VOLUME 19, NUMBER 2, 1993 ISSN 0160-4120

ENVIRONMENT INTERNATIONAL

A Journal of Science, Technology, Health, Monitoring and Policy

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ENVIRONMENT INTERNATIONAL

A Journal of Science, Technology, Health, Monitoring and Policy

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Production Editor: *Lorraine Petrella, Pergamon Press, Tarrytown, New York.*

Editorial Office: *Environment International,* P. O. Box 7166, Alexandria, Virginia 22307, USA.

Publishing, Subscription and Advertising Offices: Pergamon Press Inc., 660 White Plains Road, Tarrytown, NY 10591-5153, USA INTERNET "PPI@PERGAMON.COM" and Pergamon Press Ltd., Headington Hill Hall, Oxford, OX3 0BW, England.

Published Bimonthly. *Annual Institutional Subscription Rate* (1993): £270.00 (US$432.00). Sterling prices are definitive. US dollar prices are quoted for convenience only, and are subject to exchange rate fluctuation. Prices include postage and insurance and are subject to change without notice.

ENVIRONMENT INTERNATIONAL

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Pergamon Press
New York • Oxford • Seoul • Tokyo

Pergamon Press Offices:

U.S.A.: Pergamon Press, 660 White Plains Road, Tarrytown, NY 10591-5153, USA

U.K.: Pergamon Press, Headington Hill Hall, Oxford, OX3 0BW, England

KOREA: Pergamon Press, K. P. O. Box 315, Seoul 110-603, Korea

JAPAN: Pergamon Press, Tsunashima Building Annex, 3-20-12 Yushima,
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The Item-Fee Code for this publication is: 0160-4120/93 $6.00 + .00.

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EDITORIAL

SAVING THE EARTH OR SAVING PEOPLE

The United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro was the culmination of efforts by many to revitalize the spirit of The Stockholm Conference that occurred twenty years earlier. The Rio Conference achieved a great deal of agreement among third world nations to receive aid from developed countries to enhance environmental protection in their respective countries. It is rather easy for a group to reach a consensus to receive funding for worthy causes. During the Rio Conference, there were repeated calls to save the Earth. This call is misplaced and overlooks the geologic history of the planet Earth.

The atmosphere of the Earth at one time was incapable of supporting life, any life. The temperature of the globe was at one time above 100°C and yet later there was an ice age. There have been several continental shifts moving an entire continent. There have been earthquakes significantly harsher than the most sever recent earthquakes.

Given the history of the Earth, changes in the carbon dioxide by a factor of two or three or more are insignificant as compared to the previous carbon dioxide concentrations. Similarly, any other physical change in the globe that can be induced by human activity becomes insignificant as compared to conditions that existed in the Earth's history.

It is obvious that it is not the Earth that is of concern, but living things, particularly humans. It is most unfortunate that political environmentalism based on ideology appears to be the driving force behind environmental decisions.

Certainly biodiversity is worth preserving. The questions are what is a species and who determines it? Certainly, tinkering with the globe's climate is cause for concern, but who determines if one is tinkering and who decides what actions are to be taken? Is Earth of primary concern or are the people? All of these must be placed in the context of other causes of human misery and the need for development. Does an individual care if carbon dioxide concentration increases by a few percent if he or she has children to feed and a family to protect and has the means to do so? What is being overlooked is poverty as the ultimate form of pollution. Poverty denigrates humans to animals and causes more adverse effects than any other form of pollution. The Earth does not need to be saved. People do.

A. Alan Moghissi

Environment International, Vol. 19, pp. 109-119, 1993
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0160-4120/93 $6.00 +.00

VENTILATION AND INDOOR AIR QUALITY IN FINNISH DAYCARE CENTERS

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EI 9211-202 M (Received 23 November 1992; accepted 23 December 1992)

The purpose of this study was to assess the performance of ventilation and the indoor air quality in Finnish daycare centers and to evaluate the effect of ventilation and building design on indoor air quality. A random sample of 30 daycare centers in the city of Espoo (part of the Helsinki metropolitan area) was selected for the study. The measurements during October and November 1990 consisted of air flows, temperature, relative humidity, concentrations of CO_2, VOC and formaldehyde, and odor intensity. The measurement period was one day. The air flows in the children's rooms varied remarkably, the range being 0-11 L/s per person (average 3.8 L/s per person). Only 30% of the rooms achieved the Finnish guide value of 5 L/s per person. The air temperature varied from 19°C to 26°C (average 22.2°C). The carbon dioxide concentration measured when the room was occupied varied from 400 to 2500 µL/L (average 810 µL/L). On average, the CO_2 concentration was statistically significantly higher in the older daycare centers (constructed before 1981) with mechanical exhaust than in the newer buildings (constructed from 1981 onward) with balanced mechanical ventilation. Correspondingly, the air flows and temperatures were significantly lower on average. The workers were asked to state their experience of poor indoor air quality during the past twelve months; the most common perception was unpleasant odors (60%). Water damage and moisture problems were also common in the daycare centers (70%). The results indicate that there is much room for improvement in the indoor air quality of daycare centers.

INTRODUCTION

Approximately one third of the Finnish preschool children aged 1 to 6 y are enrolled in daycare centers. Little is known of the indoor air quality of daycare centers, where such a large proportion of children spend one third of their time. It has long been known that infectious diseases are more common among children in daycare centers than among children in other forms of care, but the effects of different indoor environmental factors have not been sufficiently studied (Hesselvik 1949; Vihma 1969; Strangert et al. 1976; Ståhlberg 1980).

Recently, Daneault and colleagues (1992) reported alarmingly high concentrations of carbon dioxide, with over 90% of daycare centers exceeding 1000 µL/L, indicating poor air quality in the greater Montreal area. Inadequate ventilation rates and high concentrations of CO_2 and chemical and biological pollutants have also been measured in daycare centers in the Nordic countries and North America: Denmark (Lundqvist et al. 1982; Olsen and Døssing 1982; Steensberg 1984; Iversen et al. 1985; Jørgensen-Birch et al. 1986; Pejtersen et al. 1991), Norway (THF 1987; Bakke and Levy 1990), Sweden (Berglund et al.

1982; Sverdrup et al. 1990), Finland (Nevalainen et al. 1987), and Canada (Dionne and Soto 1990). The indoor air quality of Finnish daycare centers has not been studied systematically.

The main objective of this study was to assess the performance of ventilation and the indoor air quality in Finnish daycare centers and to evaluate the effect of ventilation and building design on indoor air quality. Another objective was to determine to what extent the Finnish guide values were followed.

METHODS

Daycare centers

From 112 daycare centers in the city of Espoo, a random sample of 30 daycare centers (27%) was selected for the study. Espoo is an urban-suburban municipality with a population of 170 000. It is part of the Helsinki metropolitan area, where the mean annual outdoor temperature is approximately 5°C. The daycare centers were built between 1910 and 1990, and the median construction year was 1982. More than half the daycare centers (57%) were detached daycare buildings, and the rest of them (43%) were situated on the ground floor of blocks of flats. Most centers (67%) were one-story, and the rest (33%) were two-story. The floor area varied from 140 to 950 m^2 (average 560 m^2, standard deviation 260 m^2). The floor area per child was between 4 and 29 m^2/person ($\bar{x}$ 10 m^2/person, SD 4 m^2/person). The number of children in the daycare centers varied from 17 to 104 ($\bar{x}$ 56, SD 28) and the number of workers from 5 to 25 ($\bar{x}$ 14, SD 6). The number of children per daycare worker was between 3 and 9 ($\bar{x}$ 5, SD 1). The ventilation system in most of the daycare centers (63%) was balanced ventilation (mechanical supply and exhaust), while the rest of the centers (37%) had mechanical exhaust only. The majority of the daycare centers (93%) were fitted with hot water radiators; floor and ceiling heating were both used as the main heating system in one center. The characteristics of the 30 daycare centers are presented in Table 1.

Data collection

Measurements of the ventilation performance and the indoor air quality were made during October and November 1990. The measurement period in each daycare center was one day. The measurements consisted of air flows, temperature, relative humidity, concentrations of CO_2, volatile organic compounds (VOC), formaldehyde, and odor intensity. The temperature, relative humidity, and CO_2 concentration of the indoor air were monitored for a period of 7 h in two rooms, one room used for infants 0-2 y old and one used for children 3-6 y old. Temperature, humidity, CO_2 concentration, and exhaust air flows were measured with momentary point measurements in all the children's rooms (resting and playrooms) when the rooms were normally occupied. The measurements were made at the same time of the day, i.e., 1.45 pm ±15 min, in all the buildings and rooms. According to the monitoring measurements, the CO_2 concentrations reached their equilibrium levels at this time. In addition, odor intensity was determined concurrently by two researchers (R. Ruotsalainen and N. Jaakkola, members of a trained panel). One-hour concentrations of VOC and formaldehyde were measured right after the other measurements in one of the rooms for 3-6 y old children.

A self-administered questionnaire was distributed to each worker of the 30 daycare centers studied in March 1991, inquiring symptoms and perceived indoor air quality during the previous 12 months. The questionnaire was returned by 339 workers (96.0% of all). The assessment of indoor air quality was based on 268 female nursing workers (two male nursing workers were excluded), whose characteristics are described in Table 2. The outcomes of interest consisted of the presence of the following indoor air quality perceptions: warmness, coldness, dryness, and unpleasant odor.

Measurement techniques

The air flows were measured from the exhaust valves with a hot wire anemometer and an anemometer tube (Wallac). The temperatures were measured with a thermistor and the relative humidity with a capacitive bulb (Rotronic). The CO_2 concentrations were measured with an infrared analyzer (Binos). A datalogger (Grant-Squirrel) was used with these measurements. The VOC concentrations were measured using an active sampling method and tenax-absorbers; the samplers were analyzed in a laboratory with a gaschromatograph. The formaldehyde concentrations were measured using a chromotrope acid method, and they were analyzed in a laboratory.

Statistical methods

The measured indoor air quality parameters were compared according to building type, construction year, and ventilation system. The statistical significance of the differences was tested with an unpaired t-test or Wilcoxon rank sum test. The mutual linear correlation of the indoor air factors was estimated by regression analysis (Armitage 1971).

Table 1. Characteristics of the 30 daycare centers studied.

