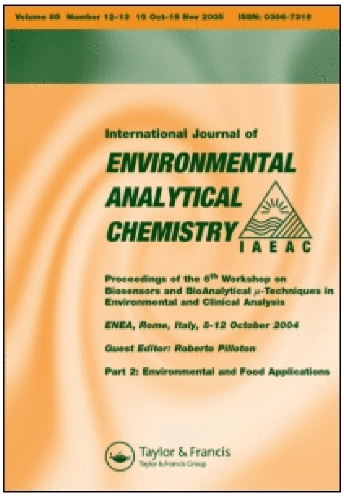


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Volatilization and Mineralization of [3-^{14}C]Fluoranthene After Soil Incorporation and Soil Surface Application

H. Ophoff[a]; A. Stork[a]; W. Veerkamp[b]; F. Führ[a]
[a] Institute of Radioagronomy, Forschungszentrum Jülich GmbH, Jülich, Germany [b] SHELL Internationale Petroleum Maatschappij B. V., The Hague, The Netherlands

To cite this Article Ophoff, H. , Stork, A. , Veerkamp, W. and Führ, F.(1996) 'Volatilization and Mineralization of [3-^{14}C]Fluoranthene After Soil Incorporation and Soil Surface Application', International Journal of Environmental Analytical Chemistry, 64: 2, 97 — 109

To link to this Article: DOI: 10.1080/03067319608028339

URL: http://dx.doi.org/10.1080/03067319608028339

Intern. J. Environ. Anal. Chem., Vol. 64, pp. 97–109
Reprints available directly from the publisher
Photocopying permitted by license only

VOLATILIZATION AND MINERALIZATION OF [3-^{14}C]FLUORANTHENE AFTER SOIL INCORPORATION AND SOIL SURFACE APPLICATION

H. OPHOFF[1]*, A. STORK[1], W. VEERKAMP[2] and F. FÜHR[1]

[1]*Institute of Radioagronomy, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany;* [2]*SHELL Internationale Petroleum Maatschappij B. V., P.O. Box 162, NL-2501 The Hague, The Netherlands*

(Received, 15 October 1995; in final form, 20 May 1996)

The gaseous losses of [3-^{14}C]fluoranthene from bare soil were measured in a glass wind tunnel under field-like conditions. Four experiments of 14 days each were performed under individual climatic situations. In two studies, [3-^{14}C]fluoranthene was incorporated into the 0–1 cm soil layer (approx. 670 µg kg^{-1}), in the other two experiments [3-^{14}C]fluoranthene was sprayed onto the soil surface (approx. 120 g ha^{-1}). The data obtained will be used for validation of the HESP computer model (*H*uman *E*xposure of *S*oil *P*ollutants).

In all experiments the major fraction of radioactivity (60.0 – 97.6% of the applied radioactivity (AR)) was recovered in the 0–2 cm soil layer. The mineralization of [3-^{14}C]fluoranthene was strongly temperature dependent and slightly higher for surface application (Σ 6.6 and 3.3% AR) than for soil incorporation (Σ 1.9 and 5.3% AR), possibly because of stronger adsorption in the soil and the resulting lower availability for microbial degradation.

After surface application, the volatilization of [3-^{14}C]fluoranthene was considerably higher (Σ 33.6 and 12.4% AR) than after soil incorporation (Σ 1.4 and 1.8% AR). The initially high volatilization rates decreased rapidly within 2 to 3 days in all experiments. Subsequently volatilization continued at a low level, showed a clear temperature dependence and thus followed a diurnal rhythm. Largely unchanged [3-^{14}C]fluoranthene was characterized by radio-HPTLC both for soil and air samples.

KEY WORDS: PAH, fluoranthene, volatilization, mineralization, soil residues, wind tunnel experiment, radio-HPTLC.

INTRODUCTION

Ecosystems may be polluted by numerous organic chemicals originating from various sources. In former times volcanic eruptions or forest fires used to be responsible for contamination with environmental chemicals. Today, anthropogenic processes such as traffic, industrial production or emissions from private households play a major role in dispersing substances of this type, e.g. polycyclic aromatic hydrocarbons (PAH) or pesticides. Both non-target areas and also food chains are influenced depending on the fate of the substance, e.g. volatilization, translocation, plant uptake and degradation

---

* To whom correspondence should be addressed.

processes. The fate of these environmental chemicals can be examined in detail in lysimeter studies making use of undisturbed soil cores[1]. Furthermore, mathematical models are becoming more and more significant for the simulation of environmental hazards, although there is an evident lack of complete data sets for modelling.

The HESP simulation model (*H*uman *E*xposure to *S*oil *P*ollutants)[2–4] serves to estimate the risk exposure potential of a soil contaminated by environmental chemicals. Direct uptake by the soil, consumption of food originating from the site studied, as well as dermal uptake and gaseous inhalation are regarded as the major input paths.

This paper presents the findings obtained with the wind tunnel constructed at the Institute of Radioagronomy of the Forschungzentrum Jülich, thus providing data sets to validate and further develop the HESP model.

From a number of substances considered, ^{14}C-labelled fluoranthene from the group of PAHs was selected as the model chemical because of its ecotoxicological significance, moderate degradability, certain volatilization potential from various surfaces and its availability as a ^{14}C-labelled substance.

The physico-chemical properties most relevant are shown in Table 1 indicating a high adsorption coefficient with respect to the organic matter in the soil. At the same time a low water solubility and a moderate vapour pressure.

