

**CENTRE FOR ECOLOGY AND HYDROLOGY
(NATURAL ENVIRONMENT RESEARCH COUNCIL)
CEH Project No. 0556**

Report to NERC Finance and Information Systems Directorate

Final Report GST/03/1566

Environmental Diagnostics Thematic Programme

J N Cape, U M Skiba & J Binnie

**CEH
Bush Estate
Penicuik
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January 2001

RESEARCH GRANT FINAL REPORT (Form PA1)

*Please send this form and your detailed report with four copies to reach
NERC within 3 months of the end date of the research grant*

NB: This form must accompany the final expenditure statement and the detailed report

1.	INVESTIGATOR(S): J N Cape START DATE: 1/7/97 END DATE: 31/12/00 (no cost extension from 30/6/00 agreed) GRANT REF NUMBER: GST/03/1566 IF THE RESEARCH INVOLVED ANY COLLABORATING ORGANISATION OTHER THAN PIs, ENTER NAME AND ADDRESS BELOW K C Jones (Lancaster), A Meharg (Aberdeen, formerly CEH Monkswood) joint award	
2.	TITLE OF RESEARCH PROJECT: Transfer, partitioning and processing of organic contaminants between and within air-soil-plant systems.	
3.	OBJECTIVES OF THE RESEARCH A: Field measurements of air concentrations of volatile organics B: Experimental determination of air-plant partition coefficients C: Field measurement of fluxes between the surface and the atmosphere D: Modelling	List main objectives in order of priority agreed at the award stage
4.	ACHIEVEMENTS OF THE RESEARCH A: Development of methods for long-term integrated sampling of VOCs at remote sites. Long-term (> 1 year) dataset on air concentrations of target VOCs (benzene, toluene, 1,1,1-trichloroethane, tetrachloroethene) from 3 rural sites (1 remote, 1 near-motorway, 1 agricultural), showing range of exposure of non-urban vegetation to VOCs, and dependence on weather conditions. Two campaigns with short-term data showing variation throughout day. The toluene:benzene ratio shows the average transport time since emission, if motor vehicle emissions are the major source. Ratios from the remote site implied atmospheric transport over 1 day prior to sampling. B: Successful development of methods to measure partitioning at relevant air concentrations, where 'equilibrium' leaf content of VOCs is on the scale of ng g ⁻¹ dry weight. We showed that partitioning cannot be described by a simple physico-chemical ratio, because grass appears to metabolise both benzene and toluene, but not the chlorinated solvents studied, at rates similar to uptake rates from the atmosphere. This finding has implications for the fate of VOCs at the earth's surface, as the products of VOC degradation in the plant are not known. C: We demonstrated that fluxes to grass (dry deposition velocities) of VOCs are too small to be measured with available micrometeorological technologies. This implies that exchange at the ground is a (negligibly) small loss mechanism for these compounds from the atmosphere. D: The modelling work requires data from all 3 collaborating institutions, and is mainly centred at Lancaster. Results from Prof. A. Meharg are awaited.	Describe briefly the extent to which the objectives of the research have been achieved and outline the principal outcomes of the work and their significance to the field
5.	RESEARCH PROGRESS	
(i)	Did the research proceed as expected and on time?	YES/NO If NO give details
	The start was delayed because of a delay in releasing funds to purchase thermal desorption apparatus, which was not commissioned until late autumn 1997. There was a knock-on effect on development of the analytical methods that underpinned all subsequent research measurements. The analytical difficulties were underestimated, especially the use of thermal desorption tubes at low levels, where artefact contamination by benzene and toluene was only controlled after intensive work on sample tube clean-up.	

