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INVESTIGATION OF ORGANIC XENOBIOTIC TRANSFERS, PARTITIONING AND PROCESSING IN AIR-SOIL-PLANT SYSTEMS USING A MICROCOSM APPARATUS. PART II: COMPARING THE FATE OF CHLOROBENZENES IN GRASS PLANTED SOIL

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ABSTRACT

A microcosm system was used to investigate and compare transfers of ^{14}C labeled-1,2-dichlorobenzene (DCB), 1,2,4-trichlorobenzene (TCB) and hexachlorobenzene (HCB) in an air-soil-plant system using single grass tillers planted into spiked soil. This study was the second phase of a development investigation for eventual study of a range of xenobiotic pollutants. Recoveries from the system were excellent at > 90 %. The predominant loss pathway for ^{14}C labeled-1,2-DCB and 1,2,4-TCB was volatilization with 85 % and 76 % volatilization of parent compound and volatile metabolites over 5 weeks respectively. Most of the added label in the hexachlorobenzene spiked system remained in soil. Mineralisation was <1 % for all compounds. ^{14}C plant burdens expressed as µg parent compound/g plant fresh weight were significant and suggest that plant uptake of chlorobenzenes from soil may be an important exposure pathway for grazing herbivores. Both shoot and root uptake of ^{14}C was detected, with foliar uptake of volatilised compounds dominating shoot uptake, and being greatest in TCB spiked systems. The microcosm is shown as potentially an ideal system with which to investigate organic xenobiotic partitioning in air-soil-plant systems to improve understanding of the equilibria and kinetics of exchanges. However, limitations imposed by the lab based conditions must be recognized and data should be compared with field based data sets as a consequence.

INTRODUCTION

Organic xenobiotic compounds may transfer between and within individual soil, gaseous, aqueous and biota compartments in a soil-air-plant system and transfers may be related to their physical-chemical properties influenced also by environmental conditions (Hung et al., 2001; Trapp and McFarlane, 1995). They may also be processed during transfer by mechanisms such as photolysis and biodegradation. Compounds may transfer from air-soil-plant systems to terrestrial foodchains and the more persistent may transfer to top predators and humans (McKone and Ryan, 1989). Full understanding of the equilibrium partitioning and kinetics of transfer, partitioning and processing of organic contaminants between and within environmental compartments is important to accurately develop and calibrate models to predict the fate of xenobiotics in environmental systems.

Models developed to predict realistic estimates of the supply of organic compounds to terrestrial food chains and, used for risk assessment purposes (Riederer, 1990; Trapp and Matties, 1995; Severinsen and Jager, 1998) suffer from a lack of reliable data to confirm model predictions (Polder et al., 1998) and also accurate input data (Dowdy and McKone, 1997). There is also particular current interest in improving our understanding about the influence of vegetation on the fate of semivolatile xenobiotics organic compounds because vegetation can serve as an important exposure route to humans and wildlife being a major sink for these compounds. It also has an important impact on environmental concentrations (McCrady and Maggard, 1993; McLachlan, 1999; Ugrekhelidze et al., 1997).

In a previous paper (Wilson and Meharg, 1999), we have described the development of a novel microcosm system to quantify transfers of certain xenobiotics in a grassed soil system. This microcosm is intended to provide detailed kinetic process data obtained under controlled conditions which can be compared with field observations to provide better understanding of compound fate mechanisms.

In this study we describe how the microcosm system was used to investigate the fate of three specific chlorobenzenes; 1,2-dichlorobenzene, 1,2,4-trichlochlorobenzene and hexachlorobenzene, in a grass planted soil and use the data to illustrate how the microcosm can be used to provide partitioning and equilibria data for a number of different xenobiotics. These specific chlorobenzene compounds were selected because they provide a range of physico-chemical properties with which to study compound fate processes in a microcosm system. Chlorobenzenes are also widespread industrial pollutants, are found in high concentrations in sewage sludge (Wang and Jones, 1991) and hexachlorobenzene in particular has been applied as a seed dressing fungicide and accumulation in agricultural food chains is of concern (McLachlan, 1996).

MATERIALS AND METHODS

Plants and soil

Holcus lanatus grass plants (Herbiseed, UK) were used in experiments. Single tillers were grown in soil (approximately 34 g dw) in a 100 mL Erlenmeyer flask until a mature root system developed (6 weeks). An agricultural loam (25 % clay, 45 % sand, 30 % silt) with pH 4.3 (3.9 in 0.01M $CaCl_2$) and an organic carbon content of 32.9±0.8 mg g^{-1} dw was used in experiments. The soil was seived to < 2 mm at field moisture content (not dried) and then Milli-Q water added so that soil was at 60 % maximum moisture holding capacity.