	N	%
Building type		
Detached building	17	56.7
Blocks of flats	13	43.3
Year of construction		
-1970	3	10.0
1971-1975	5	16.7
1976-1980	5	16.7
1981-1985	5	16.7
1986-1990	12	40.0
Floor area (m^2)		
-299	5	16.7
300-499	7	23.3
500-699	7	23.3
700-899	8	26.7
900-	3	10.0
Volume (m^3)		
- 999	9	30.0
1000-1999	5	16.7
2000-2999	11	36.7
3000-	5	16.7
Ventilation system		
Natural ventilation	0	0.0
Mechanical exhaust	11	36.7
Balanced ventilation	19	63.3
Number of children		
-29	3	10.0
30-49	12	40.0
50-69	5	16.7
70-89	5	16.7
90-	5	16.7
Number of day-care workers		
- 4	2	6.7
5- 9	13	43.3
10-14	8	26.7
15-19	4	13.3
20-	3	10.0
Children per day-care worker		
-<4	3	10.0
4-<5	12	40.0
5-<6	9	30.0
6-<7	4	13.3
7-	2	6.7
Floor area per child (m^2/person)		
-< 8	5	16.7
8-<10	10	33.3
10-<12	9	30.0
12-	6	20.0

RESULTS

The 30 daycare centers studied had a total of 103 children's rooms. Measurements were made in 83 of these rooms, which were occupied as usual, i.e., the children had been in the room for at least an hour.

Ventilation

The ventilation systems were operated for at least 8 h and on average 17 h/d, at full power for 12 h and at half power for 5 h. Defects in the ventilation systems were quite common. In eight daycare centers, the fans worked only partially: in four daycare centers, one of the fans did not work at all; in two daycare centers, the fan did not work at full power; and in two daycare centers, the control of the fans was not functioning properly. Furthermore, there were minor malfunctions with the timer-control of the ventilation systems in five daycare centers. In addition, water damage and moisture problems were common in the daycare centers (70%). The most common cause of water damage was a leaking roof.

The air flows in the 83 children's rooms varied remarkably. The range was 0-11 L/s per person and the average was 3.8 L/s per person (SD 2.7 L/s per person). The distribution of the air flows was within the limits of normal distribution (skewness 0.46, kurtosis -0.54). The Finnish guide value of 5 L/s per person (ME 1987) was achieved in 30% of the rooms. The exhaust air flows calculated per floor area varied from 0 to 4 L/sm^2 (average 1.2 L/sm^2, SD 0.8 L/sm^2); only 18% of the children's rooms achieved the Finnish guide value of 2 L/sm^2. The ventilation rates calculated were below 5 m^3/hm^3 ($\bar{x}$ 1.5 1/h, SD 1.0 1/h). The measured air flows were lower than the design air flows (or guide values) in the majority of the rooms (95%). The measured air flow varied between 0% and 106% of the design value (average 53%). The distribution of the air flows is presented in Fig. 1.

Table 2. Characteristics of the study population of female nursing workers (N=268).

	N	%		N	%
Age			Job		
15-24	71	26.5	Manager	20	7.5
25-34	74	27.6	Teacher	75	28.0
35-44	61	22.8	Nurse	97	36.2
45-54	51	19.0	Assistant	76	28.4
55-64	11	4.1			
Marital status			Smoking		
Married	173	64.8	Current smoker	71	28.3
Single	94	35.2	Ex-smoker	36	14.3
Data missing	1		Never smoker	144	57.4
			Data missing	17	
Education					
Non-professional	66	24.8			
Trade school	79	29.7	Atopy [1]		
College or university	121	45.5	Yes	89	33.2
Data missing	2		No	179	66.8

[1] Doctor-diagnosed asthma, allergic rhinitis, allergic conjunctivitis or atopic eczema

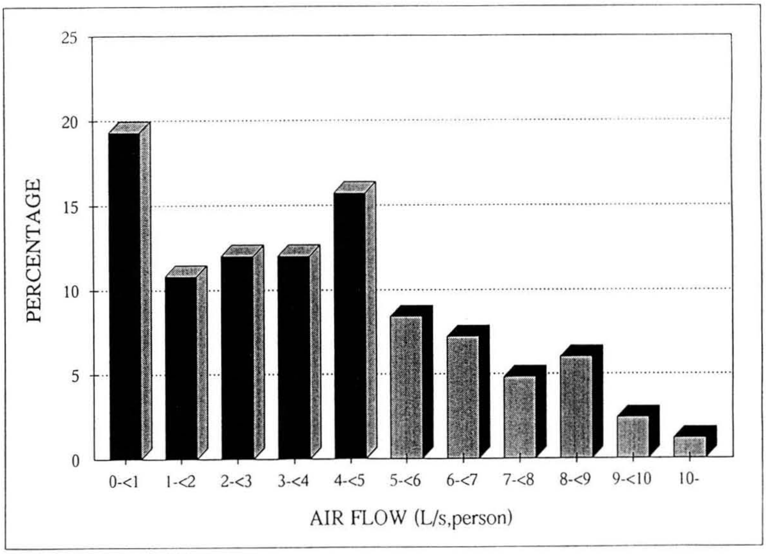

Fig. 1. The distribution of the air flows of the children's rooms in the 30 daycare centers studied (N=83).

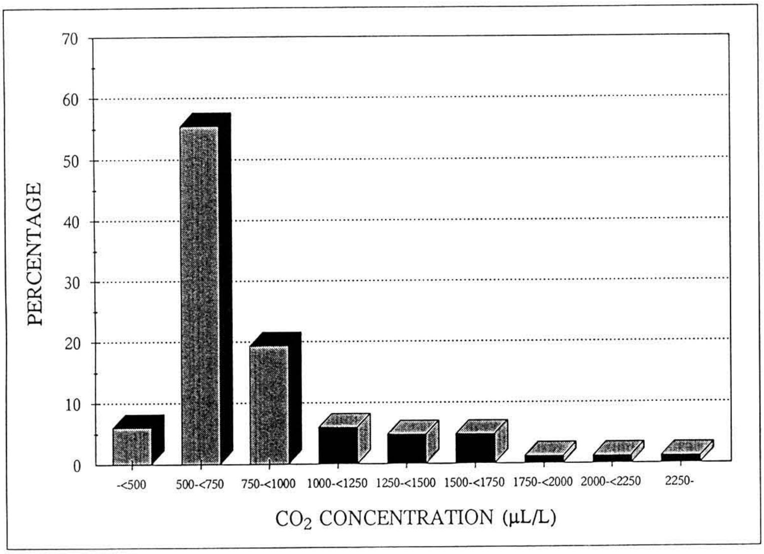

Fig. 2. The distribution of the CO_2 concentrations of the children's rooms in the 30 daycare centers studied (N=83).

The magnitude of the air flows in the daycare centers did not differ essentially according to building type. In the detached daycare buildings (59 children's rooms), the average air flow was 4.0 L/s per person (SD 2.9 L/s per person), and in the daycare centers situated on the ground floor of blocks of flats (24 rooms), the average was 3.4 L/s per person (SD 2.2 L/s per person). The magnitude of the air flows was related to both the construction year and the type of ventilation system. In the daycare centers with mechanical exhaust that were built before 1981 (32 rooms), the average of the air flows was 1.8 L/s per person (SD 1.7 L/s per person) and in the daycare centers with balanced ventilation that were built from 1981 onward (47 rooms), the average was 5.5 L/s per person (SD 2.2 L/s per person). The difference was statistically significant (p<0.001, t-test and Wilcoxon rank sum test).

Carbon dioxide

The CO_2 concentration measured in the 83 children's rooms when occupied varied from 400 to 2500 µL/L (ppm) (average 810 µL/L, SD 390 µL/L). The distribution was log-normal and the median was 670 µL/L (0.067 %). In the majority of the rooms (96%), the metabolical CO_2 concentration was below the Finnish guide value of 1500 µL/L (ME 1987). In 18% of the rooms, the CO_2 concentration was above 1000 µL/L, which is considered as the comfort limit (ASHRAE 1989). The distribution of the CO_2 concentrations is presented in Fig. 2.

During the time the children were indoors, the CO_2 concentration of the room rose 200-1500 µL/L (500 µL/L on average) due to the metabolism. In some rooms, the CO_2 concentration was high all day; at the lowest it was 800 µL/L. The CO_2 concentration profile during the day is presented in Fig. 3.

The association between the quantity of air flows and the CO_2 concentration was nonlinear (best fit found: power curve regression, $y=886*x^{-0.187}$, R^2 0.29) (Fig. 4). With low air flows (below 2.5 L/s per person), the CO_2 concentration was highest on average ($\bar{x}$ 1050 µL/L), but in the categories of higher air flows, the CO_2 concentrations were of the same magnitude (2.5-5.0 L/s per person: 710 µL/L and above 5 L/s per person: 630 µL/L). The average CO_2 concentration was statistically significantly higher in the category of lowest air flows than in the other categories (p<0.01 and p<0.001).

In the older daycare centers (constructed before 1981) with mechanical exhaust, the CO_2 concentration was higher on average than in the newer buildings (constructed from 1981 onward) with balanced ventilation (averages 980 µL/L / 690 µL/L, standard deviations 500 µL/L/230 µL/L). The difference was

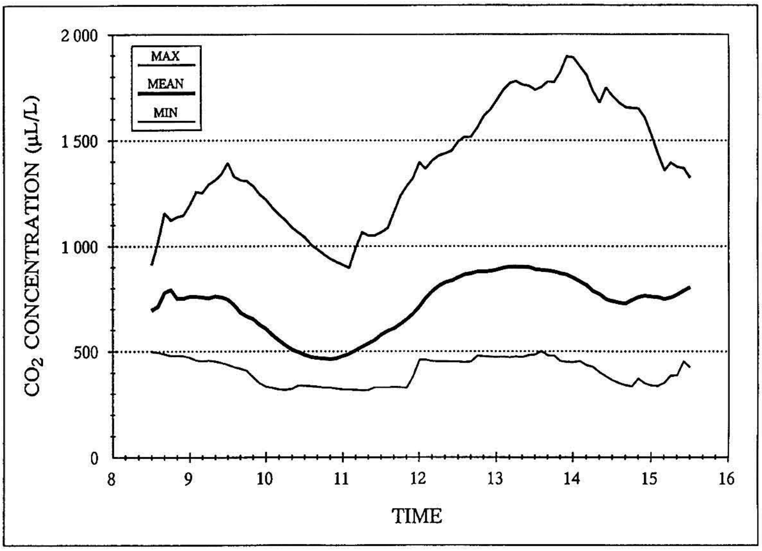

Fig. 3. The CO_2 concentration in the children's resting rooms during the day (N=26).