<p>(ii) Was there any significant change in the research compared with the original proposal?</p> <p>The final modelling stage could not be completed because of the delays caused by A. Meharg's move to Aberdeen. The way forward has been discussed at length with the Programme Manager. For similar reasons, much of the proposed fieldwork was curtailed, with only 2 major field campaigns conducted, one at Bush and one at Lancaster. There was no effective collaboration with Prof. Meharg during the period of the grant.</p> <p>(iii) Were there any circumstances which aided or impeded research progress?</p> <p>Major breakdown of the bench-top mass spectrometer occurred twice during the period, causing several months' loss of analytical time. The staffing problems at ITE Monkswood meant that much of the proposed joint fieldwork did not happen.</p>	<p>YES/NO</p> <p>YES/NO</p>	<p>If YES give reasons for changes</p> <p>If YES explain how the work was affected and how any problems were overcome or opportunities exploited.</p>
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<p>6. RESEARCH DEVELOPMENT</p>		
<p>(i) Has the research led to further NERC grant applications?</p>	<p>YES/NO</p>	<p>If YES give details of outcome. List grant applications with dates and reference numbers. Indicate value of any grants awarded</p>
<p>(ii) Has the research led to further work in any other ways?</p> <p>The discovery that plants can utilise/degrade aromatic VOCs at ambient concentrations raises the possibility of induced changes in the plant itself caused by exposure to VOCs.</p> <p>New work has started, jointly with AstraZeneca (Brixham) and the University of Plymouth, on the potential for VOCs to have effects on plants. A pilot study was completed in November 2000, funded by AstraZeneca.</p> <p>A contract with DETR 'New Horizons' Programme has been awarded to J N Cape for a desk study into the potential effects of VOCs on vegetation.</p>	<p>YES/NO</p>	<p>If YES give details of outcomes. List grant applications and links, industrially supported work etc...</p>

<p>7. MANPOWER</p>
<p>List all staff employed directly on the grant and give details of training and career development opportunities offered during the grant</p> <p>J Binnie, Band 6(S) U M Skiba, Band 6(S)</p> <p>J Binnie attended a one-day training course in the use of the Perkin-Elmer Automated Thermal Desorption equipment, and a one-day training course on gas chromatographic techniques. Other training and career development opportunities were not specifically related to this award.</p>

8. COLLABORATION

Did any other external body or person(s) collaborate in the research? ~~YES~~/NO If YES give details and describe the extent and nature of collaboration.

9. EXPENDITURE

(i) Has expenditure exceeded or fallen short of the total sum awarded under any particular head by more than 20% ~~YES~~/NO If YES explain unexpected patterns/virement of expenditure

(ii) Have funds been used for attendance at any conference/meeting not specified in the research grant announcement? ~~YES~~/NO If YES give details, state benefits obtained, and how attendance furthered the research

(iii) Were any other funds used to support the research in any way? YES/~~NO~~ If YES describe how used

The staff time of J N Cape (Band 3/4 S) exceeded that estimated on the proposal. CEH therefore contributed approx. £45k as staff time (at FEC) over 3 years. CEH also supported a summer student placement (N. Mackie) from Heriot-Watt University Department of Chemistry in 1999, who worked full-time on this project for 5 months.

10. DISSEMINATION OF RESULTS

(i) List numbers of each of the following type of output: papers, and reports directly arising from the research, refereed papers, conference proceedings; book chapters etc

2 papers in press in refereed journals, 1 submitted
Presentations (oral or poster) at 5 international conferences and one UK conference

(ii) Detail any other means whereby research results have already been disseminated including contribution to the public understanding of the science.

Article in NERC Annual Report for 1999-2000

(iii) Has any major publicity been received for this work? Did you refer to NERC as the provider of support ~~YES~~/NO YES/NO

11. EXPLOITATION OF RESULTS

Is there anything patentable/commercially exploitable arising from the research? ~~YES~~/NO If YES give details and state how and when NERC was informed

12. BENEFICIARIES OF RESEARCH

Who are the likely beneficiaries of research eg other researchers, business and commerce, local or central government, other users.

Rural measurements will inform regulatory agencies such as EA and DETR. Results showing plant degradation of VOCs are of interest to industrial producers and users of solvents (c.g. AstraZeneca, as noted above) and will be of interest to plant biochemists/physiologists, and to regulatory agencies if deleterious effects of VOCs on plants are demonstrated in future.

13. DETAILED REPORT

Please attach:

- (i) a detailed report of not more than four sides of A4 inclusive of text, figures and references and of single-spaced typescript. Minimum font size should be 12 point but the full list of references arising from the research can be in a smaller font size. The report should outline the scientific and/or technological achievements summarised in section 12 above. Do NOT submit lengthy internal reports, PhD theses etc....
- (ii) a separate one page summary of the research suitable for general publication aimed at lay readers and describing the achievements made in the research grant. Include title, investigators, institutions, and key words, and name one person whom readers could contact.