EXPERIMENTAL

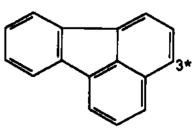
Test compound

^{14}C-labelled radioactive fluoranthene (^{14}C-FLA) was obtained from SIGMA-ALDRICH GmbH, Deisenhofen. The 4-ring molecule was labelled in the third C-position (Table 1).

Wind tunnel and air analyses

As an extension of the lysimeter concept[1], a glass wind tunnel was set up above a 0.5 m^2 lysimeter to measure the gaseous losses of environmental chemicals. Having direct air sampling, the system permits the measurement of radioactively labelled substances in the

Table 1 Physico-chemical data of fluoranthene[5,26].

Structural formula: (* = ^{14}C-label)	
Molecular mass:	202.26 g mol^{-1}
Melting point:	110–111°C
Vapour pressure:	7.0.10^{-6} hPa (20°C)
Water solubility:	0.21 mg l^{-1} (20°C)
Henry's law constant (K_H):	2.7.10^{-4}
Adsorption coefficient (K_{OC}):	31000–52000

soil/plant, leachate and air compartments under conditions similar to the field. A detailed description of the system (Figure 1) can be taken from Stork[6,7].

The adjustable lid of the wind tunnel (max. height 110 cm) enables experiments to be performed both with plants at various stages of development as well as with bare soil. In contrast to conventional field studies, it is possible with this system to compile radioactivity and mass balances with respect of the volatilization behaviour of environmental chemicals applicated as radionuclides.

Automatic measuring and control devices continuously adapt the climate inside the wind tunnel to outside conditions. Precipitation events in the field are simulated using an irrigation unit. The glass construction of the side walls and the lid of the wind tunnel made of UV-permeable acrylic glass ensure sufficient radiation with a corresponding field quality. With a tunnel lid setting of 30 cm, wind velocities of 0.3–2.0 m s^{-1} can be achieved, corresponding to a flow rate of 500–1500 m^3 h^{-1}. Field-like flow profiles have been realized in order to obtain outdoor soil moisture conditions (Figure 2). Equal wind profiles (same wind speeds in different heights) would unnaturally dry out the soil surface and have a considerable impact on the volatilization and mineralisation behaviour of the test compounds.

After intensive mixing of the outlet air, two representative aliquots are taken from the exhaust. A differentiation is made between volatilized radiolabelled organic parent substance, its metabolites and $^{14}CO_2$ as the product of the mineralisation process.

An adsorption unit[7] composed of a glass-fibre filter (185 mm ø, Machery & Nagel) and three polyurethane foam plugs (PUF) (100 mm ø × 150 mm, Ziemer GmbH) is used for the qualitative and quantitative determination of the ^{14}C-labelled organic substances in the exhaust air of the wind tunnel. Aliquots are taken isokinetically on the basis of industrial guidelines for sampling from stack air[8,9]. The maximum collection rate is about 50 m^3 h^{-1}. Integration period of the adsorption unit was between 1 h to max. 24 h. Filter samples were extracted with 70 ml toluene in a Soxhlet apparatus, PUF extraction was performed 1 – 4x with 450 ml of toluene in a special squeezing apparatus[10]. All samples were measured by liquid scintillation counting (Tri-Carb 2500 TR, Packard).

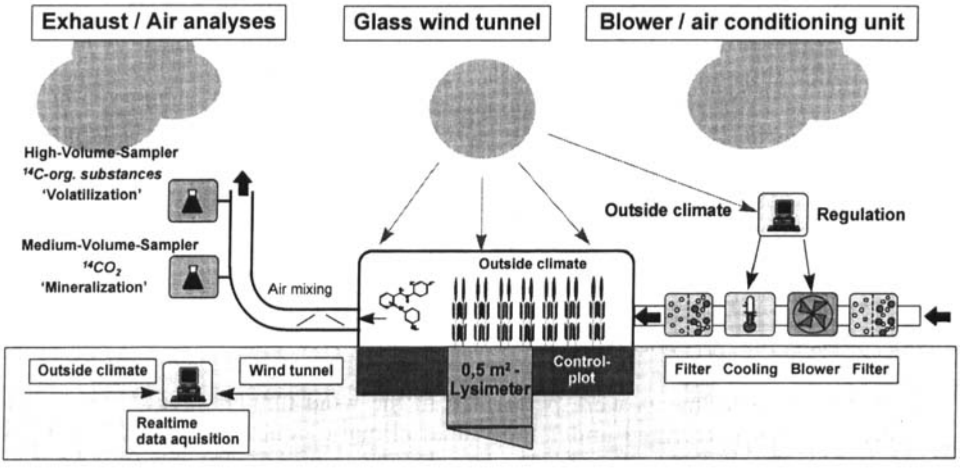


Figure 1 Diagram of the wind tunnel at the Institute of Radioagronomy, Forschungszentrum Jülich GmbH.