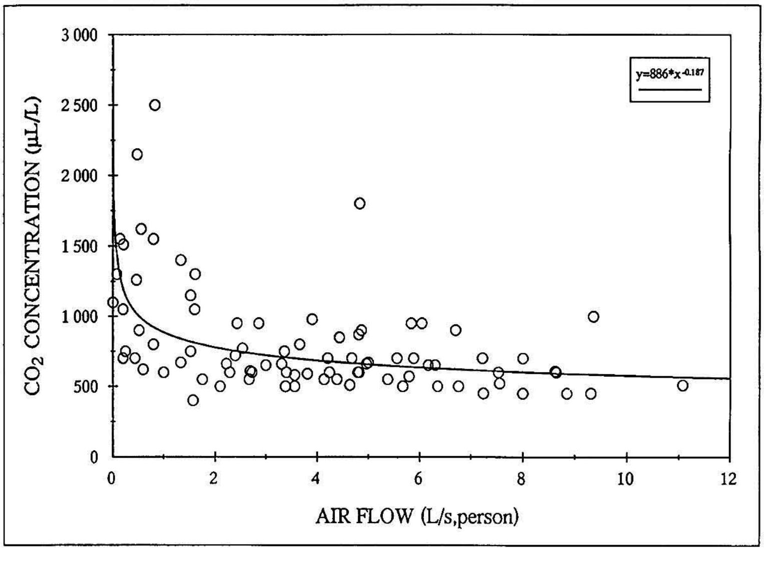

Fig. 4. The association between the air flows and the CO_2 concentration of the children's rooms in the 30 daycare centers studied (N=83).

statistically significant ($p<0.01$, Wilcoxon rank sum test).

Odor intensity

The odor intensity evaluated by two members of a trained panel varied in the 83 children's group rooms when occupied from 0.5 to 8 (butanol-scale 0-10). The odor intensity was normally distributed (Fig. 5) and the average was 3.2 (SD 1.4), which means 2.9 decipol or 33 percentage of dissatisfied (Hujanen et al. 1991). The main source of the odor was human bioeffluents. In most rooms, the researchers also judged the air stuffy and unacceptable.

There was an association between the CO_2 concentration and the odor intensity (best fit found: logarithmic regression, $y=-11.81+2.27*(\ln x)$, R^2 0.36). When the CO_2 concentration was low (below 700 µL/L), the odor intensity was lower on average ($\bar{x}$ 2.4) than when the CO_2 concentrations were higher (700-1000 µL/L: $\bar{x}$ 3.6 and above 1000 µL/L: $\bar{x}$ 4.7). The differences were statistically significant ($p<0.001$). On the other hand, no significant correlation was found between the air flows and the odor intensity.

Volatile organic compounds and formaldehyde

The range of the concentrations of total volatile organic compounds in the 30 daycare centers was 0.05-0.63 mg/m^3 (average 0.17 mg/m^3, SD 0.14 mg/m^3). The distribution was log-normal and the median was 0.13 mg/m^3. In three daycare centers, the one-hour average concentration was clearly higher than in the others, being above 0.5 mg/m^3, but according to repeated measurements, the VOC concentrations might have been only momentarily higher.

The range of measured formaldehyde concentrations was 0.002-0.038 mg/m^3 (average 0.015 mg/m^3, SD 0.008 mg/m^3, normally distributed). The concentrations were well below the Finnish guide value of 0.15 mg/m^3.

Temperature and humidity

The air temperatures in the 30 daycare centers, following normal distribution, varied from 19°C to 26°C and the average was 22.2°C (SD 0.9°C). In 46% of the 83 occupied children's rooms, the temperature was 20-22°C, i.e., close to the Finnish guide value of 21°C. During the time when the children were in the room, the air temperature rose by 0.5-3.0°C (1.5°C on average). In the afternoon, the temperature was 1°C higher on average than in the morning. The distribution of the temperatures is presented in Fig. 6.

In the older daycare centers (constructed before 1981) with mechanical exhaust, the air temperature was lower on average than in the newer daycare centers (constructed from 1981 onward) with balanced ventilation (averages 21.7°C / 22.4°C, standard devia-

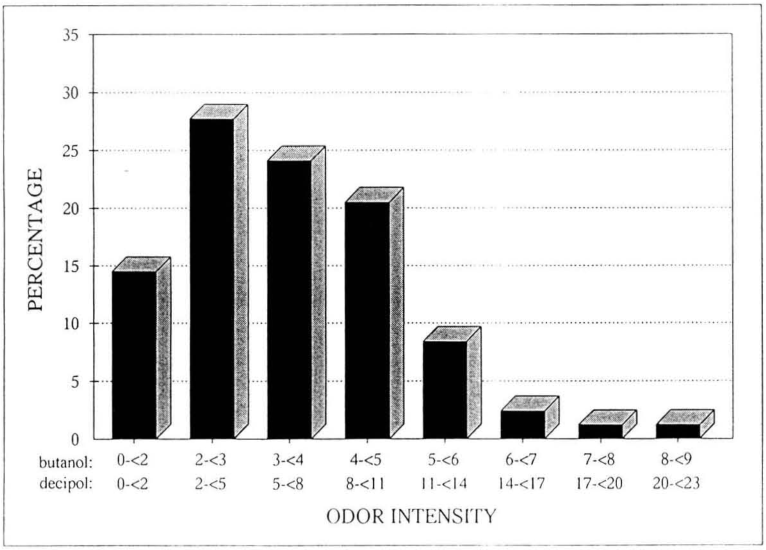

Fig. 5. The distribution of the odor intensities of the children's rooms in the 30 daycare centers studied (N=83).

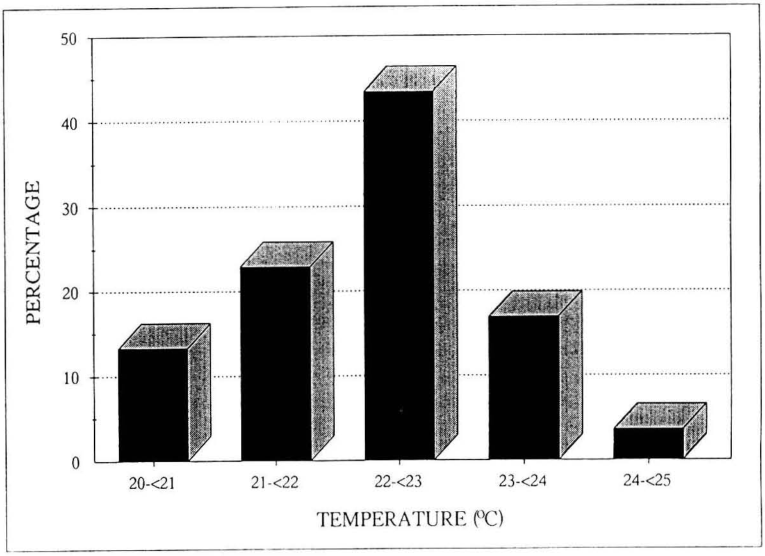

Fig. 6. The distribution of the temperatures of the children's rooms in the 30 daycare centers studied (N=83).

tions 1.0°C / 0.7°C). The difference was statistically significant ($p<0.001$, t-test and Wilcoxon rank sum test).

The relative humidity varied from 7 to 66% (average 31%, SD 4.0%). The outdoor thermal conditions are the main factor influencing the relative humidity of the indoor air (the outdoor temperature varied from -12°C to +11°C, average +2.6°C). During the time the children were inside the room, the humidity rose 5%RH on average.

Perceived indoor air quality

The workers in the 30 daycare centers studied were asked to state their experience of poor indoor air quality during the past twelve months (Table 3). According to 268 female nursing workers, the most common perception was unpleasant odor. 60% (95% confidence interval 54-66%) of the workers reported a sensation of unpleasant odors and 43% (95% CI 37-49%) experienced them daily or at least weekly. The most common odors were odors from human bioeffluents (30%, 25-36%) and stuffiness (25%, 19-30%), but the smell of sewage was also common (20%, 15-25%). Mold odor was experienced by 6% (3-9%) of the nursing workers. Thermal discomfort was quite common: coldness (38%, 32-44%), warmness (28%, 22-33%) and dryness (28%, 22-33%). Experience of too humid air was uncommon (3%, 1-5%).

In the older daycare centers (constructed before 1981) with mechanical exhaust, the nursing workers more often reported a sensation of unpleasant odors (70%/56%, $p<0.05$) and warmness (30%/21%, $p<0.01$) than the workers in the newer buildings (constructed from 1981 onward) with balanced ventilation. The differences were also statistically significant according to the stratified analysis by the workers' ages.

DISCUSSION

The performance of ventilation and the indoor air quality were assessed in 30 daycare centers selected randomly from a part of the Helsinki metropolitan area. Thus the results are unbiased estimates of conditions in the designated area. Because the building construction technology is relatively homogenous in Finland, the results well represent the conditions throughout the country.

The results indicate that the indoor air quality in the majority of Finnish daycare centers does not satisfy the existing guide values, although there are some daycare centers with good air quality. The ventilation is inadequate in most of the daycare centers. This leads to the accumulation of carbon

Table 3. The occurrence of perceptions of poor indoor air quality among female nursing workers during the past twelve months (N=268).

	N	%
Too high temperature		
Yes	74	27.7
No	193	72.3
Data missing	1	
Too low temperature		
Yes	100	37.7
No	165	62.3
Data missing	3	
Too dry air		
Yes	73	27.8
No	190	72.2
Data missing	5	
Too humid air		
Yes	7	2.7
No	255	97.3
Data missing	6	

	N	%
Unpleasant odors		
Yes	159	60.2
No	105	39.8
Data missing	4	
Odors		
Metabolical	80	30.3
Stuffy	65	24.6
Sewage	52	19.7
Mold	16	6.1
Engine exhaust	11	4.2
Tobacco smoke	9	3.4
Food	7	2.7
Chemical	6	2.3
Other	6	2.3
How often odors		
No	105	40.7
Almost daily	87	33.7
1-3 days a week	23	8.9
1-3 days a month	23	8.9
Less often	20	7.8

dioxide, which is an indicator of the accumulation of other indoor air pollutants. The average air flows of the mechanical ventilation in the day-care centers varied from nonexistent to above design values. In the daycare center with the highest average air flow, the air flow was forty times as high as in the daycare center with the lowest average air flow. As expected, the concentration of CO_2 was inversely related to the ventilation rate. The difference in CO_2 concentrations was threefold between the daycare centers with the highest and lowest average CO_2 concentrations.

The Finnish guide values were not achieved in the majority of the daycare centers. The air flow was below 5 L/s per person in 70% of the children's rooms. The variations in the average ventilation rates (0.1-4.0 1/h [ach], $\bar{x}$ 1.5 1/h) and air flows (0.2-8.8 L/s per person, $\bar{x}$ 3.8 L/s per person) in the 30 daycare centers studied were of the same magnitude as in the other studies in daycare centers (DCCs) in the Nordic countries (Olsen and Døssing 1982: 10 DCCs, 0.3-1.1 1/h; Lundqvist et al. 1986: 1 DCC, 0.3-3.0 1/h; Sverdrup et al. 1990: 71 DCCs, $\bar{x}$ 1.3 1/h; Pejtersen et al. 1991: 10 DCCs, 0.3-4.1 1/h, $\bar{x}$ 2.4 1/h; 3.6-11.8 L/s per person, $\bar{x}$ 6.9 L/s per person).