Materials

^{14}C labelled compounds used in experiments included 1,2-dichlorobenzene (Sigma) (specific activity 144.3 MBq $mmol^{-1}$), 1,2,4-trichlorobenzene (Sigma) (specific activity 136.9 MBq $mmol^{-1}$) and hexachlorobenzene (Sigma) (specific activity 588.3 MBq $mmol^{-1}$). These were made up in *n*-hexane to give an approximate activity of 37 KBq mL^{-1}. Solvents (*n*-hexane and acetone) were obtained from Rathburns (Pangbourne, Berkshire, UK) and scintillation cocktails (Hionic-Flour and Opti-Flour) were obtained from Packard (Pangbourne, Berkshire, UK).

Sample analysis

Polyurethane foam plugs (column plugs, flask top plugs and outlet plugs) and whole plant parts (tops, stems and washed and dried roots) if not analysed immediately were stored in 40 mL *n*-hexane. Wet soil samples (10 g) were stored in 30 mL *n*-hexane and 10 mL acetone.

Plant and soil samples were dried with anhydrous sodium sulphate (1 g and 10 g, respectively) (BDH, Lutterworth, Leicestershire, UK) prior to extraction. Polyurethane foam plugs and plant samples were soxhlet extracted for 6.5 h with 100 mL *n*-hexane. Soil samples were also extracted for 6.5 h but using a 20 mL acetone:80 mL *n*-hexane mixture. The cooled extract was made up to volume with *n*-hexane, an aliquot mixed with scintillation cocktail Opti-Flour O in a ratio of 1:2 and the activity counted using a liquid

scintillation counter (Tricarb 2500TR (Packard, Pangbourne, Berkshire, UK)). Spiking of a least three replicate blank samples showed mean recoveries from foam plugs of 100.1±1.1% for 1,2-dichlorobenzene, 88.2±1.2% for 1,2,4 trichlorobenzene and 90.3±2.9 for hexachlorobenzene; from plant parts 83.0±1.4% for 1,2-dichlorobenzene, 87.7±4.5% for 1,2,4 trichlorobenzene and 98.5±0.5 for hexachlorobenzene and from soils 89.1±2.0% for 1,2-dichlorobenzene, 88.3±1.4% for 1,2,4 trichlorobenzene and 93.1±1.3 for hexachlorobenzene.

Extracted plant parts and soil samples were subsequently digested with chromic acid to determine non extractable compound (*i.e*. that not extractable with solvent). Chromic acid digestion mixture consisted of 100 mL of a 2:1 mixture of concentrated sulphuric and phosphoric acids (BDH) added to 25 g chromuim (VI) oxide (BDH, Lutterworth, Leicestershire, UK) on ice. Whole extracted plant samples and 1g subsamples of the extracted dry homogenised soil/anhydrous sodium sulphate sample mixture were digested using 2 mL of the chromic acid by autoclaving at 120^{o}C for 0.5 h then allowing the digestion to stand overnight. $^{14}CO_2$ was trapped in 2 mL of 4M NaOH and a 0.25 mL aliquot mixed with 4 mL Hionic-Flour scintillation cocktail and counted on the liquid scintillation counter. Mean recoveries from plant parts were 84.9±5.2% for 1,2-dichlorobenzene, 92.2±1.8% for 1,2,4 trichlorobenzene and 93.6±3.2 for hexachlorobenzene and from soils were 89.7±3.7% for 1,2-dichlorobenzene, 89.2±7.6% for 1,2,4 trichlorobenzene and 93.6±3.9% for hexachlorobenzene.

Compound mineralisation was determined by counting 1mL aliquots of 1M NaOH carbon dioxide traps with 4 mL Hionic-flour. Based on previous work (Wilson and Meharg, 1999) < 0.01% of added label adsorbed to glass surfaces in these systems so this was not determined in these experiments. Microcosm inlet foam plugs were not soxhlet extracted but were saturated for five days in hexane and the activity of the hexane recorded. Mean recovery of 1,2-dichlorobenzene from spiked plugs was 99.2±3.1 %.

Blank samples were analysesd throughout experimental procedures and also blank solvent samples run on the scintillation counter. Sample results were adjusted for blank sample values and also for determined compound recoveries from foam plugs, soil and plant parts.

EXPERIMENTAL

The microcosm apparatus described in detail elsewhere (Wilson and Meharg, 1999) and illustrated in Figure 1 was used for experiments. The microcosm consisted of an outer glass chamber into which the pre-grown grass planted soils in flasks (single tiller per flask) were placed. From this a narrow glass tube exited to a glass adsorption column. The adsorption column contained a series of polyurethane foam plugs (BDH, Lutterworth, Leicestershire, UK) for trapping of volatile compounds (applied parent compound or volatile metabolites) and a liquid trap (10 mL oil bubbler (Radleys, Walden, Essex, UK)) containing 10 mL 1M NaOH for trapping of carbon dioxide produced as a result of compound mineralisation. Air was drawn through the system by peristaltic pump at a low flow rate of 3 mL min^{-1} to maintain aerobic conditions for plant growth and equilibrium conditions between soil and air. The flow rate was intended to mimic atmospheric conditions under still weather conditions. The whole system was kept under constant negative pressure. A small polyurethane foam plug was positioned at the exit of the liquid trap to assess any volatile compound carryover and another at the system inlet port to ensure air entering the system was free of organic compounds.