14. SIGNATURES		
	Signatures	
	Principal Investigator	Co-Investigator(s)
Investigators	<i>[Signature]</i>	
Head(s) of Department	<i>[Signature]</i>	

FINAL REPORT ON GRANT GST/03/1566 (Environmental Diagnostics)

J N Cape, U M Skiba, J Binnie: CEH Edinburgh

Transfer, partitioning and processing of organic contaminants between and within air-soil-plant systems: development of a generic framework, mechanistic understanding and modelling approach.

Background

This project was conceived as an integrated approach to understanding the behaviour of organic contaminants across a wide range of classes of compound, from volatile organics (VOCs) to semi-volatiles (SVOCs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). CEH Edinburgh was assigned the study of VOCs, with 'target' molecules benzene, toluene, 1,1,1-trichloroethane and tetrachloroethene, and with dichlorobenzene as the molecule that would 'overlap' with studies at ITE Monkswood (Dr Meharg).

Objectives

The work package at Edinburgh had 3 major objectives:

1. Measurement of rural air concentrations of target VOCs at 3 sites over one year, to encompass seasonal variations, with intensive monitoring during joint field campaigns to explore diurnal changes. This was to supplement the available urban measurements of VOCs from DETR's Enhanced Urban Network and provide a comparison of rural and urban values.
2. Measurement of the uptake kinetics and equilibrium partitioning of target VOC molecules with grass under controlled conditions and exposures similar to those observed in ambient air. These measurements were to provide the core data for subsequent use in the modelling, and were specifically aimed at providing relevant information – the few published (laboratory) partitioning experiments had used very much larger air concentrations than observed in the field, and there was evidence that data obtained from such experiments could not be extrapolated safely to ambient concentrations.
3. Direct field measurement of fluxes of target VOCs to/from the earth's surface using existing micrometeorological techniques.

The results would be used to develop the overall generic modelling approach to predicting the transport and fate of organic contaminants in the (terrestrial) environment.

Methods

The development of new measurement techniques was an integral part of the proposal, given the requirement to work at low concentrations (in rural air) and to measure plant uptake at near-ambient concentrations. It was recognised that gas chromatography-mass spectrometry (GC-MS) would be required to ensure positive identification of VOCs in plant tissue, and the use of (automated) thermal desorption was specified to avoid the interference caused by contamination of any solvents used to extract analytical samples, especially as the target VOCs are in widespread use in laboratories.

Chemical analysis: A Perkin-Elmer ATD500 automated thermal desorption unit was purchased with the grant, and commissioned in late 1997. There then followed an intensive period of method development, which identified a serious problem arising from the artefact production of both benzene and toluene in the packed sampling tubes, despite the use of Chromosorb106 rather than Tenax, which has a known problem with artefact production of benzene. Although adequate for air sampling, it was only in summer 1999 that analytical techniques were adequate to resolve the uptake of VOCs by grass. All samples were analysed using capillary GC (SGE BP624, 25m x 0.53 mm i.d.) with He as carrier, using a temperature programme from 50-210°C. The ion trap (mass spectrometric) detector (Finnegan-Mat ITD) was used in full scan mode, with selective ion monitoring at $m/z=78$, 91, 97 and 146-148 for benzene, toluene, trichloroethene and tetrachloroethene, respectively. Quantitation was achieved using external standards, purchased as gravimetric solutions in methanol from Supelco, applied to clean ATD sampling tubes to cover the appropriate analytical range. Sample blanks were routinely included in all analyses.

Air monitoring: Packed sample tubes were exposed in duplicate for 1 to 2 weeks, with air sucked through the tubes at 25 ml min^{-1} using a small diaphragm pump. The 3 sites are shown in Table 1. During intensive campaigns, and in the partitioning experiments, an automated carousel sampler (Perkin-Elmer) was used to sample for 1-3 hour intervals, usually at a higher sample flow rate.