The highest CO_2 concentration measured was 2500 µL/L and the concentration was above 1000 µL/L in 18% of the children's rooms. This could indicate sensations of stuffiness and unpleasant odors. The variation in the CO_2 concentrations was of the same magnitude but the average was higher in the two most recent studies (Pejtersen et al. 1991: 900-2600 µL/L; Daneault et al. 1992: 860-2440 µL/L). In some studies, CO_2 concentrations even as high as 4000 µL/L have been reported (Lundqvist et al. 1982; Iversen et al. 1985; Bakke and Levy 1990).

The assessment of exposure to chemical indoor air pollutants is difficult due to the strong daily and seasonal variation in the concentrations. We carried out short-term measurements of total volatile organic compounds and formaldehyde concentrations. The TVOC concentration was at least momentarily above 0.2 mg/m^3 in three daycare centers. This concentration may increase symptoms and dissatisfaction together with other factors of poor indoor air quality (Mølhave 1991). The average TVOC concentration was lower in our study (0.17 mg/m^3) than in a Swedish study in 71 daycare centers (Sverdrup et al. 1990: 0.27 mg/m^3). The formaldehyde concentrations were well below the Finnish guide value of 0.15 mg/m^3 and also below the human odor threshold of 0.06 mg/m^3 (Ahlström et al. 1986).

Another way to assess chemical and microbiological indoor air pollution is to use human odor perception. Two trained members of the research group assessed the odor intensity in each daycare center. The odor perceptions of the nursing workers during the past year were also requested in the questionnaire. In a Danish study, the perceived air quality was evaluated by a trained panel of 13 persons in 10 daycare centers (Pejtersen et al. 1991). The average pollution load from the building itself (ventilation system and materials) was as high as from the occupants (0.4 olf/m^2 floor). The variation in the odor intensities in our study was higher (1-13 decipol, $\bar{x}$ 3.0 decipol/2-7 decipol, $\bar{x}$ 3.6 decipol); the large variation is partly due to the small size of our panel.

The percentage of nursing workers perceiving unpleasant odors in the 30 daycare centers studied varied from 20% to 100%. The experience of thermal comfort also varied remarkably from one daycare center to another (coldness 0-100%, warmness and dryness 0-88%).

Mold odor was reported by 6% of the nursing workers: in two daycare centers over half of the workers and in three centers one worker experienced mold odor. These daycare centers had also suffered water damage. Water damage and moisture problems appeared in 70% of the daycare centers. Mold odor and water damage were associated with respiratory symptoms among preschool children in Finnish dwellings (Jaakkola et al. 1993).

Controlling the temperature is a problem in daycare centers. In 54% of the children's rooms, the air temperature was above 22°C; this temperature was associated with excessive symptoms of the sick building syndrome in a Finnish cross-sectional study of office workers (Jaakkola et al. 1989). On the other hand, in 13% of the rooms, the air temperature was below 21°C, which may affect the sensation of coldness and draught. The air temperature in the daycare center with the highest average temperature was on average 4°C higher than in the daycare center with the lowest average temperature. Variations in temperature between different parts of a daycare center were also common.

The relative humidity may be low in winter in the daycare centers. During cold periods, the relative humidity was below 20%, which may increase dryness of the skin, eyes and respiratory tract, as suggested in a Finnish cross-over study of office workers (Reinikainen et al. 1992).

The measured indoor air quality did not differ between building types (detached daycare buildings /daycare centers situated on the ground floor of blocks of flats). In the older daycare centers (constructed before 1981) with mechanical exhaust, the CO_2 concentration was higher on average than in the newer buildings (constructed from 1981 onward) with balanced mechanical ventilation. Correspondingly, the air flows and temperatures were significantly lower on average. Perceptions of unpleasant odors and warmness were also more common.

CONCLUSIONS

The results indicate that there is much room for improvement in the indoor air quality of Finnish daycare centers. The air flows are below the designed values, and the pollutant concentrations and odor intensity may be high. The temperature is often too high, as it tends to lead to symptoms of the sick building syndrome and unnecessary energy consumption. In addition, perceptions of poor indoor air quality are quite common. The frequency of mold odor and moisture problems indicated microbiological growth, which may have respiratory health effects. Thus there are both good and bad daycare centers in all types of buildings. We consider that the study addresses an important public health issue and we intend through further analysis to estimate the effect of poor indoor air quality on the health and comfort of workers and children in daycare centers.

Acknowledgment — This study was supported by the Ministry of the Environment, the National Agency for Welfare and Health, and the Medical Research Council of the Academy of Finland. The authors wish to thank researcher Kristiina Saarela of the Technical Research Center of Finland for the analysis of the VOC measurements. The assistance of all the employees of the city of Espoo who contributed to the study is gratefully acknowledged.

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Environment International, Vol. 19, pp. 121-132, 1993
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0160-4120/93 $6.00 +.00

A STUDY OF BUS COMMUTER AND PEDESTRIAN EXPOSURE TO TRAFFIC AIR POLLUTION IN HONG KONG

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EI 9208-176 M (Received 8 August 1992; accepted 25 October 1992)

Exposure of bus commuters and pedestrians were measured in Hong Kong, a densely populated Asian city. The study found that bus commuters were exposed to an average NO, NO_2, SO_2 and CO of 0.490 µL/L, 0.077 µL/L, 0.020 µL/L and 1.6 µL/L respectively, for trips lasting between 20 and 45 min. Exposure levels of pedestrians to hourly average NO, NO_2, SO_2 and CO were 0.156 µL/L, 0.051µL/L, 0.011µL/L and 0.9 µL/L, respectively. Spatial and temporal variation of exposure levels were detected with ANOVA. In-bus concentrations were higher than out-bus concentrations at roadsides. Linear regression models were used to predict in-bus levels of NO, NO_2 and SO_2 from out-bus levels which in turn could be estimated from traffic flow. Fixed-station data were found to give an unreliable representation of exposure level.

INTRODUCTION

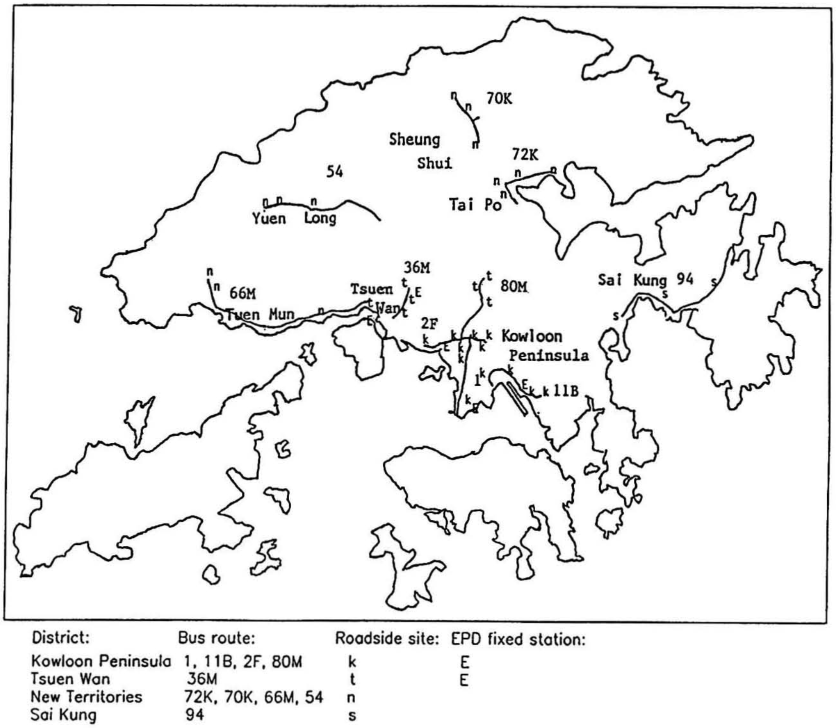
Hong Kong is one of the most densely populated territories in the world. It is hilly with a land area of only 1068 km^2. Most of its population of more than 5.7 million live in an urban area around one of the world's busiest harbours. The streets are crowded with people and every day more than 8 million passenger trips are made on the public transport system which includes high capacity railways, buses, trams, minibuses, taxis, and ferries. It is worth noting that more than half of the passenger commuting is spent on buses every day. Thus, the exposure to traffic air pollution in the in-transit trips including the bus and roadside trips are likely to contribute heavily to a citizen's total exposure to air pollution.

Most of the surveillance on air pollution in Hong Kong is conducted by the Environmental Protection Department (EPD). Ambient air pollutant concentrations are mainly measured on rooftop-fixed locations (EPD 1989, 1990). There were also several short-term curbside measurements using a mobile laboratory undertaken by EPD. However, there is no field measurement in Hong Kong like the present one which aims at the study of the exposure level of bus commuters and pedestrians to traffic-related air pollutants, NO, $NO2$, $SO2$, and CO under different traffic and street conditions. Akland et al. (1985) measured human exposure to CO in two urban areas and found that commuter exposure was significantly higher than noncommuter exposure. Ott and Flachsbart (1982) determined CO concentrations at indoor and outdoor locations of commercial settings in four towns and cities, and showed that CO concentrations outdoors were statistically higher than indoors. The exposure to CO in commuting was also assessed by other researchers (Holland 1983; Petersen and Allen 1982; Ziskind and Fite 1982), and a common phenomenon revealed that fixed station data of ambient air quality were not able to represent exposure of commuters. Colwill and Hickman (1980) showed that CO concentration present in vehicles travelling in London was higher than those generally found at the curbside of busy streets, but less than those immediately outside the vehicles.

Only a limited amount of work has so far been made to determine bus commuter exposure to CO (Flachsbart et al. 1987). In addition to CO measurement, Chan et al. (1991), Luria et al. (1990), Petersen and Sabersky (1975) and Rudolf (1990) determined exposures to NO_x in cars or vans. Most of the research was done in cities of western countries. Here, presented is a study of bus commuter and pedestrian exposure to traffic air pollution in a densely populated Asian city, Hong Kong, based on microenvironmental field measurements and statistical analysis of the data collected. It is also interesting to see how these measurements of in-bus and curbside levels of NO, NO_2, SO_2, and CO compare with measurements from fixed stations operated by EPD in Hong Kong.