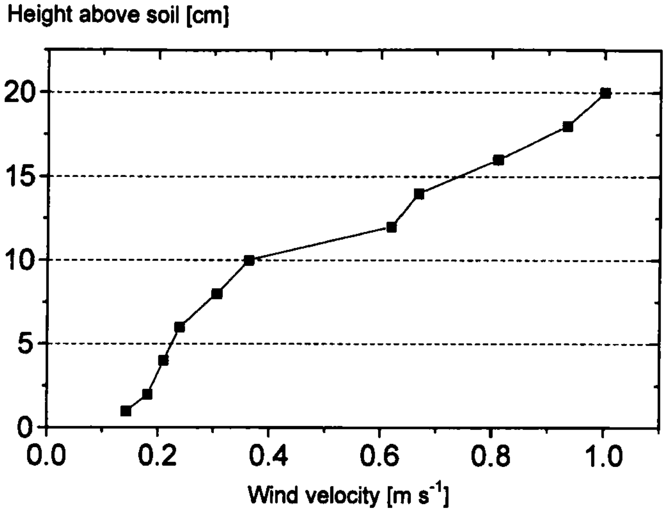


Figure 2 Flow profile inside the wind tunnel above bare soil.

The $^{14}CO_2$ arising from the complete mineralization of the test compound is collected in a special apparatus[7]. The maximum flow rate amounts to 3.5 L min^{-1}. After adsorption of volatile organics, XAD-4 (Amberlite, Sigma), the sample gas is completely dried by silica gel and phosphorus pentoxide. $^{14}CO_2$ is subsequently absorbed by 2-methoxypropylamine (Carbosorb E$^+$, Packard) using a special cooled intensive wash bottle (reflux temperature of –40°C). The collecting time amounts to a maximum of 48 h, corresponding to about? 10 m^3 of air sample. At the end of the experiments, all contaminated parts of the wind tunnel are rinsed with an appropriate solvent in order to obtain complete radioactivity balances. Aliquots of the upper soil layers (0–2 cm and 2–7 cm) were taken, extracted in Soxhlet apparatus for 16 h with 70 ml of acetone and subsequently combusted for ^{14}C-measurement (Oxidizer 306, Packard). A characterization of the test compound and the metabolites was performed by radio high performance thin-layer chromatography (HPTLC) with thin-layer plates specially developed for PAH analysis, i.e. impregnated with caffeine (HPTLC-FPKG 60 F_{254S}, Merck). Both the ^{14}C extracts as well as a non-radioactive reference standard were spotted cochromatographically in 10 mm bands (Linomat IV, Camag) and the HPTLC plates were developed with $CHCl_2$ at –20°C. The evaluation was performed with a Bio Imaging Analyser (Fujix BAS 1000, Fuji) and a special software (TINA, Raytest). A verification by radio high performance liquid chromatography (HPLC) is in preparation.

Description of the experiments

In 1994, four experiments were performed in the wind tunnel using ^{14}C-FLA. Each experiment was performed under individual climatic conditions (Table 2). In two experiments, ^{14}C-FLA was incorporated into the upper soil layer (0–1 cm) in a benzene solution to simulate moderate soil contamination. As a second variant, soil surface

Table 2 Experimental conditions of the wind-tunnel studies with [3-^{14}C]fluoranthene.

Soil application type[a]	*1st Incorp.*	*2nd Incorp.*	*1st Surface*	*2nd Surface*
Start:	26 Apr. 94	22 Aug. 94	06 Jun. 94	11 Oct. 94
End:	10 May 94	05 Sept. 94	20 Jun. 94	25 Oct. 94
Net applied (^{14}C-radioactivity):	664.6 μg kg^{-1} (9.72 MBq)	667.6 μg kg^{-1} (5.78 MBq)	112.4 g ha^{-1} (2.06 MBq)	125.3 g ha^{-1} (1.97 MBq)
Spec. radioactivity:	1733 kBq mg^{-1}	950 kBq mg^{-1}	407 kBq mg^{-1}	350 kBq mg^{-1}
Formulation:	–	–	SC[b]	SC[b]
Application volume:	–	–	450 l ha^{-1}	450 l ha^{-1}
Climatic parameters (mean during experimental periods)				
Air temperature:	14.7°C	18.5°C	16.8°C	10.1°C
Soil temp., 5 cm:	13.6°C	18.2°C	15.9°C	10.1°C
Air humidity:	83.5% rel.	85.5% rel.	81.1% rel.	89.1% rel.
Irrigation:	1st week none, 2nd week irrigation programme (Σ 17 mm)			
Wind velocity[c]:	0.2/1.0	0.3/1.1	0.3/0.9	0.3/1.0

[a] Gleyic cambisol (Kaldenkirchen Lower Rhine (0.99% $C_{org.}$ 73.3% sand, 3.6% clay));
[b] Suspendable concentrate based on cyclohexanone;
[c] 1 cm height/20 cm height.

application was performed in two further experiments where ^{14}C-FLA was applied to the soil surface, mixed in a blank pesticide formulation based on cyclohexanone by a semi-automatic application device[6,11]. A gleyic cambisol with a high proportion of sand (73.3%) and a relatively low content of C_{org} (0.99%) was used in all experiments. Constant wind velocity of 1 m s^{-1} was adjusted (wind tunnel lid at 30 cm; measurement of wind velocity at a height of 20 cm in all experiments). In the first week no irrigation was given and at the beginning of the second week of the experiments, a precipitation programme with a total of 17 mm was realized by the irrigation unit (Table 2).

Each experiment represents a unique scenario, which is shown in Figure 3 after soil incorporation of ^{14}C-FLA. The diurnal rhythm of the irradiation, air/soil temperature and soil moisture document the varying field-like conditions. The content of soil water decreases perceptibly in the first week of the experiment and rises at the start of the irrigation programme.