Plant exposure to VOCs: Four species of grass were raised from seed in standard compost in a cool greenhouse before transferring to open-top chambers (OTCs) at CEH Edinburgh. The OTCs are provided with a flow of charcoal-filtered air (ca. $15 \text{ m}^3 \text{ min}^{-1}$) to give two air changes per minute. Controlled fumigation was achieved by pumping air using a peristaltic pump (ca. 1 ml min^{-1}) through a flask held at 40°C containing pure VOC liquid. The saturated vapour was then introduced into the main airflow upstream of the OTC, and thoroughly mixed into the OTC in the turbulent flow. Concentrations measured at floor level using sampling tubes were in good agreement with the measured loss of solvent from the thermostatted flask and measured airflow rates. In windy conditions, air ingress through the top of the OTC diluted the target air concentrations.

Results

1. Air concentrations of selected VOCs at 3 rural sites

The three sites are described in Table 1. Median annual concentrations of benzene, 1,1,1-trichloroethane and tetrachloroethene were the same at all sites, but toluene concentrations were 4 times larger at Lancaster than the Edinburgh sites (Table 2). The toluene to benzene ratio at Lancaster and Bush was 2.8 and 2.1, respectively (median ratio). The emission ratio from transport

Site name	Grid reference	Site description	Sampling dates
Lancaster	SD 492 573	Rural area within 1 km of M6 at the southern outskirts of Lancaster	Oct 1998 - Oct 1999
Auchencorth Moss	NT 223 565	Drained peat bog in a rural area 15 km south of Edinburgh	Aug 1998 - Dec 1998, Feb 1999 - Mar 2000
Bush Estate	NT 245 639	Rural agricultural area at CEH 5 km south of Edinburgh's city bypass	Aug 1998 - Dec 1998, Feb 1999 - Mar 2000

sources is 2.3 and from non-transport sources is 9 (PORG, 1997). At the remote rural site at Auchencorth Moss the measured ratio was always smaller than at the Bush site or the more polluted rural site at Lancaster (Figure 1). The annual median ratio of 1.5 implies an average distance from sources (if assumed to be from vehicles) of around 1 day, based on reaction with OH radical as the major loss mechanism in the atmosphere.

Clear seasonal variations were only observed at the Lancaster site, with minimum concentrations of all VOCs measured in summer (May - July). The pattern is in agreement with observations at

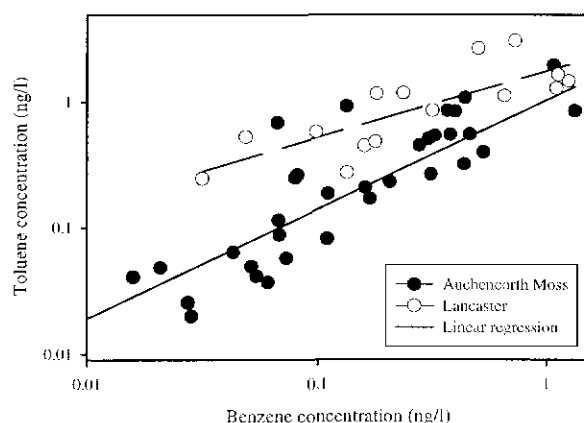


Figure 1. The toluene / benzene ratio at a rural and remote rural site

Mace Head, Ireland, (PORG, 1997). Diurnal variations (3 hourly means) were studied in detail at Auchencorth Moss (August 1998) and at Lancaster (June 1999) during intensive campaigns. No obvious diurnal pattern was observed, and variations were mainly controlled by wind direction. For example, at Lancaster the VOC concentrations measured over 3 hour periods for 5 days reflected the annual averages. Benzene, trichloroethane and tetrachloroethene concentrations decreased by 77% (benzene) and 40 % (chlorinated hydrocarbons) when the wind direction veered from the west to the east and rain fell. Toluene concentrations were not affected. At the

Auchencorth Moss campaign concentrations of all compounds were larger than the annual median due to predominantly north and north westerly air flow (bringing air from central Scotland) and low wind speeds ($< 2 \text{ m s}^{-1}$).

The concentrations at the 3 sites are similar in magnitude to those measured at Mace Head, Ireland, but are an order of magnitude lower than measurements made at a range of urban and rural sites (PORG, 1997; <http://www.aeat.co.uk/netcen/airqual>). Only the toluene concentration at Lancaster approaches the median annual toluene concentrations at the 'rural' site at Harwell.