Grass shoots were separated from the roots by wrapping a polyurethane foam plug around the grass stem at the entrance to the flask in which the plants were grown.

Microcosms were kept in an incubator (MLR 350, Sanyo) with constant diurnal light and temperature conditions. The incubator cycle was a 12 h day cycle with temperature of 20^{o}C followed by a 12 h night cycle with temperature of 15^{o}C.

Three microcosm systems were prepared to independently investigate the fate and distribution of 1,2-dichlorobenzene, 1,2,4-trichlorobenzene and hexachlorobenzene in grass planted soils, respectively. For

each experimental system, four flasks each containing one grass tiller in soil were placed in each glass chamber, two were pre-spiked with the appropriate chlorobenzene and two left unspiked. The spike volume was 50 µl made up of cold chlorobenzene and ^{14}C label in hexane. This was added by injecting the spike volume in approximately 20 discrete amounts throughout the soil volume using a Hamilton syringe for want of any other recommended method for spiking intact plant rhizospheres. This spiking procedure did not damage plant roots because spiked plants showed no impairment compared to unspiked plants over the period of the experiment The spike had been made up so that the number of moles of each individual chlorobenzene added to each soil was the same. 0.044 mmol of both 1,2-dichlorobenzene and 1,2,4-trichlorobenzene were present in the 50 µl spike (5 µl and 5.5 µl of chlorobenzene compound, respectively) which gave soil concentrations of 0.20 mg g^{-1} dry soil and 0.24 mg g^{-1} dry soil respectively. Due to problems dissolving hexachlorobenzene in hexane only 0.53 µmol of hexachlorobenzene in hexane was added to the soil giving a soil concentration of 0.005 mg g^{-1} dry soil (However, this is within the range used by other workers (Scholl and Scheunert, 1992; Sotiriou et al., 1994)). The activity added to each soil ranged from 1 – 2.5 KBq depending on the compound (approximately 35 µl of ^{14}C standard). The spike volume prepared initially was greater than that required in experiments so that the exact spike activity used for experiments could be measured on the scintillation counter in Opti-Flour O at the start of the experiment.

After the soils had been spiked the microcosms were sealed and the experiment run for 5 weeks. Each different spiked system was set up in triplicate. The plants were not watered over the experimental period because of impracticalities for dismantling the system to enable watering. However, there was less than 2% moisture loss from soil in each flask over the experimental period because of low air flow rates through the system.

At week 2 and week 5 one spiked planted soil, one unspiked planted soil and also all foam plugs and NaOH traps were collected from each system (plugs and traps replaced at week 2) for analysis to assess the chlorobenzene distribution throughout the system at these intervals. In addition, at weeks 1 and 3, foam plugs and NaOH traps were collected for analysis and replaced so that the extent of mineralisation and volatilisation could also be determined at these intervals between plant/soil harvests. Results were used to

assess the distribution of the three chlorobenzenes throughout the microcosm system over the experimental period of 5 weeks.

RESULTS AND DISCUSSION

Mass balances for total ^{14}C added to the experimental systems averaged 91±2%, 98±2% and 108±5% for DCB, TCB and HCB spiked microcosms respectively over the two harvests of the experiment (Tables 1, 2, and 3). These data show excellent compound recovery for ^{14}C label in all three systems. The lower recovery of DCB was probably due to its relatively high volatility and possible losses during spiking procedures. The slightly high figure for HCB was a result of soil subsampling for analysis and subsequent data work up when HCB concentrations in soil were high (see later discussion).

The distribution of ^{14}C in each microcosm system over the experimental period is presented in Tables 1 to 3. Results have been calculated to show the distribution as % of initially added spike to one spiked/unspiked pair of grass planted soils at each harvest over the 5 weeks of the experiment, noting that plants were harvested only at weeks 2 and 5.

$^{14}CO_2$ detected in each system was < 1 % of initially added label over the five week experimental period. There was little mineralisation of di and tri chlorbenzene, maybe because the soil spiking technique used in these experiments enhanced volatilization rates and precluded the contact with soil biomass necessary for significant degradation. However, Scheunert et al. (1994) also reported low % mineralisation for these chlorobenzenes in a different microcosm set up using a different spiking technique. Mineralisation of HCB was not expected to be high (Scholl and Scheunert, 1992; Sotiriou et al., 1994).