In view of the expected high volatilization rates after application to the soil surface, the adsorption unit was replaced in a high time resolution (1, 3, 6, 12, 18 h after application) in order to provide an improved description of the kinetics of the volatilization process directly after application. Sampling was subsequently performed in a 12 h rhythm. Due to the lower volatiliation rates after soil incorporation, sampling intervals of 12 h or 24 h were selected.

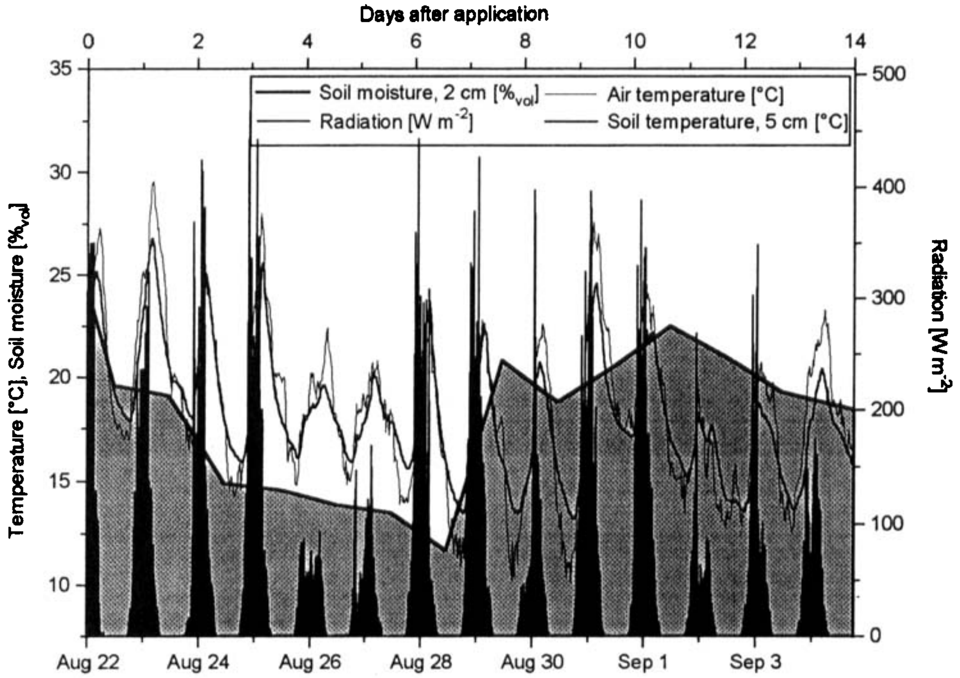


Figure 3 Climatic situation of wind-tunnel experiments with [3-^{14}C]fluoranthene: 2nd soil incorporation, Aug 22th–Sep 5th 1994).

RESULTS

Radioactivity balances

The recoveries are shown in Table 3. The functionality of the experimental apparatus and air analysis is documented by a ^{14}C recovery of 98.8 ± 3.4% AR. System contaminations were very low at < 0.1% AR, which can be attributed to the use of glass as the main construction material and high air change rates.

The major fraction of the applied radioactivity (AR) was recovered in the soil (61–98% AR). No radioactivity was detected in the leachate.The gaseous losses resulting from volatilization ranged between < 2% AR after incorporation into the soil and 12–33% AR after soil surface application. A moderate mineralization of 1.9–6.6% AR was observed in the experiments.

Soil

The radioactivity recovered in the soil at the end of experiments predominantly remained in the upper 2 cm of the soil, only traces of AR were detected in the underlying layer (Table 3). On average, approx. 80% of the soil radioactivity was extractable with acetone, approx. 95% of the extractable ^{14}C corresponded to unchanged ^{14}C-FLA. Thus

Table 3 ^{14}C recoveries of wind-tunnel experiments with [3-^{14}C]fluoranthene. Net applied radioactivity = 100%, all data in % of applied radioactivity.

Soil application type	*1st Incorp.*	*2nd Incorp.*	*1st Surface*	*2nd Surface*
Net applied [MBq]	9.72	5.78	2.06	1.97
Contamination[a]	< 0.1	< 0.1	< 0.1	< 0.1
Soil 0–2 cm:	96.7	87.8	60.0	76.8
Soil 2–7 cm:	1.0	0.2	1.4	4.0
Leachate:	n.d.	n.d.	n.d.	n.d.
Volatilization:	1.4	1.8	33.6	12.4
Mineralization:	1.9	5.3	6.6	3.3
Sum:	*101.8*	*95.2*	*101.6*	*96.6*

[a] Contamination of the wind tunnel and the high-volume sampler;
n.d. = not detectable.

after soil incorporation in duplicate experiments, 74.6% AR (1st Incorporation) and 68.8% AR (2nd Incorporation) were characterized as unchanged substance and 44.4% AR (1st Surface) and 58.4% AR (2nd Surface) after soil surface application (Table 4).

Mineralization

The cumulative mineralization from the C3 position of the ^{14}C-FLA molecule is shown in Figure 4. In all the experiments, a more or less distinct linear rise in mineralization can be observed without a lag phase.

A higher cumulative mineralization was observed in the experiments with higher mean temperatures (6.6% and 3.3% AR after soil surface application and 1.9% and 5.3% AR after soil incorporation) (Table 3).

Table 4 Analysis of soil (0–2 cm) of the wind-tunnel investigations with [3-^{14}C]fluoranthene at the end of the experiments in 1994.