Site	n [†]	Benzene	Toluene	Trichloroethane	Tetrachloroethene
Lancaster	17	0.18 ± 0.10	0.85 ± 0.21	0.090 ± 0.026	0.080 ± 0.042
Auchencorth Moss	37	0.11 ± 0.05	0.21 ± 0.07	0.083 ± 0.057	0.034 ± 0.030
Bush Estate	27	0.097 ± 0.019	0.24 ± 0.20	0.056 ± 0.010	0.011 ± 0.016

* median and standard error of the mean. † number of observations over the study period (Table 1).

2. Dynamics of exchange and partitioning of VOCs between air and grass

All the experiments used perennial ryegrass (*Lolium perenne*) as plant material, which was maintained fully-watered throughout. In dynamic experiments, samples were initially taken at hourly intervals after starting the exposure, and then less frequently, up to 24 h, when the grass

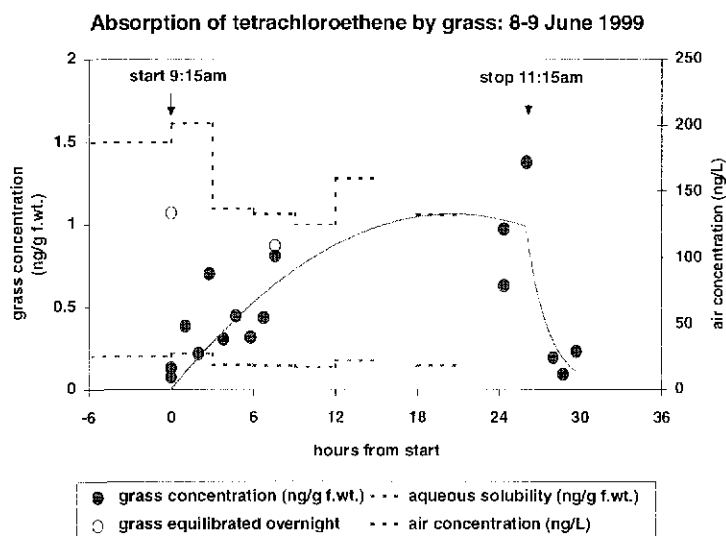


Figure 2. Absorption of tetrachloroethene by grass. Grass was transferred to exposure OTC at time=0. Upper dashed line shows air concentration (RH axis) and lower dashed line shows expected concentration of solvent in leaf water. Open symbols show concentrations from grass equilibrated over previous 24 h.

was removed from the VOC atmosphere and again sampled approximately hourly. In equilibrium experiments, grass was equilibrated at a given air concentration for 24 h and sampled, before the air concentration was changed for a subsequent 24 h period, for up to one week. Initial uptake of VOCs by grass was relatively rapid, with grass concentrations approaching the 24 h value after a few hours (Figure 2). The rate of uptake was not limited by air turbulence, which in the chambers is very efficient (maximum transfer rates of 5 cm s^{-1} or more). A typical uptake rate, even for initial measurements, was very slow compared with uptake of inorganic gases; equivalent deposition velocities were of the order of 10^{-6} m s^{-1} or less (cf. up to several cm s^{-1} for gases such as HNO_3 , and several mm s^{-1} for NO_2). The resistance to uptake presumably stems from the low aqueous solubility, and the rapid equilibration of surface sinks followed by slow transfer and equilibration within the leaf. At equilibrium, the deposition velocity should fall to zero, assuming no net loss of VOC within the plant-soil system. On removal from the exposure, leaf concentrations of VOCs fell rapidly to below the detection limit (Figure 2). This behaviour shows a typical partitioning response, with leaf uptake much greater than expected from simple partitioning into leaf water (ca. 80% leaf fresh weight), shown by the lower dashed line, calculated from aqueous solubility. The partitioning into leaf dry matter was 20 times greater than into water, as expected for a lipophilic molecule. Similar behaviour was shown for 1,1,1-trichloroethane.