The predominant loss mechanism for 1,2-DCB was volatilization. 71 % of added label volatilised after 2 weeks with 85 % volatilisation after 5 weeks (Table 1). The volatile compounds would constitute parent material and volatile metabolites but not $^{14}CO_2$ given the results described above. This agrees with previous work (Wilson and Meharg, 1999; Scheunert et al., 1994). 16 % of added label remained in the soil after 2

weeks, decreasing to 2 % after 5 weeks reflecting the increase in volatilized compound in this period. Data in Table 1 shows no evidence for compound incorporation in soils over the 5 week experimental period with all ^{14}C solvent extracted from the soil matrix. A low percentage of ^{14}C was detected in the soil of the unspiked plant at weeks 2 and 5. Based on previous work by these authors where flasks with unplanted soil were also investigated in microcosms (Wilson and Meharg, 1999) this is likely to be a result of diffusion of volatilised ^{14}C compound through the foam plug at the flask neck of the spiked plant and diffusion from the outer glass chamber through the foam plug of the unspiked vessel and sorption by the soil, rather than the plant acting as a conduit.

The predominant loss process for 1,2,4-trichlorobenzene was also volatilization of ^{14}C labeled TCB and volatile metabolites (Table 2). 52 % of added label volatilised after two weeks with 76 % volatilised after 5 weeks. Volatilisation rates were lower than those for 1,2-dichlorobenzene, as expected. A significant proportion of added label remained in soil, 42 % after 2 weeks with 20 % remaining after 5 weeks. Again, all ^{14}C in soil was solvent extractable with the % in digested soil insignificant. Transfer of added ^{14}C from the spiked soil to the unspiked soil was also seen in this system, again most likely occurring by the same diffusion process as described for the DCB spiked system, although the % transfer was lower.

Less than 1 % volatilisation of added ^{14}C label was observed in the hexachlorobenzene spiked system over the whole experimental period of 5 weeks. The results in Table 3 show that most of the ^{14}C added to soil remained in the soil over the 5 week experimental period (102 ± 2 %), in agreement with other studies (Sotiriou et al., 1994). There was no evidence for ^{14}C compound incorporation into the soil matrix (% ^{14}C in digested soil was insignificant). The final % ^{14}C in soil at the experiment end was calculated using results from extraction and digestion of subsamples collected from the whole volume of spiked soil (approx 30-40 g). Although the soil was well mixed before subsampling, obviously some inhomogeneity remained, particularly because it also necessarily remained wet. This has resulted in some over estimation of the final soil ^{14}C content for some samples although results are within the experimental error.

Between 1-2 % of initially added label for all compounds was detected in plant parts at experiment completion. Although conversion of added parent compounds to hydrophilic and non-polar metabolites in soil may influence plant uptake rates and volatile metabolites would make up a part of ^{14}C taken up by foliage, Scheunert et al. (1994), using similar chlorobenzenes in plant uptake short-term experiments over one week, demonstrated that the proportion of metabolites in soil was <1% of the ^{14}C in soil extracts and plant uptake was nearly only in the form of parent compounds. This is also supported by the work of Wang et al. (1996). Therefore, following the work of Scheunert et al. (1994), ^{14}C plant burdens have been

expressed as μg parent compound per g plant fresh weight in Table 4. For experiments conducted over long time scales, the proportion of volatile metabolites would require further assessment.

The data in Table 4 shows highly significant plant concentrations. After two weeks ^{14}C in the spiked plant as μg 1,2-DCB was 35.9±4.8 μg g^{-1} and this increased slightly to 41.7±6.6 μg g^{-1} by week 5. Similar concentrations were detected in the unspiked plant by week 5. Most compound in both unspiked and spiked plants was associated with plant tops and stems and a significant amount was extracted only by digestion (incorporated). These results suggest that equilibrium between plant and air DCB concentrations in this system were attained within the experimental period.

^{14}C in plants as μg TCB was present at greater concentrations than in DCB spiked systems, increasing from 64.0±8.2 μg g^{-1} (spiked plant) at week 2 to 129.4±21.4 μg g^{-1} by week 5, suggesting that plant-air equilibrium conditions were not observed within the experimental period. TCB was detected at lower concentrations in the unspiked plant possibly because of less contact time with volatilised compound. A significant proportion of compound was extracted by digestion (incorporated) but also a significant proportion of TCB was associated with the roots, explained by greater potential for root sorption because of lower volatilization rates.

^{14}C in spiked plants as μg HCB was < 1.5 μg g^{-1} by week 5 with most of the sorbed compound, not incorporated, but solvent extractable from the foliage and roots. At week 5, almost equal HCB concentrations were detected in the foliage and roots of spiked plants (Table 4).