Soil application type	*1st Incorp.*	*2nd Incorp.*	*1st Surface*	*2nd Surface*
% of applied radioactivity:	97.6	87.8	60.0	76.8
Radioactivity in soil (0–2 cm, after soil combustion BR = 100%)				
acetone-extractable [% of BR]	79.0	84.1	77.0	79.6
not extractable [% of BR]	20.5	9.3	22.8	13.5
^{14}C-recovery [% of BR]	99.5	93.4	99.8	93.1
Characterization by Radio-HPTLC: (acetone-extractable radioactivity ER = 100%)				
^{14}C-fluoranthene [% ER]:	97.7	93.2	96.5	95.6
NIR[a] [% ER]:	2.3	6.8	3.5	4.4
% of appl. ^{14}C-FLA[b]	*74.6*	*68.8*	*44.6*	*58.4*

[a] = not identified radioactivity. [b] = appl. ^{14}C-FLA = 100%

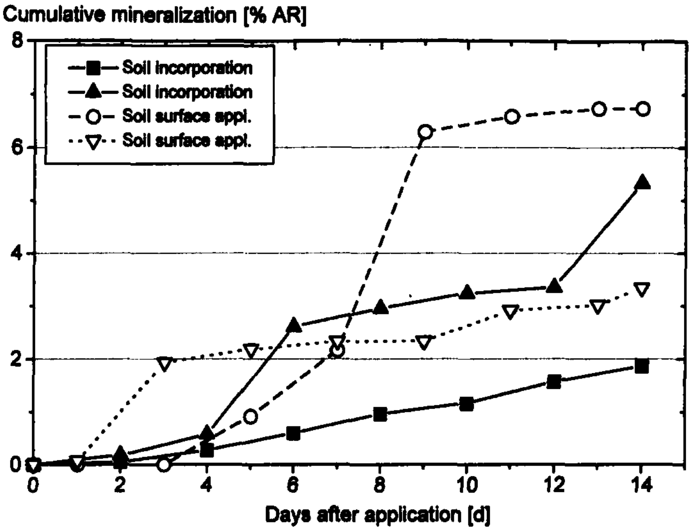


Figure 4 Cumulative mineralization in wind-tunnel experiments with [3-^{14}C]fluoranthene. Applied radioactivity = 100%.

Volatilization

^{14}C-FLA shows a clear volatilization tendency as a function of the type of application. After soil surface application, 33.6% and 12.4% AR were volatilized in the total experimental period. After soil incorporation cumulated volatilization was more than one order of magnitude lower (1.4% AR and 1.8% AR respectively) (Figure 5).

The highest volatilization rates were measured for the first sampling dates directly after application. As already observed as a trend during mineralization, a clear dependence of the average experimental temperatures of the volatilized radioactivity can be established (Figure 5, Table 2).

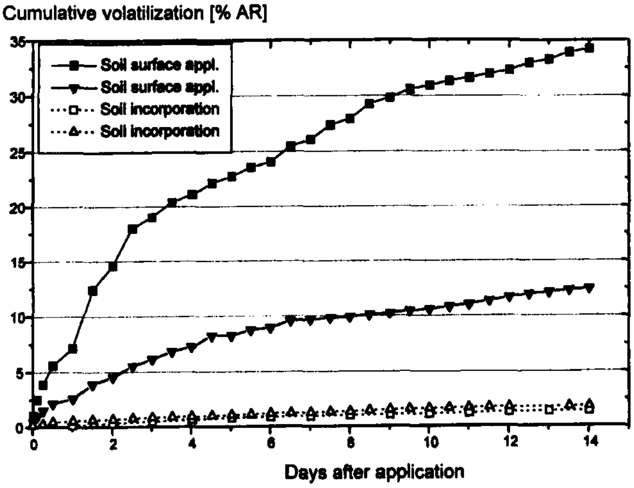
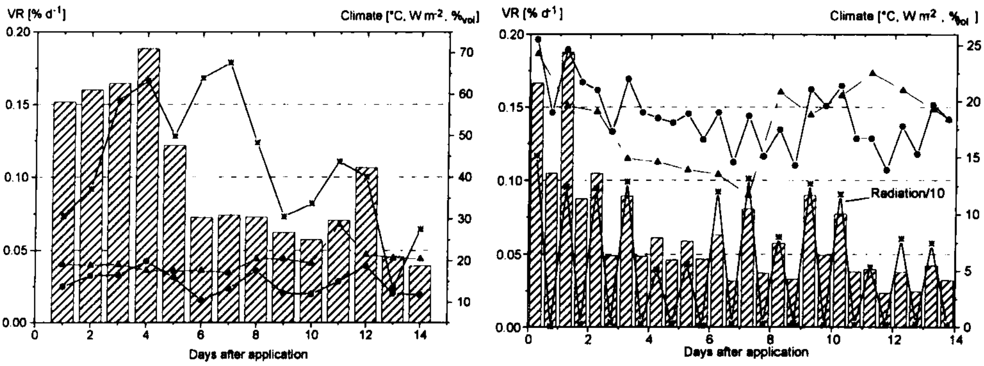


Figure 5 Cumulative volatilization in wind-tunnel experiments with [3-^{14}C]fluoranthene. Applied radioactivity = 100%.

