the range of concentrations from 0 to 25  $\mu\text{g/mL}$  with  $R^2$

value ranging from 0.974 to 0.996 (Table 2). Adsorption isotherms for all soils had slopes of  $(1/n)$  close to 1, suggesting that the percentage of this herbicide adsorbed by soil decreased with the increase of the solution concentration, and that there was a potential for the herbicide leaching particularly at higher application rates.



**Fig. 1** Adsorption isotherms of napropamide in the five soils

The Freundlich adsorption coefficient  $K_f$  ranged from 1.56 to 9.61  $\mu\text{g}^{1-n}\text{mL}^n/\text{g}$ , implying that napropamide was not strongly adsorbed to the above mentioned five soils for the concentration range in this study (Table 2 and Fig. 1). The adsorption affinity followed a descending order of soil  $A > B > C > D > E$ . The adsorption of pesticide by soil could be significantly influenced by soil properties, such as OM and clay contents<sup>[17-18]</sup>. The correlation of adsorption with soil properties can be used either to predict the adsorption of pesticides on different soils, or to determine the dominating factors in adsorption process. Thus, the stepwise regression analysis was used to assess the relationship between the adsorption coefficient of napropamide and the soil property

**Table 2** Parameters of adsorption, degradation and bioavailability of napropamide in soils

Soil	Adsorption			Degradation			Bioavailability	
	$K_f$	$1/n$	$R^2$	$t_{50}$	$k$	$R^2$	$C_w$	BAF
A	9.61 ± 0.19 a	0.720	0.987	61.3 ± 1.57 d	0.011 3	0.973	0.71 ± 0.04 d	0.15 ± 0.011 c
B	7.15 ± 0.16 b	0.730	0.996	70.7 ± 1.46 c	0.009 8	0.976	0.88 ± 0.04 c	0.17 ± 0.015 c
C	4.56 ± 0.12 c	0.778	0.974	73.7 ± 1.32 c	0.009 4	0.987	0.85 ± 0.05 c	0.16 ± 0.012 c
D	2.28 ± 0.14 d	0.893	0.991	78.8 ± 1.61 b	0.008 8	0.977	1.11 ± 0.05 b	0.21 ± 0.014 b
E	1.56 ± 0.11 e	0.894	0.987	97.6 ± 1.78 a	0.007 1	0.995	1.42 ± 0.07 a	0.29 ± 0.016 a

Note: Values followed by different letters in the same column are significantly different at  $P < 0.05$  level.

parameter. This procedure shows that  $K_f$  of napropamide was highly correlated between and OM content ( $r = -0.994$ ,  $P < 0.01$ ) and clay content ( $r = -0.864$ ,  $P < 0.1$ ) (Table 3), meaning that among the various factors influencing napropamide adsorption, OM content appeared to be the most influential factor followed by clay content. In previous studies to investigate the soil adsorption of napropamide, Gerstl and Yaron<sup>[10]</sup>, Kim<sup>[11]</sup> and Guo *et al.*<sup>[12]</sup> also found that OM and clay content affected the napropamide adsorption more significantly than other soil parameters, implying less adsorption in soils with lower OM and clay contents and greater leaching potential of napropamide after passage through the soil profile. Similar phenomena were also observed in studies on the adsorptive behavior of other chloroacetamide herbicides, such as acetochlor, butachlor, pretilachlor and metolachlor<sup>[19-20]</sup>.

**Table 3** Correlation coefficients between  $K_f$ ,  $t_{50}$ ,  $C_w$  and BAF of napropamide and soil properties

Parameter	OM	Clay	Sand	Silt	CEC	pH
$K_f$	0.994***	0.864*	-0.119	-0.162	0.738	-0.446
$t_{50}$	-0.904**	-0.802	-0.030	0.269	-0.542	0.558
$C_w$	-0.886**	-0.768	-0.004	0.237	-0.407	0.491
BAF	-0.815*	-0.680	0.027	0.184	-0.304	0.536

Note: \*, \*\* and \*\*\* represents  $P < 0.1$ ,  $< 0.05$  and  $< 0.01$ , respectively.