FIELD STUDY

Field studies were carried out in four districts (Fig. 1) representing environments with distinct traffic patterns. The district of Kowloon Peninsula represents urban traffic, which is characterised by heavy traffic volume, frequent stops, and congestion. Many roads are lined by tall buildings. The four satellite towns, Tai Po, Sheung Shui, Tuen Mun, and Yuen Long in the district of the New Territories are characterised by moderate traffic. Roads are usually without tall buildings on both sides. The district of Sai Kung represents rural traffic which is characterised by low traffic volume and few stops. The bus route traverses some country parks. Tsuen Wan is an industrial district where traffic volume is intermediate between urban traffic and rural traffic. Many roads are surrounded by factories. Ten designated bus routes in these four districts were selected for in-bus measurements, four routes being in the urban area, Kowloon Peninsula, one route traversing industrial area, Tsuen Wan, four routes in the New



District:	Bus route:	Roadside site:	EPD fixed station:
Kowloon Peninsula	1, 11B, 2F, 80M	k	E
Tsuen Wan	36M	t	E
New Territories	72K, 70K, 66M, 54	n	
Sai Kung	94	s	

Fig. 1. Geographical distribution of bus routes and roadside sites.

Territories including the four different satellite towns, and one route being in the rural area, Sai Kung. A total of 35 roadside sites were used to estimate the exposure of pedestrians. The selection was based on traffic flow so that three sites representing the heavy, medium, and light traffic were selected along each route. When the bus route traversed industrial area, one more site was included for that route.

The sampling of the air at the respiratory level of passengers at the lower deck and at the height of 1-1.5 m above ground at the roadside was performed in three different hours (8:30-9:30 am, 1:30-2:30 pm, 4:30-5:30 pm) for four days (Saturday, Sunday, two weekdays) from July to August 1990. Air was collected in Tedlar sampling bags which were then transported to the central laboratory for analysis. NO_x (including NO and NO_2), SO_2, and CO were measured with a Thermo Electron 14B/E Chemiluminescent NO_x analyser, a Thermo Electron 43 Pulsed Fluorescence SO_2 analyser and a Horiba APMA-300E nondispersive infrared ambient CO analyser, respectively. Zero calibration and span calibration were performed regularly. A Monitor Labs Inc calibrator 8550 was used to calibrate the NO_x analyser and SO_2 analyser, first with zero air and then with span gas from a NO_2 permeation tube and SO_2 permeation tube, respectively. The CO analyser was calibrated with CO span gas from a gas cylinder. The number of vehicles passing the road site was counted concurrently with air sampling at the roadside sites.

RESULTS AND DISCUSSION

Spatial and temporal variation

Table 1 shows the average in-bus and roadside levels of NO, NO_2, SO_2, and CO measured in three time periods, 8:30-9:30 am, 1:30-2:30 pm, and 4:30-5:30 pm, on Saturday, Sunday, and weekdays. In-bus concentrations and roadside concentrations of NO and NO_2 decreased in the order: Kowloon Peninsula, Tsuen Wan, New Territories, and Sai Kung. In-bus CO concentration also followed the above order but

Table 1. Concentration means of various pollutants in the lower deck of buses and at roadside sites.

District	Inbus concentration (µL/L)					Roadside concentration (µL/L)				
	NO	NO_2	SO_2	CO	n	NO	NO_2	SO_2	CO	n
Kowloon Peninsula	0.648	0.100	0.023	2.3	48	0.239	0.061	0.012	0.9	144
	(0.224-1.122)	(0.020-0.222)	(0.006-0.060)	(0.9-3.7)		(0.009-0.922)	(0.004-0.213)	(0.004-0.058)	(DL2-4.2)	
Tsuen Wan	0.479	0.078	0.026	1.4	12	0.170	0.053	0.019	0.8	48
	(0.243-0.835)	(0.044-0.123)	(0.008-0.044)	(0.6-2.9)		(0.007-0.610)	(0.023-0.244)	(0.006-0.044)	(0.2-1.6)	
New Territories	0.387	0.066	0.019	1.2	48	0.114	0.048	0.010	0.9	192
	(0.103-1.001)	(0.005-0.369)	(0.003-0.066)	(0.4-2.3)		(0.001-0.524)	(0.007-0.180)	(DL1 -0.049)	(DL2-2.1)	
Sai Kung	0.279	0.029	0.005	0.6	12	0.030	0.026	0.003	1.3	36
	(0.104-0.678)	(0.014-0.076)	(DL1 -0.010)	(0.2-1.0)		(0.001-0.107)	(0.001-0.056)	(DL1 -0.007)	(0.4-2.2)	
Average	0.490	0.077	0.020	1.6	120	0.156	0.051	0.011	0.9	420
	(0.103-1.122)	(0.005-0.369)	(DL1 -0.066)	(0.2-3.7)		(0.001-0.922)	(0.001-0.244)	(DL1 -0.058)	(DL2-4.2)	

The range is given in parentheses ( ).

n - sample size

DL1 - less than lower detectable limit of 0.002 (µL/L)

DL2 - less than lower detectable limit of 0.2 (µL/L)

Table 2. ANOVA of gaseous pollutant concentrations in the lower deck of buses.

		p values				degree of freedom
		NO	NO_2	SO_2	CO	
Effect	District	<0.001	<0.001	<0.001	<0.001	3,96
	Sampling day	0.033	0.187	0.022	0.006	2,96
	Sampling time	0.499	0.507	0.069	0.080	2,96
Interaction	District x day	0.218	0.664	0.443	0.626	6,96
	District x time	0.640	0.959	0.724	0.096	6,96
	Day x time	0.892	0.613	0.854	0.328	4,96

roadside CO concentration was highest in Sai Kung, second highest in both Kowloon Peninsula and the New Territories, and lowest in Tsuen Wan. Both in-bus and roadside SO_2 concentrations were highest in Tsuen Wan, then decreased in the order: Kowloon Peninsula, New Territories, and Sai Kung. Generally speaking, traffic-related air pollution in buses and at roadsides was most severe in urban areas and mild in rural areas. In-bus and roadside SO_2 concentrations were influenced by factory emissions and were highest in industrial areas. High roadside CO concentration in Sai Kung might be due to the nearby local source from barbequing in the country park.

Spatial variation and temporal variation of gaseous pollution in running buses and at roadside sites were also analysed using analysis of variance (ANOVA) with F-tests. In previous studies (Colome and Spengler 1982; Ott and Flachsbart 1982; Tosteson et al. 1982), ANOVA was applied to look for differences among the effects. Ryan et al. (1988) stated that clustering of samples might be temporal, spatial, or both. In the present survey, the effects were district (Kowloon Peninsula, Tsuen Wan, New Territories, and Sai Kung), sampling day (Saturday, Sunday, and weekday), and sampling time (8:30-9:30 am, 1:30-2:30 pm and 4:30-5:30 pm). The results of the F-tests could be interpreted in much the same way as the other hypothesis

Table 3. ANOVA of gaseous pollutant concentrations at roadside sites.

		p values				degree of freedom
		NO	NO_2	SO_2	CO	
Effect	District	<0.001	<0.001	<0.001	<0.001	3,396
	Sampling day	0.009	0.013	0.020	<0.001	2,396
	Sampling time	0.030	<0.001	<0.001	<0.001	2,396
Interaction	District x day	0.012	0.008	0.007	0.010	6,396
	District x time	0.831	0.716	0.221	0.159	6,396
	Day x time	0.733	0.093	0.582	0.020	4,396

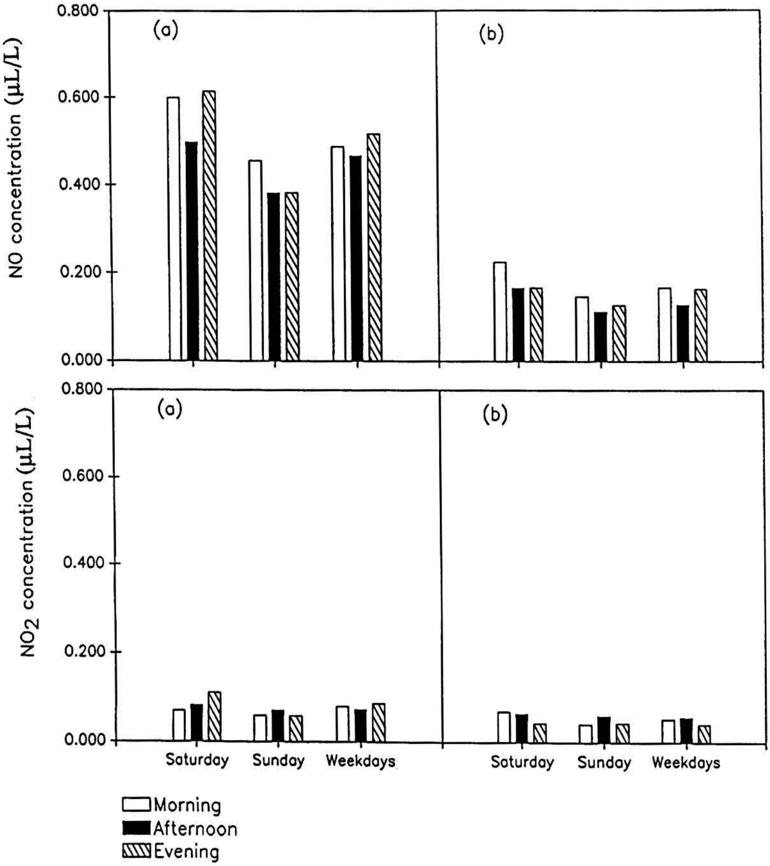


Fig. 2. Temporal variation of NO concentration and NO_2 concentration (a) in lower decks of buses (b) at roadside sites.

tests. For all pollutants tested, ANOVA of concentrations showed that significant differences of in-bus concentrations (Table 2) and of roadside concentrations (Table 3) existed among various districts.

From the result of ANOVA (Table 2), the in-bus levels of NO, SO_2 and CO were found to depend on day of measurement (weekday, Saturday, Sunday) but not on time of measurement (8:30-9:30 am, 1:30-2:30 pm, 4:30-5:30 pm). In-bus level of NO_2 was independent of both day and time of measurement, i.e., the level during weekday-commuting was approximately the same as during the Saturday commuting or Sunday commuting, and the level in the morning was also approximately the same as in the afternoon or in the evening. As shown in Figs. 2a, 3a, and 4a, in-bus NO, SO_2, and CO concentrations were lowest on Sunday. Temporal variation of roadside levels was different from that of in-bus levels. Roadside levels of all pollutants showed significant day and time effects (Table 3). Roadside NO concentration was lowest on Sunday for different times, and highest in the morning, second highest in the evening, and lowest in the afternoon on various days (Fig. 2b). Roadside NO_2 concentration was highest on Saturday for different times and lowest in the evening on various days. Roadside SO_2 concentration was also lowest on Sunday for various times and increased from morning to evening on various days (Fig. 3b). Roadside CO concentration decreased from morning to evening on various days (Fig. 4b). In the afternoon and evening,

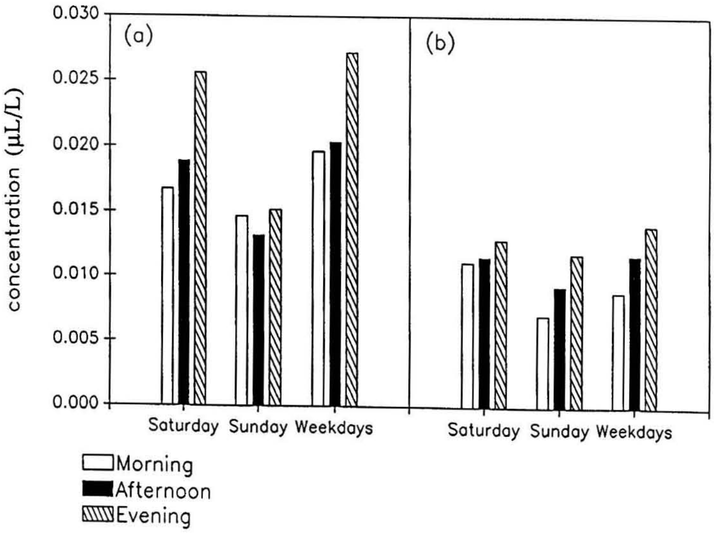


Fig. 3. Temporal variation of SO_2 concentration (a) in lower decks of buses (b) at roadside sites.