The experiment shows that uptake of ^{14}C spiked to soil by both shoots and roots of grass tilters occurred in the microcosm systems. Most of this uptake was considered to be foliar uptake of volatilised parent compound because compound mineralisation was demonstrated to be negligible, and other workers have shown that conversion of parent compound to volatile metabolites is low (Scheunert et al., 1994). Foliar uptake (rather than translocation from plant root to shoot)was considered the major plant uptake mechanism also because of similar foliage concentrations in spiked and unspiked plants by week 5 shown particularly

for DCB. We assume foliar uptake by both spiked and unspiked plants occurred following compound volatilisation from soil and diffusion through the foam plug in the spiked flask neck to the main microcosm chamber. This observation corresponds with other work where translocation of organic xenobiotics from roots to shoots has been demonstrated not to be an important uptake pathway compared to foliar uptake (McLachlan et al., 1995, Trapp et al., 1990; Wang and Jones, 1994). In addition, the results suggest that there is comparatively greatest foliage uptake of TCB, the chlorobenzene of intermediate volatility, also corresponding with other work (Wang and Jones, 1994). Higher volatilization potential of DCB allows revolatilisation from foliar surfaces to the atmospher and the low volatilization potential of HCB results in low foliage uptake with resulting lower foliar concentrations because of inefficient volatilization from soil.

The system has demonstrated that plant uptake of chlorobenzenes is potentially a significant fate pathway and may be an important route of exposure to grazing herbivores (grazing cattle ingest approximately 12 Kg DM/day) and humans via foodchain transfers.

There has been much recent work to improve prediction of organic xenobiotic plant uptake from soil or air using physico-chemical parameters for more accurate assessment of risks associated with exposure (McLachlan et al., 1995). Uncertainty however exists in estimating doses because of unreliable or unrealistic data with which to calculate bioconcentration potentials and partition coefficients. Results from the microcosm experiment have been used to calculate plant/soil bioconcentration factors (BCF) for whole (spiked) plant fresh weight and for foliage fresh weight (Table 5) to demonstrate its potential for such data generation. To acheive this, we have again assumed most of the plant uptake was in the form of parent compound based on the above discussion. BCFs were greatest for DCB and lowest for HCB and increased for all compounds over the experimental period although the increase was greatest for DCB, presumably because of low soil concentrations. Log BCF (whole plant) was correlated with Log Kow values (Dowdy & McKone, 1997, Scheunert et al., 1994) and correlations were highly significant with r^2=0.984 (week 2) and r^2=0.983 (week 5). For more volatile compounds BCF (plant /air) is primarily determined by the octanol/air partition coefficient (Koa) as well as other factors such as temperature (McLachlan et al., 1995). The correlations of Log BCF (foliage) with Log Koa were calculated as r^2=0.99 (week 2) and r^2=0.73 (week 5). The poor correlation at week 5 may be explained because BCFs for foliage were calculated using soil

concentrations instead of air concentrations, and there may be less impact on foliage concentration by the soil for the more volatile compounds at this stage.

These data demonstrate the potential for the system to provide useful lab based data for better understanding of the mechanistic plant uptake of persistent organic pollutants. However, it must be noted that the data generated will obviously depend on limitations under laboratory conditions and comparison with field based data is also necessary.

CONCLUSIONS

The microcosm system has been used here to investigate the behaviour of three chlorobenzenes in grass planted soil. Compound recoveries in the system were excellent and the distribution and partitioning of the chlorobenzenes in the air-soil-plant system was demonstrated. The predominant loss process for 1,2-dichlorobenzene and 1,2,4-trichlorobenzene was volatilisation whereas most hexaxhlorobenzene remained in the soil after 5 weeks. Plant burdens of added label expressed as µg parent compound were highly significant and data from the system was used to calculate bioconcentration factors to demonstrate that the system can be used for improved understanding of relationships with physico-chemical data. Obviously in a system of this type data generation is limited by laboratory conditions. Although the microcosm shows good potential to study and compare persistent organic compound partitioning and distribution in an air-soil plant system, in a real system a number of additional effects should be considered such as, canopy effects, environmental conditions and soil type. This will be the focus of further studies and comparison with field based data sets is planned as well as an expansion of the range of pollutants studied.