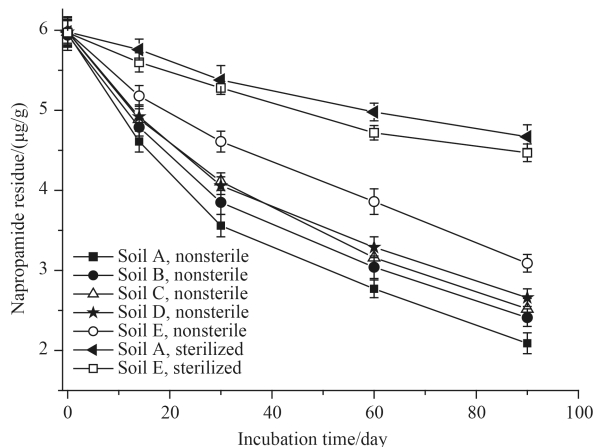
The organic carbon adsorption coefficient  $K_{oc}$  (mL/g) can be obtained by normalizing adsorption from a total soil basis to an organic carbon basis and is generally regarded as independent of soil for nonionic compounds.  $K_{oc}$  can be calculated according to the following equation:

$$K_{oc} = K_f / W_{oc} \times 100 \quad (4)$$

Where  $K_f$  is Freundlich adsorption coefficient and  $W_{oc}$  is the percentage of soil organic carbon. Based on the measured  $K_f$  and  $W_{oc}$  values, the calculated  $K_{oc}$  values were 420.49, 453.18, 377.95, 322.19 and 320.17 mL/g for soil A, B, C, D and E, respectively. These  $K_{oc}$  values suggest that the adsorption of napropamide was generally weak in soils, which accordingly implied that napropamide may have a leaching potential to contaminate the groundwater.

## 2.2 Persistence of napropamide in soil

The persistence of napropamide in the tested soil was evaluated using the degradation behavior. The degradation of napropamide in all unsterilized soils was fitted to the first-order reaction kinetics model and showed good performance for all treatments (Fig. 2), with  $R^2$  values  $> 0.97$  (Table 2). The observed half-lives ( $t_{50}$ ) (from 61.3 to 97.6 days) for napropamide in nonsterile soils were similar to those previously reported varying from 25 to 152 days<sup>[12, 19, 21]</sup>. In all cases, napropamide was more persistent in soils with lower OM content as compared to soils with higher OM content (Table 3). A significantly negative correlation was observed between the half-lives and the soil OM content ( $r = -0.904$ ,  $P < 0.05$ ), which suggests that soil OM is a predominant factor determining the persistence of napropamide in soils, although the degradation of napropamide in soils also depended on clay content and other property parameters of soils.



**Fig. 2** Degradation kinetics of napropamide in nonsterile and sterilized soils

Concerning correlations between the degradation half-life of napropamide and the soil property, there are some contradictory comments. Walker *et al.*<sup>[21]</sup> reported, for instance, that the half-life of napropamide was positively correlated with both soil OM and clay contents, but correlation between the half-life and clay content was higher than that between the half-life and OM content. While Guo *et al.*<sup>[12]</sup> reported that the half-life for napropamide was negatively and positively related to soil OM and clay content, with

correlation coefficients of  $-0.979$  and  $0.432$ , respectively. The present study demonstrates that the  $t_{50}$  of napropamide decreased with the increase of the OM level and clay content, and correlation coefficient between  $t_{50}$  and OM content was higher than that between  $t_{50}$  and clay content (Table 3). These disagreement results show that the degradation of napropamide in soil is a complicated process, which may not only depended on physical and chemical properties of the soil, but also depended on biological properties of the soil, such as soil microbial population and napropamide availability to those microorganisms.

Napropamide degradation in sterilized soil A and E also obeyed well the first-order kinetics with  $R^2$  values of  $0.986$  and  $0.974$ , respectively (Fig. 2). As expected, sterilization treatment resulted in a significant decrease in the degradation rate of napropamide in two soil samples investigated ( $P < 0.05$ ). In soil A, sterilization increased the half-life from  $61.3$  to  $223.6$  days, or by  $72.57\%$ . In soil E, the persistence increased from  $97.6$  to  $203.8$  days or by  $52.11\%$ . The degradation rate coefficient  $k$  for napropamide in sterilized soils A and E was  $3.65$  and  $2.09$  times smaller than that in the corresponding unsterilized soil, indicating that microbial degradation may be the dominant pathway for napropamide degradation in soils. There was strong evidence indicated that microbial transformation was the primary mechanism of napropamide dissipation in soil<sup>[22]</sup>.