CO level was highest on weekdays, second highest on Saturday, and lowest on Sunday whereas Sunday morning was higher in concentration than other days.

Interaction of effects for in-bus measurement was not significant (Table 2). However, for roadside measurement, there was significant interaction between district and day effects for all pollutants measured and between day and time effects for CO only (Table 3). Weekly variation of pollution level might be district dependent and characteristic of particular roadside sites.

Interrelationship between in-bus concentration and roadside concentration

The total average of concentrations at all the roadside sites measured along each bus route was treated as the average out-bus concentration along that route. From the paried t-tests, average in-bus concentra-

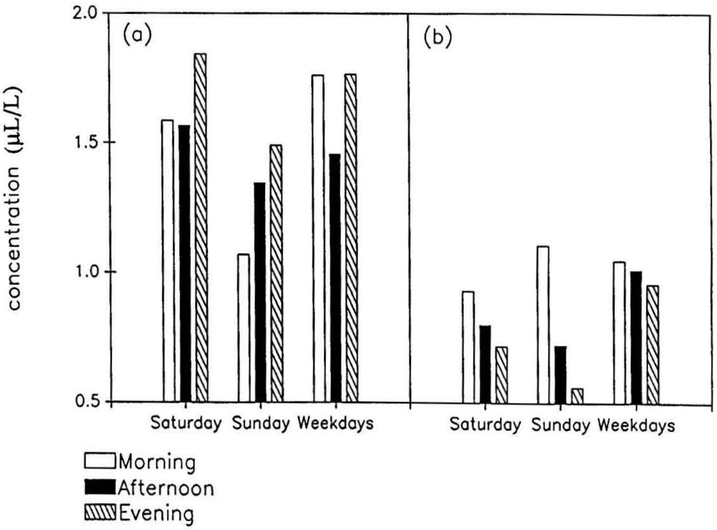


Fig. 4. Temporal variation of CO concentration (a) in lower decks of buses (b) at roadside sites.

tions of NO ($t=7.00$, $p<0.001$), NO_2 ($t=3.55$, $p<0.006$), SO_2 ($t=4.40$, $p<0.002$), and CO ($t=2.75$, $p<0.023$) over the whole trip were significantly greater than the average out-bus concentrations along the ten bus routes. Windows were opened, particularly in summer, allowing the outside air and bus exhaust to enter the bus compartment freely. Roadside sites in this field study were selected not near road junctions or bus stops, or along slopes. Besides cruising on road, buses decelerate on approaching road junctions, idle in waiting behind traffic lights and accelerate on leaving the junctions which were shown to emit higher concentration of pollutants (Al-zanaidi and Singh 1991; Colwill and Hickman 1980; Ott and Flachsbart 1982;

Fig. 5. Relationship between average in-bus concentration (inbus NO) and average out-bus concentration (outbus NO) for NO along various routes.

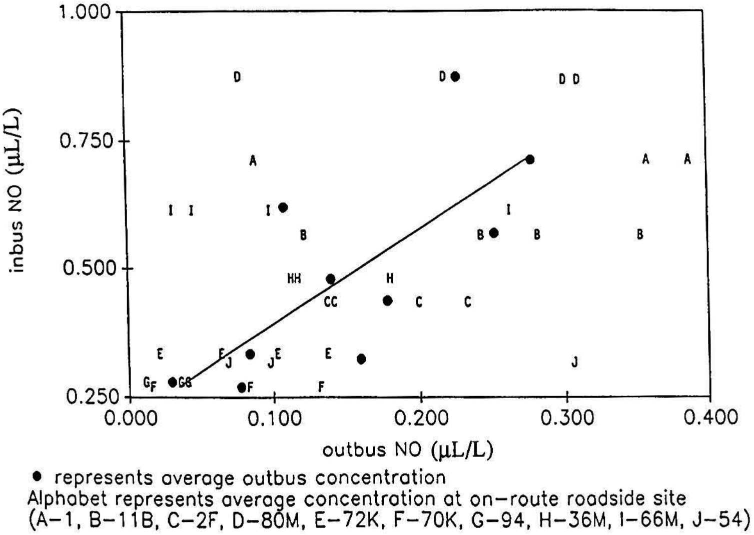
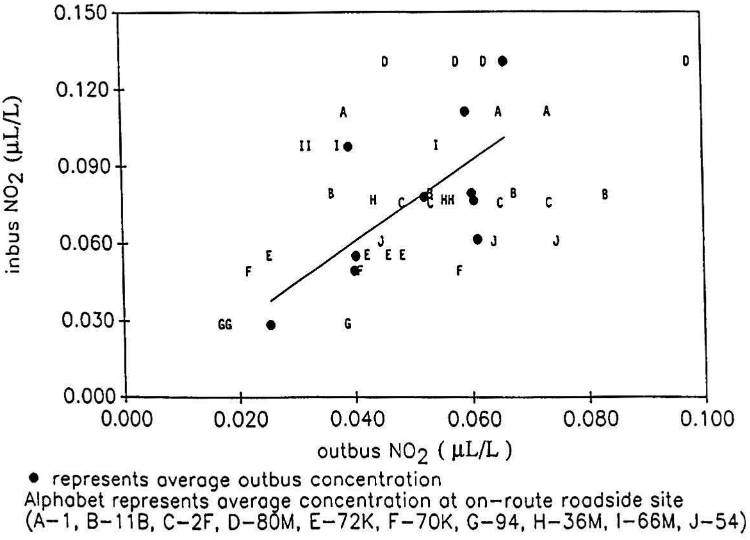


Fig. 6. Relationship between average in-bus concentration (inbus NO) and average out-bus concentration (outbus NO_2) for NO_2 along various routes.



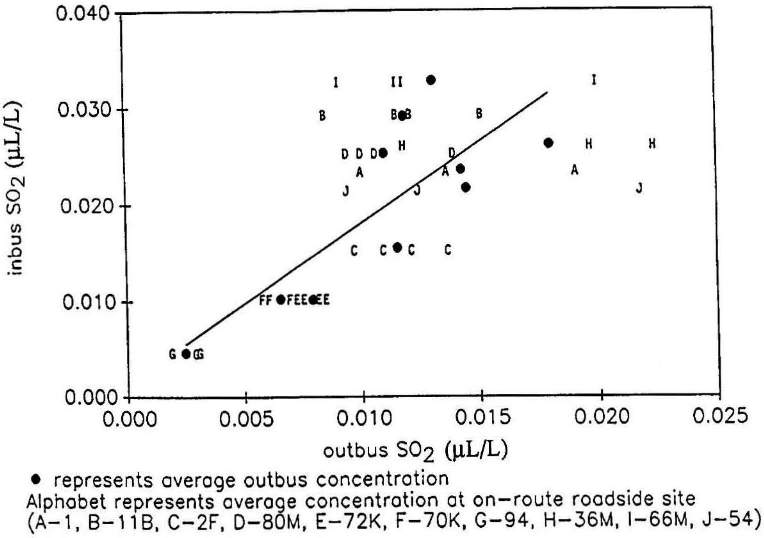


Fig. 7. Relationship between average in-bus concentration (inbus SO_2) and average out-bus concentration (outbus SO_2) for SO_2 along various routes.

Laxen and Noordally 1987; Luria et al. 1990; Tonkelaar et al. 1987). Passing vehicles during ascends were also found to give rise to high NO_x and CO values (Rudolf 1990). Thus, infiltration of bus exhaust, contribution at junctions and more emission upslope accounted for higher in-bus levels.

Nevertheless, the in-bus concentration could be inferred from the out-bus concentration as there was a high degree of correlation between the two sets of data (r ranging from 0.68 to 0.80) for NO, NO_2, and SO_2 except CO (r=-0.30). Their relationships are illustrated in Figs. 5 to 7, with ten different alphabets representing scatter plot of average in-bus concentration vs. average concentration at respective roadside sites representing heavy, medium, low traffic and industrial area along each of the ten routes. The filled circles represent the scatter plot of average in-bus concentration vs. average out-bus concentration along respective routes. The variation of concentrations at roadside sites along each route could be obtained from the spread of each type of alphabets relative to the horizontally aligned filled circle. In-bus concentration could be estimated from the out-bus concentration using the regression equations (1) to (3), regression lines of which were drawn through the filled circles in Figs. 5 to 7. Although only a limited number of roadside sites were taken in calculating the out-bus concentration for each route, linear relationships between in-bus and out-bus concentrations could be obtained for NO, NO_2, and SO_2. Generally speaking, the higher the in-bus pollution levels, the higher were the roadside levels within the area traversed by the bus route, with the exception of CO.

$$\text{in-bus NO } (\mu L/L) = 1.84 \times \text{out-bus NO } (\mu L/L) + 0.207 \quad (1)$$

$$\text{in-bus } NO_2 \ (\mu L/L) = 1.56 \times \text{out-bus } NO_2 \ (\mu L/L) - 0.002 \quad (2)$$

$$\text{in-bus } SO_2 \ (\mu L/L) = 1.66 \times \text{out-bus } SO_2 \ (\mu L/L) + 0.002 \quad (3)$$

Effect of traffic flow on pollution levels

The effect of traffic flow on NO, NO_2, SO_2, and CO levels became apparent from the correlation coefficients between the respective concentration and traffic flow at the 35 roadside sites (Table 4). The traffic counts were categorised into two groups which were the hourly average of the diesel vehicle counts (diesel) and the hourly average of the petrol vehicle counts (petrol). The NO and NO_2 concentrations correlated significantly with all traffic counts,

Table 4. Correlation coefficients of roadside concentrations with traffic flow.