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REFERENCES

1. Dowdy, D.L., McKone, T.E., 1997. Predicting plant uptake of organic chemicals from soil or air using octanol/water and octanol/air partition ratios and a molecular connectivity index. Environ Toxicol Chem. 16, 2448-2456
2. Hung, H., Thomas, G.O., Jones, K.C., Mackay, D., 2001. Grass-air exchange of polychlorinated biphenyls. Environ Sci Technol. 35, 4066-4073.
3. McCrady, J.K., Maggard, S.P., 1993. Uptake and photodegradation of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin sorbed to grass foliage. Environ Sci Technol. 27, 343-350.
4. McKone, T.E., Ryan, P.B., 1989. Human exposures to chemicals through food chains: An uncertainty analysis. Environ Sci Technol. 23, 1154-1163.
5. McLachlan, M.S., Welsch-Pausch, K., Tolls, J., 1995. Field validation of a model of the uptake of gaseous SOC in lolium multiflorum (Rye grass). Environ Sci Technol. 29, 1998-2004.
6. McLachlan, M.S., 1996. Bioaccumulation of hydrophobic chemicals in agricultural food chains. Environ Sci Technol. 30, 252-259.
7. McLachlan, M.S., 1999. Framework for the interpretation of measurements of SOCs in plants. Environ Sci Technol. 33, 1799-1804.
8. Polder, M.D., Hulzebos, E.H., Jager, D.T., 1998. Bioconcentration of gaseous organic chemicals in plant leaves: Comparison of experimental data with model predictions. Environ Toxicol Chem. 17, 962-968.
9. Riederer, M., 1990. Estimating partitioning and transport of organic chemicals in the foliage/atmosphere system: Discussion of a fugacity-based model. Environ Sci Technol. 24, 829-837.
10. Scheunert, I., Topp, E., Attar, A., Korte, F., 1994. Uptake pathways of chlorobenzenes in plants and their correlation with n-octanol/water partition coefficients. Ecotoxicol Environ Safety 27, 90-104.
11. Scholl, R., Scheunert, I., 1992. A laboratory system to determine separately the uptake of organic chemicals from soil by plant roots and by leaves after vaporization. Chemosphere 24, 97-108.
12. Severinsen, M., Jager, T., 1998. Modelling the influence of terrestrial vegetation on the environmental fate of chemicals. Chemosphere 37, 41-62.
13. Sotiriou, N., Moza, P., Scheunert, I., Feicht, E.A., 1994. Uptake and fate of ^{14}HCB in tobacco and wheat plants. Fresnius Environ Bull. 3, 175-180.

14. Trapp, S., Matties, M., 1995. Generic one-compartment model for uptake of organic chemicals by foliar vegetation. Environ Sci Technol. 29, 2333-2338.

15. Trapp, S., Matties, M., Scheunert, I., Topp, E.M., 1990. Modelling the bioconcentration of organic chemicals in plants. Environ Sci Technol. 24, 1246-1252.

16. Trapp, S., McFarlane, J.C., 1995. Introduction. In: Trapp, S., McFarlane, J.C. (Eds). Plant Contamination: Modelling and simulation of organic chemical processes. Lewis, Boca Raton, FL, USA, pp. 1-10.

17. Ugrekhelidze, D., Korte, F., Kvesitadze, G., 1997. Uptake and transformation of benzene and toluene by plant leaves. Ecotoxicol Environ Safety 37, 24-29.

18. Wang, M-J., Jones, K.C., 1991. Analysis of chlorobenzenes in sewage sludge by capillary gas chromatography. Sci of Tot Environ. 121, 677-691.

19. Wang, M-J., Jones, K.C., 1994. Uptake of chlorobenzenes by carrots from spiked and sewage sludge amended soil. Environ Sci Technol. 28, 1260-1267.

20. Wang, M-J., Bokern, M., Boehme, C., Jones, K.C., Harms, H., 1996. Phytotoxicity, uptake and metabolism of 1,4-Dichlorobenzene by plant cells. Environ Toxicol Chem. 15, 1109-1114.

21. Wilson, S.C., Meharg, A.A., 1999. Investigation of organic xenobiotic transfers, partitioning and processing in air-soil-plant systems using a microcosm apparatus. Part 1: Microcosm development. Chemosphere 38, 2885-2896.