In order to evaluate the potential risks of groundwater contamination, the leaching potential of napropamide in soils was calculated using the groundwater ubiquity score (GUS) model proposed by Gustaf-son<sup>[23]</sup>:

$$\text{GUS} = \lg[t_{50} \times (4 - \lg K_{oc})] \quad (5)$$

Where  $t_{50}$  is the half-life in the soil (days),  $K_{oc}$  is the organic carbon partition coefficient (mL/g). A chemical with  $\text{GUS} > 2.8$  is considered of the high leaching potential, while a chemical with  $\text{GUS} < 1.8$  is defined as a low leaching candidate. When  $\text{GUS}$  of a chemical is between  $1.8$  and  $2.8$ , it belongs to a

“transition zone”. Using the measured  $K_{oc}$  and  $t_{50}$  values, the estimated GUS index in soil A, B, C, D and E was  $2.46$ ,  $2.49$ ,  $2.66$ ,  $2.83$  and  $2.97$ , respectively. According to the classification of the tendency of the chemical leaching, napropamide may leach easily through soils under conducive conditions, especially in the soil with relatively low OM. These results confirm the observations of the adsorption studies. However, many other factors may alter the actual dissipation rate of a pesticide under field conditions, and such factors include volatilization and photolysis. The exact leaching risk of napropamide must hence be investigated under field conditions.

### 2.3 Bioavailability of napropamide to earthworm

Napropamide was ingested from soil by *E. foetida*, which is listed in Table 2. For the five samples of soils involved, uptake of napropamide by worms decreased as the soil OM content increased. Based on the regression analysis result, there was a significant correlation ( $P < 0.05$ ) between concentrations in worm tissues ( $C_w$ ) and the soil OM contents (Table 3). This indicates that OM was also a dominant parameter in worm availability of napropamide in soils with wide variety of OM, clay, sand, silt, CEC and pH. Investigating the availability of another chloroacetamide herbicide butachlor in the five soils with different properties to earthworms, Yu *et al.*<sup>[19]</sup> also found that uptake of butachlor by *Allolobophora caliginosa* decreased with the increase in the level of soil OM content. In the experiment to examine the availability of anthracene, chrysene, pyrene, and benzo (a) pyrene in the five soils to earthworms, Tang *et al.*<sup>[24]</sup> also demonstrated that amounts of these compounds detected in *E. foetida* tissues were the greatest in the soil with the lowest OM. In other studies, the different uptake of pesticides by earthworm with different soil properties was also observed in the case with DDT, DDE, DDD and dieldrin<sup>[25]</sup>. These results suggest that accessibility of a certain contaminant to earthworm was dependent upon both characteristics of a contaminant (e.g., solubility,  $K_{ow}$ , molecular structure) and soil properties such as OM, clay content, CEC and pH.

The bioaccumulation factor BAF of earthworms for napropamide is presented in Table 2. Similar to the concentrations detected in organism tissues, the soil OM also had significant influence on the bioaccumulation of napropamide by worms ( $P < 0.1$ ) (Table 3). There was a similar variation trend between the bioaccumulation and uptake of napropamide by earthworms with the soil OM content level. Moreover, BAF was significantly correlated with  $C_w$  ( $P < 0.01$ ). The bioaccumulation of a contaminant in soil by earthworms could be affected by a complex interaction of physicochemical and biological factors<sup>[6, 25]</sup>. In general, among these physicochemical and biological factors, a crucial factor in determining the rate of entry of an organic compound into an organism is octanol/water partition coefficient determining the ability of compound to traverse the cell membrane of the organism. The octanol/water partition coefficient is perhaps the most important single factor that is used for predicting the bioavailability of environmental contaminants<sup>[9, 26]</sup>. For the herbicide napropamide, the partitioning of napropamide in soils is possibly governed by its relatively low  $\log K_{ow}$  (3.36) and hence resulted in weak sorption to soils, as evidenced by *L*-type isotherms (Fig. 1) and low adsorption coefficients (Table 2). To sum up, napropamide available to *E. foetida* was possibly the fraction in pore-water and/or weakly associated with the surface of soils<sup>[3]</sup>. As a result, the increase in adsorption of napropamide makes it less 'available' to earthworm *E. foetida*.