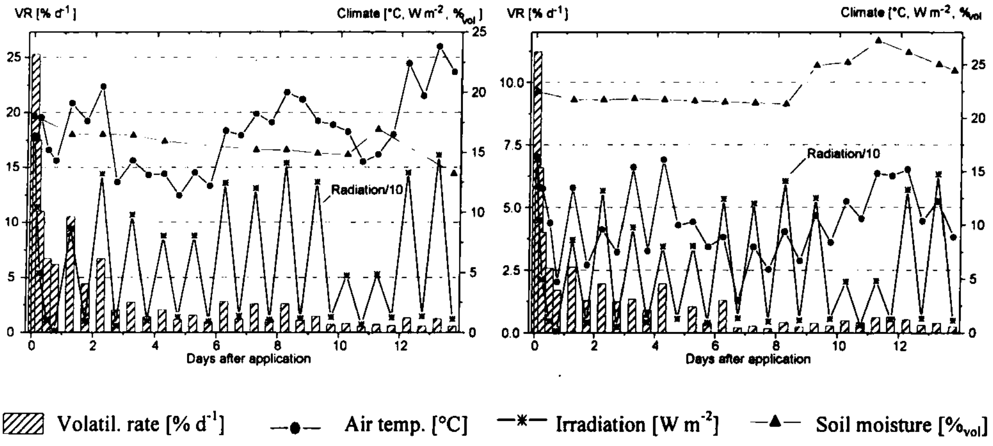
Daily volatilization rates expressed as % AR d^{-1} are much lower after soil incorporation than after soil surface application. The rates follow two-part kinetics in the course of the experiments. After initially very high volatilization rates (day 0–3, Figure 6), extremely low but constant daily rates are observed.

These kinetics could not be detected for the first soil incorporation experiment because of 24-hour air sampling. The other experiments with 12-hour air collection intervals, show clear diurnal rhythms. Volatilization of ^{14}C-FLA seems to be dependent on air temperatures. Although a clear dependence of the volatilization rate on the soil moisture has not been observed, nevertheless an indirect influence via soil water evaporation may be assumed. Only minor amounts of metabolites have been found in the air samples, 89–90% of the extracted radioactivity has been characterized as unchanged ^{14}C-FLA (Figure 7).



a) 1st soil incorporation experiment, 26 Apr.-10 May '94, Ø air temperature 14.7° C.

b) 2nd soil incorporation experiment, 22 Aug.-5 Sept. '94, Ø air temperature 18.5° C.



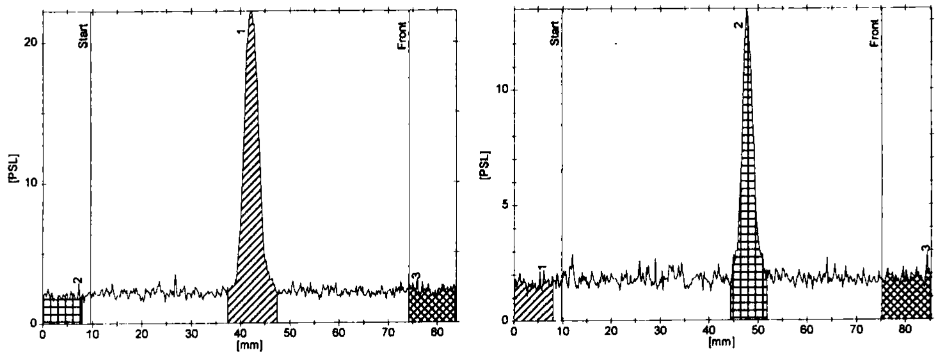
c) 1st soil surface application experiment, 6-20 Jun. '94, Ø air temperature 16.8° C.

d) 2nd soil surface application experiment, 11-25 Oct. '94, Ø air temperature 10.1° C.

Figure 6 Volatilization rates of [3-^{14}C]fluoranthene after different application types. Climatic parameters are averages within the air sampling periods.

a) 1st soil surface application:
PUF adsorption bed:
Toluene extract, 1 h after application.

b) 1st soil surface application:
PUF adsorption bed:
Toluene extract, 330 h after application.



c) 1st soil surface application:
Soil sample (0-2 cm)
Acetone extract, end of experiment.

d) 1st soil incorporation application:
Soil sample (0-2 cm)
Acetone extract, end of experiment.

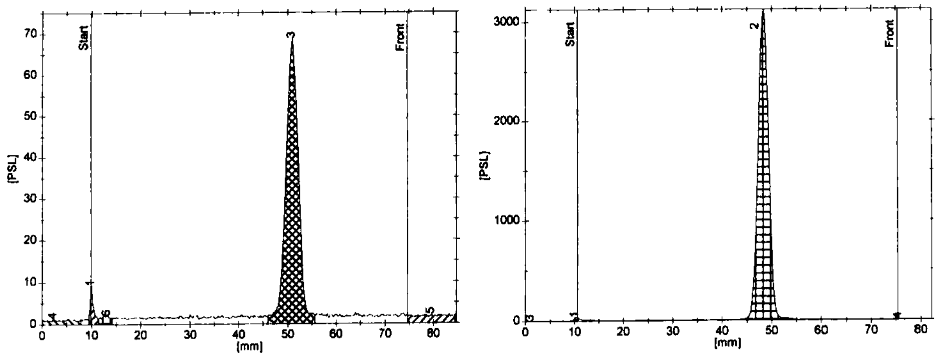


Figure 7 Examples of radio-HPTLC chromatograms of air and soil samples. PSL = '*photostimulated luminescence*' (intensity of radioactivity).