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However, benzene showed a different pattern of behaviour. Although uptake to a reproducible equilibrium value was observed, the resultant equilibrium concentration was less than that predicted from aqueous solubility alone. This implies that the concentration measured in the leaf was maintained as the balance between the rate of uptake and the rate of removal of benzene from the leaf, and that the removal rate was similar in magnitude to the uptake rate. The measurements cannot distinguish between export to the roots and degradation of benzene within the leaf, although this is known to occur at very high benzene concentrations (e.g. Ugrekhelidze *et al.*, 1997). Toluene showed intermediate behaviour, with initial rapid uptake to leaf concentrations approximately double the calculated aqueous solubility, then a decline to values similar to the aqueous solubility after 24 h, again implying active removal from the leaf.

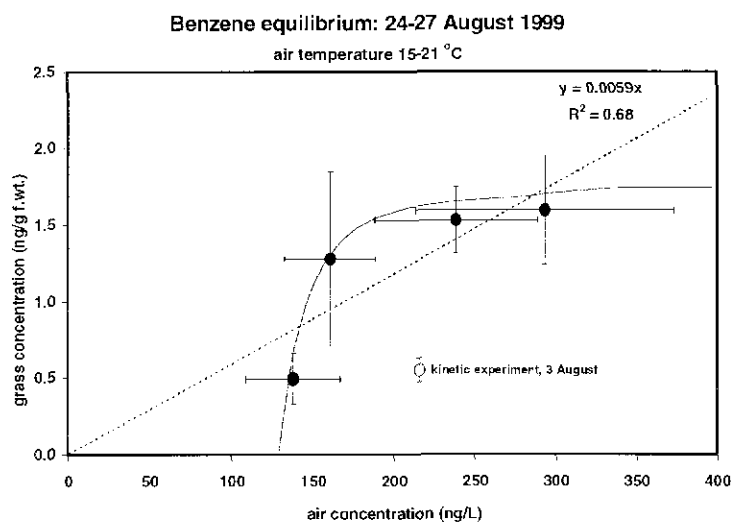


Figure 3. Partitioning of benzene between grass and air, showing the non-linearity introduced by removal processes in the leaf.

Figure 3 shows the results of an equilibration experiment where air concentrations were maintained for 24 h then changed. Simple physico-chemical partitioning would lead to a linear relationship. The data imply that, for air concentrations below about $100 \mu\text{g m}^{-3}$, benzene is removed from grass faster than it is absorbed. The difference in leaf concentration from an earlier experiment (3 August – see Figure 3), is presumably related to changes in plant metabolic activity and growing conditions over the 3-week period.

3. Flux measurements

The above results demonstrate why we were unsuccessful in measuring fluxes. Transfer rates (expressed as deposition velocities) were shown to be 10^4 times smaller than those typically observed for small inorganic molecules. The resultant vertical concentration gradients in the field, or concentration gradients across a dynamic box, were too small to measure.

Conclusions

- it is now possible to measure the partitioning of a range of anthropogenic VOCs between air and grass at concentrations that can be found in urban air, but plant processes act to maintain leaf concentrations below those that might be predicted from simple physico-chemical models. The fate of the removed VOC is not known.
- the net rate of uptake of VOCs by grass is very slow relative to the uptake rate of small inorganic gases, and is controlled by processes on or within the leaf. Conventional methods cannot be used to measure fluxes of anthropogenic VOCs between air and grassland.

References

- PORG (1997) UK Photochemical Oxidants Review Group Report. ISBN 1 870393 30 0
 Ugrekhelidze, D, Korte, F & Kvesitadze, G (1997) Uptake and transformation of benzene and toluene by plant leaves. *Ecotoxicol. Environ. Safety*, 37, 24-29

Publications

- Binnie, J., Cape, J.N., Mackie, N., Leith, I.D. (in press) Exchange of organic solvents between the atmosphere and grass- the use of open-top chambers. *Sci.Total Environ.*
 Binnie, J., Cape, J.N., Skiba, U.M., Mackie, N., Leith, I.D. (in press) Transfer of volatile organic compounds in an air-plant system. *J. Anal. Environ. Chem.*
 Binnie, J., Cape, J.N., Skiba, U.M., Mackie, N. (submitted) The importance of sample preparation and blank levels in the measurement of volatile organic compounds in rural and semi-rural sites. *Proc.5th Europ. Conf. Environ. Chem. Sep.2000, Visegrad, Czech.*