Figure 1. Experimental system

Figure 1. Experimental system

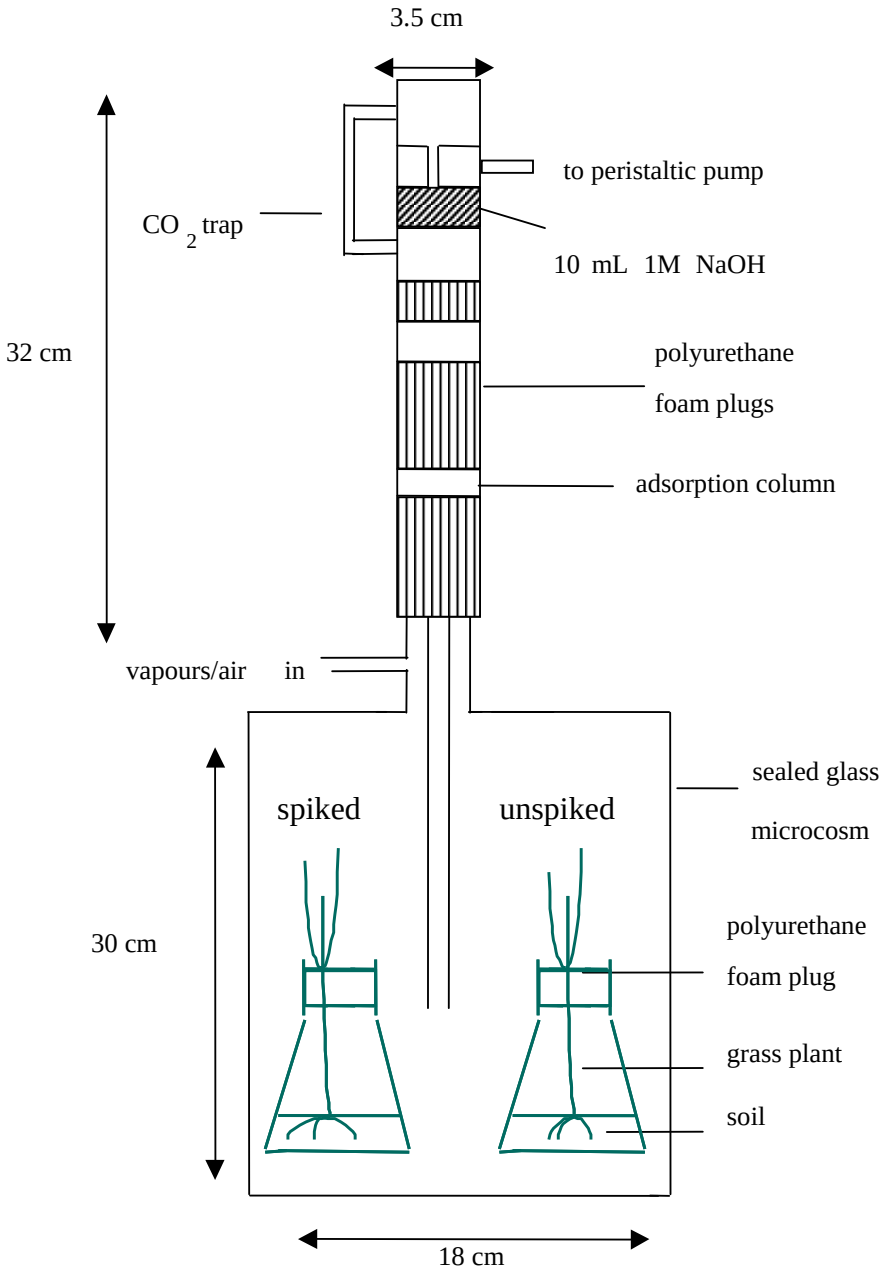

Table 1 Distribution of ^{14}C, as % of initially applied ^{14}C labeled 1,2-dichlorobenzene, in microcosm system over time

	Week 1	Week 2		Week 3	Week 5	
$^{14}CO_2$	0.09±0.02	0.03±0.004		0.05±0.01	0.06±0.003	
Volatile ^{14}C						
Trapped by column plugs	12.9±0.4	4.44±0.20		2.91±0.09	1.57±0.16	
Trapped by flask plugs	38.9±1.01	14.8±0.59		5.77±0.19	3.82±0.15	
Inlet plug		0.01±0.001			0.01±0.001	
^{14}C in plants						
		Spiked	**Unspiked**		**Spiked**	**Unspiked**
Plant extract top		0.013±0.006	0.003±0.003		0	0.105±0.064
Plant extract stem		0.026±0.014	0.012±0.005		0.132±0.075	0.169±0.036
Plant extract root		0.081±0.050	0.153±0.080		0.042±0.016	0.031±0.018
Plant digest top		0.056±0.006	0.029±0.003		0.057±0.016	0.101±0.029
Plant digest stem		0.070±0.007	0.069±0.039		0.189±0.032	0.14±0.012
Plant digest root		0.056±0.035	0.018±0.011		0.093±0.015	0.056±0.023
^{14}C in soil						
Soil extract		16.0±0.34	4.508±0.53		1.935±0.273	1.055±0.060
Soil digest		0.198±0.198	0		0	0
	92.4±1.31			89.4±2.39		

Table 2 Distribution of ^{14}C, as % of initially applied ^{14}C labeled 1,2,4-trichlorobenzene, in microcosm system over time