DISCUSSION

In our experiments, the gleyic cambisol was identified as the major sink for applied organic substances. 45–75% of the applied ^{14}C-FLA or 61–98% AR were recovered. In other lysimeter studies in which ^{14}C-FLA was incorporated in an orthic luvisol at an initial concentrations of 32.32 mg kg^{-1} [12,13], compared to our application of approx. 670 µg kg^{-1} in the wind tunnel experiments, only 5.7% AR was recovered at a depth of 0–35 cm after 132 d and 2.7% AR after duration of the study of 706 d. Thus, it can be assumed that intensive microbial conversion processes as well as a volatilization potential of ^{14}C-FLA are responsible for the decrease in concentration in the soil. This assumption is confirmed by detailed laboratory degradation studies with ^{14}C-FLA in an orthic luvisol at a concentration of 32.32 mg kg^{-1} [14,28]. With constant climatic conditions, i.e. 21°C and a soil moisture of 40% WHC$_{max}$, 63% AR was characterized as $^{14}CO_2$ after 117 d. Only 9.4% of the applied ^{14}C-FLA was recovered as the unchanged compound. The highest mineralization rates were recorded after 47–96 days, whereas $^{14}CO_2$-degradation in the first 14 days amounted $< 1\%$ AR. In contrast to this, very low to medium degradation rates in soil are described for fluoranthene in the literature[15], which are not in accordance with our experiments. An explanation for the high mineralization even in experimental durations of 14 days, may be provided by the permanently changing climatic conditions which have a considerable influence on the degradation performance of the microorganisms. The dependence of microbial activity and the associated conversion processes on climatic parameters has already been demonstrated for a number of other environmental chemicals, such as pesticides[16–18]. The influence of temperature on the persistence of pesticides is particularly emphasized[19,17]. It might be concluded, that an average temperature difference of approx. 7°C (Table 2), as measured in the experiments after soil surface application, influences the cumulative mineralization rate in the experiments by 50% (Table 2, Figure 4). The interpretation of degradation experiments by Schnöder[14] is similar. A considerably lower mineralization was recorded (12% AR) after 117 d (øtemperature; approx. 10°C) than at a constant 21°C (63% AR). It can be seen from the studies of Keck *et al.*[20] and Wild *et al.*[21] that PAHs having > 4 rings, are converted cometabolically. The $^{14}CO_2$ developed directly at the start of the ^{14}C-FLA experiments leads one to conclude an immediate cometabolic conversion by microorganisms. There is no lag phase, characteristic of an adaptation of the soil organisms, in any of the experiments (Figure 4), which supports the statements above[20,21].

It is remarkable, that the extent of mineralization after soil incorporation is lower than after soil surface application. One possible interpretation of this effect could be the high adsorption potential ^{14}C-FLA of associated with the low water solubility (Table 1). Although a more pronounced contact to microorganisms can be assumed in the soil incorporation variant, the binding mechanism in the soil seems to precede microbial activity and reduce microbial availability even further. The cumulative mineralization in the four experiments clearly indicates the complexity of interactions for the degradation of environmental chemicals in achieving experimental conditions similar to those of the field. Several parameters, such as temperature and soil moisture at the existing interfaces, display a considerable variation, which may both increase and also considerably retard the degradation rate.

The dependence of volatilization on the type of application, i.e. soil incorporation or surface application, is apparent and has already been documented for some pesticides[22,23]. The effective vapour pressure of an organic chemical is reduced by adsorption effects at the soil matrix and volatilization is correspondingly negatively influenced. In contrast to some pesticides[24,25], soil moisture has only apparently a minor influence on the volatilization tendency of ^{14}C-FLA. In a study with ^{14}C-diflufenican, Stork[6] established a clear dependence of the volatilization on the moisture situation after application onto bare soil. Compared with diflufenican ^{14}C-FLA exhibits a one order of magnitude higher adsorption coefficient, so that it is firmly adsorbed to soil matrix and is no longer desorbable even if the soil is remoistened with water. This is also confirmed by the decreasing extraction yields in Schnöder's[29] lysimeter/degradation studies. The influence of temperature on the volatilization rates is due to an increase of vapour pressure[28]. With a Henry coefficient of 2.7, ^{14}C-FLA can be classified as a category I chemical[30,31], i.e. volatilization is controlled by diffusion and there is no accumulation at the soil surface. First calculations with the HESP simulation model confirm the indication that volatilization of ^{14}C-FLA from bare soil is dependent on evaporation. Thus with high irradiation and a resulting high temperature, high volatilization rates are measured. In the second phase of the experiments low leveled volatilization rates lead to a steady state with a diurnal rhythm. Our volatilization data of ^{14}C-FLA is in accordance with the findings of Glotfelty *et al.*[23], Taylor and Spencer[31], who also observed diurnal volatilization kinetics for pesticides.

The volatilization process of organic chemicals from soils or soil surfaces depends on the physicochemical properties of a compound, the soil parameters (bulk density, adsorption potential, water content, pore volume, etc.) or the climatic parameters such as incident radiation and temperature[12,22]. In this connection, attention must be drawn to the fact that none of these studies performed with ^{14}C-FLA represents an existing pollution situation with aged residues since the test substance was applied freshly into or onto the soil. However, our experiments indicate, that one potential possibility of detoxifying problem sites could be provided by complete mineralization. Mahro and Kästner[32] have already developed biological concepts for remediation.

The wind tunnel offers a very good opportunity to study the behaviour of environmental chemicals under field-like conditions. Nevertheless, the findings presented indicate, that studies are necessary to investigate certain processes in detail.