	Diesel	Petrol	n
NO	0.5471 ****	0.5231 ****	35
NO_2	0.4953 ***	0.4285 **	35
SO_2	0.3562 *	0.2210	35
CO	-0.1545	-0.0928	35

**** significant at 0.001
*** significant at 0.005
** significant at 0.01
* significant at 0.05

and the SO_2 concentration correlated more with the diesel, whereas the CO concentration did not show any linear correlation. The contribution of various types of vehicles could be assessed using a stepwise selection method to build the multiple regression equations (4), (5) and (6). Although adding independent variables (i.e., petrol and diesel) would increase r^2, it did not necessarily decrease the standard error of the estimate. This occurred when more than the optimal number of independent variables were entered into the equation. Concentrations of NO, NO_2, and SO_2 could be predicted from the hourly flow of diesel vehicles (Equations (4) to (6)). Their relationships are shown in Figs. 8 to 10.

$$\text{NO } (\mu\text{L/L}) = 5.94 \times 10^{-5} \times \text{diesel (no./h)} + 0.095 \quad (4)$$

$$\text{NO}_2 \ (\mu\text{L/L}) = 9.01 \times 10^{-6} \times \text{diesel (no./h)} + 0.042 \quad (5)$$

$$\text{SO}_2 \ (\mu\text{L/L}) = 1.77 \times 10^{-6} \times \text{diesel (no./h)} + 0.009 \quad (6)$$

The findings of the significant correlations of the traffic flow with NO, NO_2, and SO_2 concentrations were similar to other countries. Inoue et al. (1986) showed a relationship between the traffic flow of cars and the NO_x concentration at a site in Chiba City while McCrae and Hickman (1990) found significant correlations between traffic flow and NO and SO_2

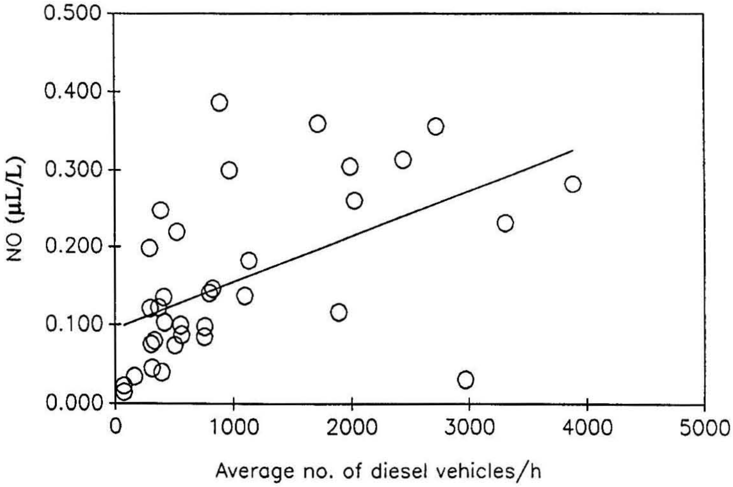


Fig. 8. Graph of average NO concentration (NO) vs. traffic flow of diesel vehicles for all roadside sites.

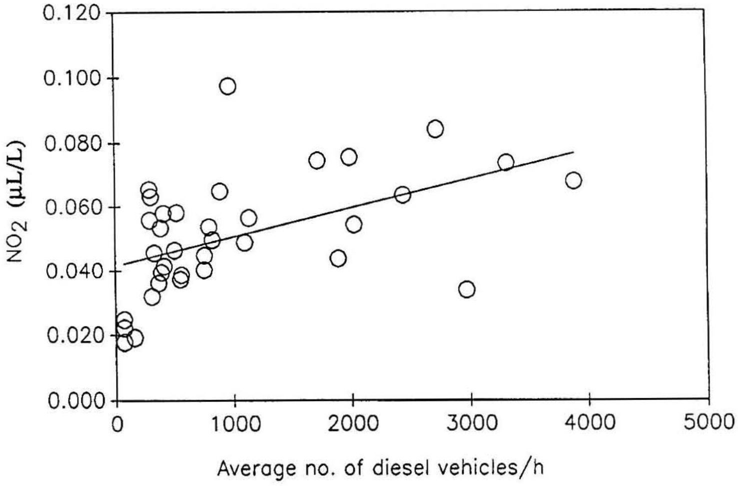


Fig. 9. Graph of average NO_2 concentration (NO_2) vs. traffic flow of diesel vehicles for all roadside sites.

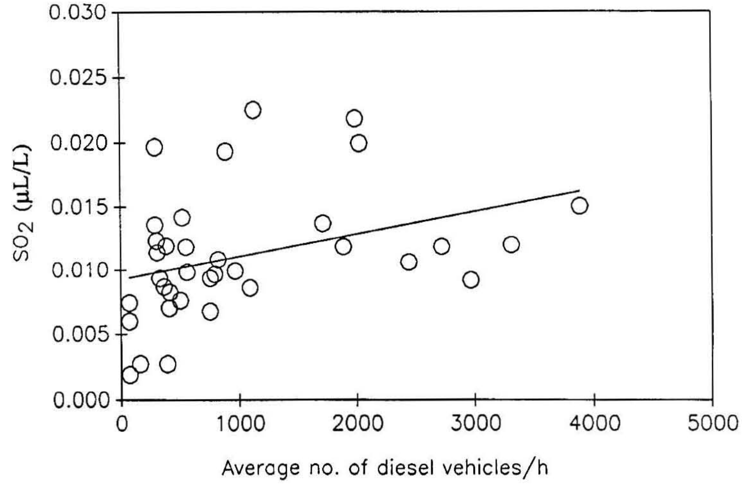


Fig. 10. Graph of average SO_2 concentration (SO_2) vs. traffic flow of diesel vehicles for all roadside sites.

concentrations at four sites in the United Kingdom. Luria et al. (1990) obtained an r value of 0.81 between NO_x level and traffic volume during travel in Jerusalem. The relative contribution of different types of traffic flow has not been considered in these studies. In Hong Kong, it was estimated that motor vehicles emitted about 75% of the NO_x, 82% of which was contributed from diesel-engine vehicles (EPD 1990). The significant correlation of NO and NO_2 concentrations with traffic flow of diesel-engine vehicles was obvious. SO_2 is generally not considered as an important primary vehicular pollutant. McCrae and Hickman (1990) explained that the relationship of SO_2 with traffic flow could be directly credited to the high percentage of diesel vehicles, particularly, taxis using fuel with a sulphur content approximately five times that of petrol. This is also true in Hong Kong as the percentage of diesel vehicles passing the roadside sites was on average 76% and ranged from 27% to 94% in the present survey. Yet, the behaviour of CO in the present study was quite different from others as an unexpected insignificant correlation with the traffic flow was observed. Ledolter and Tiao

(1979) and Kot and Lai (1985) found that concentration of CO depended on wind speed. Flachsbart et al. (1987), Petersen and Allen (1982), and Rashidi and Massoudi (1980) observed also the dependence on vehicle speed. Luria et al. (1990) detected a linear correlation between CO concentration and traffic volume at idle and the geometry of the road was found to be equally important. Traffic flow together with all these factors might affect the CO level.

Comparison of fixed-site concentrations with commuter exposures and pedestrian exposures

Ambient NO, NO_2, and SO_2 data of roof-top fixed monitoring stations during the study period were obtained from EPD. Figure 11 shows the distribution of the hourly average of NO, NO_2, and SO_2 values at five EPD fixed stations and at nine nearby fixed roadside sites, and the distribution of NO, NO_2, and SO_2 values averaged over the trip time in buses along four nearby routes. The statistics chosen for illustration included the mean, the minimum, and the maximum. The means of the EPD fixed-site data were lower than the roadside data which were lower than the in-bus data. NO and NO_2 at EPD stations varied over a narrower range than at roadside sites and in buses whereas the range of SO_2 was about the same. McCrae and Hickman (1990) stated that approximately 80-90% of NO_x emissions were in the form of NO, which upon emission was converted to NO_2 by atmospheric reactions. Chan et al. (1991) stated that NO comprised about 90-95% of NO_x emitted by vehicles. Higher percentage of NO than NO_x meant that the sampling inlet was closer to the auto emission source. NO contributed an average of 86%, 65%, and 48% to NO_x in buses, at roadside sites, and at EPD stations, respectively. The decrease in concentrations from bus to roadside site and to roof-top EPD station might be a result of concentration gradient. Sources of SO_2 included not only vehicle emission but also industrial emission from chimneys of factories. The SO_2 concentration monitored at EPD roof-top stations was subject to similar fluctuation as that experienced at ground level.

Besides difference in pollution levels, EPD fixed-site data were correlated poorly with all in-bus data and also insignificantly with most roadside data. Thus, bus commuter exposure and pedestrian exposure could not be inferred from ambient air quality measurements at the EPD fixed stations. Due to underestimation and insignificant correlation, ambient air quality data could not reflect exposures of pedestrians and commuters to pollutants at roadsides and in buses, respectively.

Comparison with ambient air quality objectives

As shown in Table 1, bus commuters were exposed to an average NO, NO_2, SO_2, and CO of 0.490 µL/L, 0.077 µL/L, 0.020 µL/L, and 1.6 µL/L, respectively for trips lasting between 20 and 45 min. Exposure levels of pedestrians to an hourly average NO, NO_2, SO_2, and CO were 0.156 µL/L, 0.051 µL/L, 0.011 µL/L, and 0.9 µL/L, respectively. For overall exposure assessment in buses, 10.0% (7.5% in Kowloon

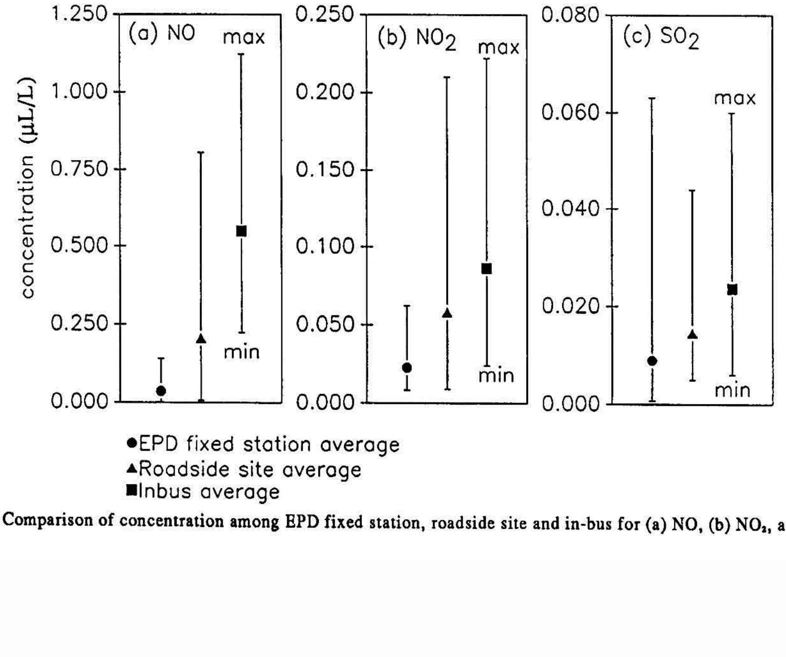


Fig. 11. Comparison of concentration among EPD fixed station, roadside site and in-bus for (a) NO, (b) NO_2, and (c) SO_2.