#### 2.4 Correlation between adsorption and persistence of napropamide

The adsorption coefficient  $K_f$  and the degradation half-life  $t_{50}$  of napropamide increased and decreased with the soil OM content, respectively. This suggests that they may be inversely related. As expected, there was a negative correlation between  $K_f$  and  $t_{50}$  ( $r = -0.885$ ,  $P < 0.05$ ) according to the result provided by a linear regression analysis. The regression equation was:  $t_{50} = 94.210 - 3.535 K_f$  (Fig. 3). The Pearson correlation coefficient test and the Spearman correlation coefficient test show that the degree of the

linearly relation between adsorption extent and degradation rate of napropamide was statistically significant at  $P < 0.05$  and  $P < 0.01$  level, respectively. It seems that the use of the adsorption coefficient would be useful in predicting the corresponding degradation or persistence for napropamide in soil.

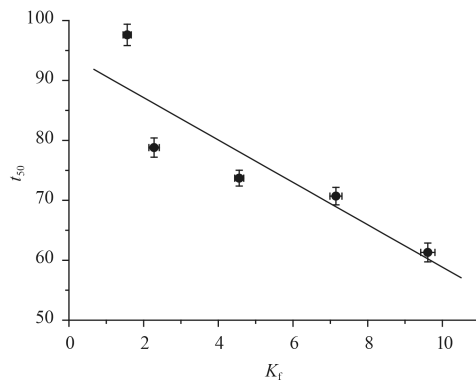


Fig. 3 Correlation between  $t_{50}$  and  $K_f$  of napropamide

Adsorption is a governing process determining the concentrations of pesticides in soil solution, and their parameters derived from standard laboratory tests can be used for the parameterization of mathematical models for the assessment of their efficacy and degradation, as well as their potential for leaching into ground water. Thus, numerous laboratory studies have been carried out to investigate the effect of adsorption on degradation of pesticides. In general, adsorption is often considered to be able to decrease the degradation by limiting the availability of organic chemicals to microbial or chemical transformations<sup>[4, 8]</sup>. However, based on the data presented here, the degradation rate of napropamide in soils increased with the enhancement of the adsorption capacity (Tables 1 and 2). Although the largest adsorption affinity for napropamide was observed in soil A, for example, the half life of napropamide in soil A was the shortest. Soil E, on the other hand, had the weakest sorption capacity for napropamide, the half life of napropamide in soil E was the longest. Similar phenomena was also observed by Guo *et al.*<sup>[12]</sup> who characterized the adsorption and degradation of napropamide in three Chinese soils. These findings suggest that degradation of herbicides also may be influenced by the microbial



population, and thereby by the soil OM content because the soil OM was known to support microbial growth<sup>[27]</sup>. It is possible that the lowest OM content in the soil E led to the relatively low microbial population, which degraded napropamide, and hence the longest half-life of napropamide was observed in this soil although adsorption capacity for napropamide is the lowest in this case.

Biodegradation of pesticides in soil is influenced by many physical, chemical, and biological properties of the soil. Biodegradation rates may related to the availability of the pesticide to the degrading microorganisms. When the pesticide such as 2, 4-D is intercalated into the clay<sup>[4]</sup> or benzonitrile is irreversibly bound to the crop-straw-derived ash<sup>[28]</sup>, they are isolated from the degrading organisms and are hence protected from biodegradation. These cases are somewhat unusual, however, because most pesticides (e.g., atrazine) re-versibly partition between the soil solution and the soil organic matter<sup>[8]</sup>. Since microbes themselves may be sorbed, it is conceivable that microbes and pesticide may be sorbed on adjacent locations on the soil surface, thereby facilitating degradation of the chemical by the sorbed microbes. Thus, pesticide sorption might either enhance or decrease microbial degradation rates in soils, relying on whether the sorbed pesticide is available. Thus, a more likely explanation for the increase in degradation rate of napropamide with adsorption extent is that sorbed napropamide to the soil matrix may be biodegraded by indigenous microorganisms. However, in the present study, we simply measured the dissipation of napropamide over time, and thus did not provide mechanistic information about the degradation pathway. There are many direct and indirect processes that could account for the increase in degradation rate and further experiments are underway that may allow a better understanding of the mechanism of the effect of adsorption on biodegradation of napropamide in soils.