	Week 1	Week 2		Week 3	Week 5	
$^{14}CO_2$	0.163±0.003	0.032±0.003		0.087±0.034	0.045±0.008	
Volatile ^{14}C						
Trapped by column plugs	1.022±0.197	0.534±0.017		1.047±0.193	0.249±0.004	
Trapped by flask plugs	31.34±0.77	19.18±0.517		11.14±0.393	11.41±0.956	
Inlet plug		0.008±0.004			0.008±0.004	
^{14}C in plants						
		Spiked	**Unspiked**		**Spiked**	**Unspiked**
Plant extract top		0.011±0.011	0.192±0.062		0.460±0.033	0.115±0.069
Plant extract stem		0.002±0.002	0.007±0.007		0.108±0.055	0.115±0.052
Plant extract root		0.297±0.041	0.008±0.008		0.511±0.134	0.205±0.016
Plant digest top		0.10±0.014	0.073±0.014		0.066±0.006	0.038±0.013
Plant digest stem		0.06±0.016	0.064±0.020		0.064±0.036	0.083±0.017
Plant digest root		0.066±0.007	0.04±0.004		0.023±0.007	0.031±0.012
^{14}C in soil						
Soil extract		42.42±1.39	1.139±0.376		20.4±1.2	0.956±0.061
Soil digest		0	0.048±0.048		0	0
	96.8±1.15			99.4±1.98		

Table 3 Distribution of ^{14}C, as % of initially applied ^{14}C labeled hexachlorobenzene, in microcosm system over time

	Week 1	Week 2		Week 3	Week 5	
$^{14}CO_2$	0.040±0.006	0.027±0.023		0.016±0.007	0.032±0.010	
Volatile ^{14}C						
Trapped by column plugs	0.017±0.017	0.060±0.056		0.126±0.121	0.059±0.030	
Trapped by flask plugs	0.232±0.068	0.084±0.058		0.004±0.004	0.116±0.048	
Inlet plug		0.002±0.001			0.002±0.002	
^{14}C in plants						
		Spiked	**Unspiked**		**Spiked**	**Unspiked**
Plant extract top		0	0.002±0.002		0.251±0.130	0.052±0.052
Plant extract stem		0.054±0.054	0.224±0.112		0.129±0.038	0.234±0.025
Plant extract root		0.201±0.108	0.164±0.058		0.371±0.183	0.022±0.022
Plant digest top		0.055±0.019	0.045±0.022		0.052±0.004	0.014±0.007
Plant digest stem		0.094±0.032	0.011±0.010		0.057±0.047	0.025±0.019
Plant digest root		0.009±0.006	0.041±0.020		0.011±0.009	0.018±0.013
^{14}C in soil						
Soil extract		108.0±12.6	1.735±0.668		101.8±2.30	0.616±0.012
Soil digest		0.405±0.406	0		0.705±0.705	0
	111.5±12.1			105.0±3.04		

Table 4. Chlorobenzene content of grass tillers expressed as μg chlorobenzene/g plant fresh weight

	Week 2		Week 5	
	Spiked plant	**Unspiked plant**	**Spiked plant**	**Unspiked plant**
Dichlorobenzene				
Extracted tops and stems	4.60±1.60	1.90±1.14	9.68±5.67	15.58±3.91
Extracted roots	9.63±6.26	14.52±4.53	2.89±1.21	1.57±0.93
Digested tops and stems	14.88±1.51	10.96±3.97	17.68±1.41	14.41±1.73
Digested roots	6.77±4.45	2.92±2.50	6.20±1.08	3.68±1.94
Total	35.87±4.82	26.19±2.47	41.74±6.63	35.24±5.27
Trichlorobenzene				
Extracted tops and stems	1.50±1.14	23.66±3.92	50.00±10.28	20.31±9.94
Extracted roots	35.37±3.91	0.66±0.66	53.37±15.04	18.72±0.73
Digested tops and stems	19.97±1.29	17.15±3.57	13.71±3.15	10.81±4.94
Digested roots	8.03±0.70	4.94±0.55	2.35±0.79	3.05±1.23
Total	64.01±8.22	46.41±6.25	129.42±21.36	50.58±13.19
Hexachlorobenzene				
Extracted tops and stems	0.12±0.12	0.74±0.37	0.69±0.22	0.53±0.06
Extracted roots	0.62±0.31	0.47±0.13	0.58±0.23	0.04±0.04
Digested tops and stems	0.45±0.13	0.12±0.08	0.30±0.09	0.13±0.09
Digested roots	0.02±0.01	1.05±1.00	0.02±0.02	0.03±0.02
Total	1.21±0.30	2.42±1.20	1.49±0.16	0.81±0.06

Table 5. Bioconcentration factors (BCF) in grass plants (expressed as concentration of parent compound in the whole plant or stems & tops as μg g^{-1} fresh weight/soil concentration as μg g^{-1} dry weight soil)

	Whole plant BCF		Foliage BCF	
	Week 2	Week 5	Week 2	Week 5
1,2-Dichlorobenzene	1.14	11.3	0.62	8.55
1,2,4-Trichlorobenzene	0.62	2.64	0.21	1.50
Hexachlorobenzene	0.25	0.33	0.12	0.24

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