Acknowledgements

The authors thank the following staff members of the Institute of Radioagronomy, Forschungszentrum Jülich GmbH, for their efforts in conducting the experiments and the analysis: S. Dupont, K. Matzerath, S. Stork, R. Witte.

The experiments were supported by: SHELL Internationale Petroleum Maatschappij B.V., The Hague, NL.

References

1. F. Führ, and R. J. Hance, (Eds.), *Lysimeter Studies of the Fate of Pesticides in the Soil.* BCPC Monograph No. **53**, (The Lavenham Press Ltd., Lavenham, Suffolk, 1992).
2. W. Veerkamp and D. E. ten Berge, *Manual on Human Exposure to Soil Pollutants,* Version 2.10a, (SHELL Internationale Maatschappij, Den Haag. 1994).
3. C. L. M. Poels and W. Veerkamp, *Toxicol. Letts.*, **64/65**, 503–510 (1992).
4. ECETOC. *Hazard assessment of chemical contaminants in soil.* European Chemical Industry Ecology & Toxicology Centre, Technical Report No. **40** (1990).
5. G. Rippen, *Handbuch der Umweltchemikalien.* 3. Ergänzungslieferung, ecomed verlagsgesellschaft, Landsberg (1991).
6. A. Stork, Ph. D. Thesis, University of Bonn, Agricultural Faculty (1995).
7. A. Stork, R. Witte, and F. Führ, *Eviron. Sci. Pollut. Res.*, **1**, 234–245 (1994).
8. VDI, 'VDI-Handbuch Reinhaltung der Luft', Band 4, (Verein Deutscher Ingenieure, Richtlinie 2066, Blatt 1, 1975).
9. VDI, 'VDI-Handbuch Reinhaltung der Luft', Band 4, (Verein Deutscher Ingenieure, Richtlinie 2066, Blatt 2, 1981).
10. R. Niehaus, B. Scheulen, and H. Dürbeck, *Sci. Total Environ,* **99**, 163–172 (1990).
11. A. Stork, C. Evers, W. Mittelstaedt, and F. Führ, 8th IUPAC Congress, Washington, poster 8a–722 (1994).
12. W. J. Farmer, K., Igue, W. F. Spencer, and J. P., Martin, *Soil. Sci. Soc. Am. Proc.*, **36**, 443–447 (1972).
13. F. Schnöder, W. Mittelstaedt, and F. Führ, In *Biologischer Abbau von polycyclischen aromatischen Kohlenwasserstoffen,* (Ed. B Weigert, TU Berlin, Schriftenreihe Biologische Abwasserreinigung, **4**, 217–230, 1994).
14. F. Schnöder, Ph. D. Thesis, University of Bonn, Agricultural Faculty (1995).
15. R. C. Sims and M. R. Overcash, *Res. Rev.* **88**, 1–68 (1983).
16. F. Führ, and W. Mittelstaedt, *Zeitschr. Pflanzenern. Bodenkunde,* **142**, 657–668 (1979).
17. K. Hurle, *Acta Phytomedica* **(8)** (Verlag Paul Parey, Berlin und Hamburg, 1982).

18. R. Kubiak, F. Führ, W. Mittelstaedt, M. Hansper, and W. Steffens, *Weed Sci.*, **36**, 514–518 (1988).
19. K. Haider, *Berichte über Landw.*, **198**, 81–92 (1985).
20. J. Keck, R. C. Sims, M. P. Coover, K. S. Park and B. Symons, *Water Res.*, **23**, 1467–1476 (1989).
21. S. R. Wild, J. P. Obbard, C. I. Munn, M. L. Berrow and K. C. Jones, *Sci. Total. Environ.*, **101**, 235–253 (1991).
22. W. J. Farmer, K. Igue, and W. F. Spencer., *J. Environ. Qual.*, **2**, 107–109 (1973).
23. D. E. Glotfelty, A. W. Taylor, B. C. Turner and W. H. Zoller, *J. Agric. Food. Chem.*, **32**, 638–643 (1984).
24. W. F. Spencer and M. M. Cliath, *J. Agric. Food Chem.*, **20**, 645–649 (1972).
25. W. F. Spencer and M. M. Cliath, *J. Agric. Food Chem.*, **22**, 987–991 (1974).
26. N. J. Fendinger and D. E. Glotfelty, *Environ.Toxicol. Chem.*, **9**, 731–735 (1990).
27. D. E. Glotfelty, M. M. Leech, J. Jersey and A. W. Taylor, *J. Agric. Food Chem.*, **37**, 546–555 (1989).
28. W. F. Spencer, W. J. Farmer and M. M. Cliath, *Res. Rev.*, **49**, 1–47, 1973.
29. F. Schnöder, W. Mittelstaedt and F. Führ, In *Fremdstoffe in Böden – Akkumulation, Bioverfügbarkeit, Bewertungsansätze,* (AGF-Meeting, Dec. 12, 1994, Bonn-Bad Godesberg, 28–30, 1994).
30. W. F. Spencer, W. A. Jury, L-Z Zhang and M. M. Cliath, *J. Environ. Qual.*, **17**, 504–509, 1988.
31. A. W. Taylor and W. F. Spencer, In *Pesticides in the Soil Environment: Processes, Impacts, and Modeling,* Number 2 (Ed.: H. H. Cheng, Soil Sci. Soc. Amer., Inc., Madison, Wi., USA, 213–269, 1990).
32. B. Mahro and M. Kästner; *Spektrum d. Wissensch.*, 10 (1993).