## 2.5 Correlation between adsorption and bioavailability of napropamide

Adsorption may decrease bioavailability of napro-

pamide by reducing uptake rate of napropamide in soil by *E. foetida*. As indicated in Table 2, based on the result of the regression analysis, the bioaccumulation factor of *E. foetida* for napropamide was closely correlated with the Freundlich adsorption coefficient, with  $r$  value of  $-0.796$ . The corresponding linear regression equation was:  $BAF = 0.264 - 0.014 K_f$  (Fig. 4). The strength of association between BAF and  $K_f$  was also statistically significant ( $P < 0.05$ ) on the basis of the Spearman correlation coefficient test result, meaning that the Freundlich adsorption coefficient might predict the availability of napropamide in soils to earthworms.

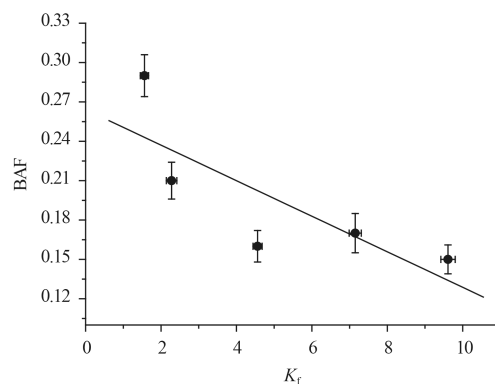


Fig. 4 Correlation between BAF and  $K_f$  of napropamide

Availability of contaminants to earthworms is of interest because these organisms contact soil directly and can act as a conduit through which pollutants enter food webs. Moreover, they are the model organisms used in certain standardized tests designed to evaluate the risk of contaminated soil<sup>[29]</sup>. However, there have been few detailed studies on the correlation of contaminant adsorption with the availability to earthworms in soil. In attempting to describe an existing relationship between soil sorption and bioavailability of pesticides, Yu *et al.*<sup>[9]</sup> investigated the effect of soil adsorption on availability of pesticides such as butachlor, myclobutanil and chlorpyrifos to *A. caliginosa*. In their experiments, the bioavailability of both butachlor and myclobutanil with relative low  $K_{ow}$  to *A. caliginosa* could be predicted by the adsorption coefficient, whilst the adsorption coefficient could not be used as a predictor of the availability of *A. caliginosa* for chlorpyrifos

with relative high  $K_{ow}$ . It is conceivable that octanol/water-partitioning coefficient should be a crucial factor in determining sorption, advective-dispersive transport and biological processes, and thereby the bioavailability of pesticides (as mentioned above).

Bioavailability is an important consideration in the risk assessment of a herbicide or other chemicals in the selection of appropriate remediation technologies for polluted sites. Adsorption is generally considered as a key to control the availability of contaminants in soil to receptors. Thus, knowledge of adsorption mechanism of a contaminant is necessary for predicting the fate of contaminants in soil ecosystems when data are lacking. Using independent datum sets and understanding how adsorption influences bioavailability of a contaminant may result in more accurate prediction of its availability in biota. Based on data presented in the current study, a Freundlich adsorption coefficient  $K_f$  can be used as a model for assessing the availability of napropamide in soil to earthworms. Nevertheless, the present investigation merely represents a step in the direction of attempting to use parameters from standard adsorption tests to predict the availability of napropamide to receptors because there were only five soils and one test organism involved. Further study should be conducted to investigate more test organisms and soils with different characteristics to obtain a more reliable predictability of napropamide bioavailability based on information of adsorption.

### 3 Conclusions

From the studies above, our results indicated that:

1) Napropamide was not strongly adsorbed to the five soils, suggesting its potential to move downward with percolating water. Adsorption followed a Freundlich isotherm and was positively correlated OM and clay contents.

2) Napropamide had relatively long persistence in soil, which was strongly controlled by soil OM. The prolonged  $t_{50}$  by sterilization means that microbial transformation was the dominant pathway for napropamide degradation in soil.

3) Uptake and bioaccumulation of napropamide in soils by earthworm *E. foetida* was also mainly depended upon soil properties, especially with level of OM content.

4)  $K_f$  of napropamide was negatively correlated with its  $t_{50}$  and BAF, indicating that adsorption coefficient might be useful for predicting degradation and bioavailability of napropamide in soil.

All these results provide valuable basis for the direction of scientific application of napropamide in China.

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