Peninsula and 2.5% in the New Territories) exceeded the Hong Kong Air Quality Objective of an 1-h average of NO_2 of 300 $\mu g/m^3$ (equivalent to 0.159 $\mu L/L$) whereas at roadside sites the exceedance, all in Kowloon Peninsula, was 1.7%. The exposures of SO_2 and CO were below the respective Air Quality Objectives of an 1-h average of 800 $\mu g/m^3$ (equivalent to 0.304 $\mu L/L$) and 30000 $\mu g/m^3$ (equivalent to 26.1 $\mu L/L$). The averaging time of in-bus concentrations in this survey did not match exactly those Air Quality Objectives referred to, as the values were averaged over trips which were usually less than 1 h. Therefore, care should be taken in the interpretation of the result of the comparison.

CONCLUSION

10.0% of in-bus measurements and 1.7% of roadside measurements of NO_2 exceeded the Air Quality Objective while other pollutant concentrations were below the Objectives. Field study results showed that in-bus concentrations of NO, NO_2, SO_2, and CO, to which bus commuters were exposed, were much higher than those measured at ambient fixed monitoring stations and even at roadside sites. Statistical analyses on spatial variation and temporal variation revealed the necessity of more data measurement in order to assess the exposure level more accurately. Correlation analysis also showed that in-bus concentrations of NO, NO_2, and SO_2 could be predicted from roadside data which could be in turn estimated from diesel vehicle flow using the linear regression models established.

As EPD fixed-site data could not reflect the actual exposure of bus commuters and pedestrians, it was realized that a more accurate method of exposure estimation in ground level had to be developed in Hong Kong. This pilot study was the first step to investigate the feasibility of using a microenvironmental monitoring technique in the bus microenvironment and roadside microenvironment. The basic methodology and analysis protocol were based on previous experiences in western countries. Such technique will then be modified to suit the situation in Hong Kong. The findings of this study will give insight into the application of this microenvironmental analysis approach in the future full-scale study, so as to obtain the characteristic pattern and spread of traffic-related air pollution to which Hong Kong citizens are exposed.

Acknowledgment — Special thanks are given to the Environmental Protection Department for provision of the fixed station data.

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Environment International, Vol. 19, pp. 133-145, 1993
Printed in the U.S.A.

0160-4120/93 $6.00 +.00
1993 Pergamon Press Ltd.

IMPACT ON INDOOR AIR QUALITY DURING BURNING OF PAKISTANI COAL BRIQUETTES

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EI 9207-172 M (Received 30 July 1992; accepted 19 December 1992)

A comparison was made of airborne emissions from combustion of new types of Pakistani coal briquettes and traditional fuels. A mud-lined Angethi stove was operated under the standard nominal conditions of burning 200 g charges of fuel inside a 12-m^3 shed with a forced rate of air exchange of 14 h^{-1}. Coal was cold briquettes with lime, clay, and oxidant. Traditional fuels were wood, charcoal, and animal dung. Compared to raw coal, the amended coal gave fourfold reduced emission of respirable-size particles (RSP) while dramatically reducing overall SO_2 release. Initial burning was restricted to the outer layers of the briquettes during which time reaction of SO_2 with lime was incomplete and early emissions of SO_2 were substantial. The measurements overall indicated that, with respect to CO, SO_2, NO_x, and RSP, substitution of amended coal briquettes for traditional fuels will not worsen indoor air quality during domestic cooking. The traditional fuels and coal briquettes emit elevated peak amounts of CO (100-250 µL/L), SO_2 (2-5 µL/L), and NO_x (1-5 µL/L) in the early phase of volatiles burning with much reduced emissions in the later char-burning phase. Stove operators can substantially lower exposures by lighting the fuel outside and later moving the stove inside.

INTRODUCTION

Firewood, charcoal, and imported kerosene are the predominant residential cooking and heating fuels in Pakistan. Wood is becoming increasingly scarce, and deforestation has reduced tree cover tenfold this century. The importing of alternate fuels such as kerosene causes heavy drain on foreign exchange. Better utilization of Pakistan's large reservoirs of coal would be an attractive alternate energy option for both economic and environmental reasons.

Unfortunately, Pakistan's coal is mostly of poor quality; it is lignitic to sub-bituminous in rank, has high sulfur (3-7%) and mineral contents, and is friable. Briquettes made from untreated coal produce copious emissions of sulfur dioxide, smoke, and fumes that have an objectionable odor.

An initial market assessment by Oak Ridge National Laboratory (ORNL) for the U.S. Agency for International Development (USAID) indicated that a substantial market exists for briquettes based on low-rank Pakistani coals (Stevenson and Willson 1988). Major markets include the poultry industry that uses heating stoves, brick kilns, space heating, and household cooking. In the period 1985-1988, laboratory facilities and coal-briquetting machinery were provided by USAID to the Fuel Research Center

(FRC) of the Pakistani Council of Scientific and Industrial Research. A major objective in the new FRC program was to develop uncarbonized coal briquettes that were both inexpensive and at least as safe environmentally as the traditional domestic fuels. The raw coals were amended with pollutant-reducing additives and shown to have a thermal value (BTU per Rupee) about twice that of wood, charcoal, or kerosene (STEDEC 1991).

The staff of the Health and Safety Research Division of ORNL was engaged to assess the quantities of toxic inorganic and organic emissions under conditions simulating stove usage in a typical Pakistani dwelling. Initial environmental measurements of emissions from 50 g charges of prototype briquettes were reported in 1987 (Wilson and Hawthorne 1987). The work reported here focuses on the measurement and interpretation of inorganic emissions relative to emissions from traditional fuels. Efforts to optimize the additives in the coal briquettes are also described. The organic emissions will be reported at a later date.

EXPERIMENTAL

Briquetting

The briquetting procedure consists of first crushing the coal to -12-mesh size. The coal fines are mixed with slaked lime (-200 mesh), bentonite clay (-200 mesh), potassium nitrate and water. The mixture is passed through a compactor and the resulting briquettes allowed to dry (Ahmad et al. 1990).

Simulated cooking environment

Fuel burns were conducted in a traditional Angethi cooking stove placed inside a metal shed. The medium-sized Angethi stove consisted of a vertically oriented metal barrel with a metal grill situated at midpoint. The inside of the upper portion was lined with baked mud. The combustion chamber was 12-cm deep and 25-cm wide. A fuel charge of 200 g was used. To encourage smoother burning, the coal briquettes were broken into cm-sized pieces and arranged to form a pyramid on the grill. Fuel was ignited by using a propane torch held below the grate for 5 min. Thereafter, the burn was allowed to proceed to completion with the shed door closed. A minimum of three, and as many as six, separate burns were conducted to generate the data on emissions for a particular sample.

The structural units of the shed were made of aluminum, including the floor. The shed volume was 12 m^3. The shed was ventilated with outside air blown into the shed through a duct to produce a constant rate of air exchange of 14 h^{-1}. Air exited the shed through openings along the wall-roof line, openings that existed because of corregations in the roof. Two floor fans were operated to ensure thorough mixing of the air inside the shed.

The particle monitoring devices were rugged enough to be operated directly inside the shed. Other devices had to be operated external to the shed because they were not designed to operate in the sometimes heavily polluted, smokey atmospheres inside the shed. This limitation was addressed by transporting shed air via a duct to a nearby monitoring van. The duct was a wide-bore, galvanized steel tube that looped from the shed, through the monitoring van and back to the shed. A fan inside the shed blew air at the mouth of the duct. Ports in the duct section inside the van allowed sampling of polluted air via short lengths of Teflon tubing connected to individual monitoring devices. The schematic in Fig. 1 illustrates the layout. This arrangement has several advantages, including a low surface-to-volume ratio for reduced memory effects in the sampling loop, and rapid (8 m/sec), low-pressure, continuous transport of air from shed to van and then back to the shed. The sample loop allowed our monitoring devices to sample at their design specifications without perturbation of the 14 h^{-1} rate of air exchange. Combustion of particular fuels was usually complete within 1-2 h. To improve the accuracy of determining integrated emission factors, monitoring was continued for 3-4 h until the response of each gas analyzer returned to baseline.

INSTRUMENTATION

The instruments used to conduct measurements of air exchange rate, respirable-sized particles and inorganic gases are listed below:

Inorganic particles:

Harvard particle sampler, 0.0035 m^3 min^{-1} flow rate, 2-μm pore, 41-μm Ø PTFE membrane filter, 200-min sampling interval. Samples analized gravimetrically and for toxic heavy metals by ICP/MS, EPA Method 200.8.

Carbon monoxide:

GasTech GX-4000 electrochemical monitor, 0-250 μL/L range.

Sulfur dioxide:

GasTech GX-4000 electrochemical monitor, 0-50 μL/L range.

Nitrogen oxides:

Columbia Scientific CSI-6000 NO_x Analyzer, 0-5 μL/L range.

Air exchange:

Foxboro Miran 1A, infrared monitor (Freon 12 tracer).

The gas monitors were calibrated twice weekly using commercially available ultra-zero grade air and CO, SO_2, and NO_2 gas standards with concentrations of 47, 1.3, and 5 μL/L, respectively.

FUEL SAMPLES

Fuel samples were provided by the Fuel Research Center (FRC) and were Pakistani wood, wood charcoal, animal dung, and coal briquettes. The compositions of the four types of coal briquette are shown in Table 1, while the characteristics of the parent coals are indicated in Table 2. The specific surface of the slaked lime additive was determined by nitrogen adsorption at ORNL to be 7.67 m^2g^{-1}. The coal in a particular type of briquette was representative of a large batch of coal which were ground and homogenized prior to briquetting.

RESULTS

Sulfur fixation

The effectiveness of both finely divided, slaked lime, and limestone were evaluated for fixing sulfur in the ash and thereby reducing emissions of sulfur dioxide. The sulfur:lime and sulfur:limestone molar ratios were varied between 1:1 to 1:3 and 1:1 to 1:2, respectively. The fixation efficiency is depicted in Fig. 2 for Sor-Range coal briquettes.

Bentonite clay was added to the briquettes in the hope of catalytically pyrolyzing and assisting in the complete combustion of products that otherwise would be emitted as smoke and tar. The effect that clay also has on sulfur fixation, in combination with an optimum amount of slaked lime or limestone, is shown in Fig. 3 for Lakhra coal briquettes.

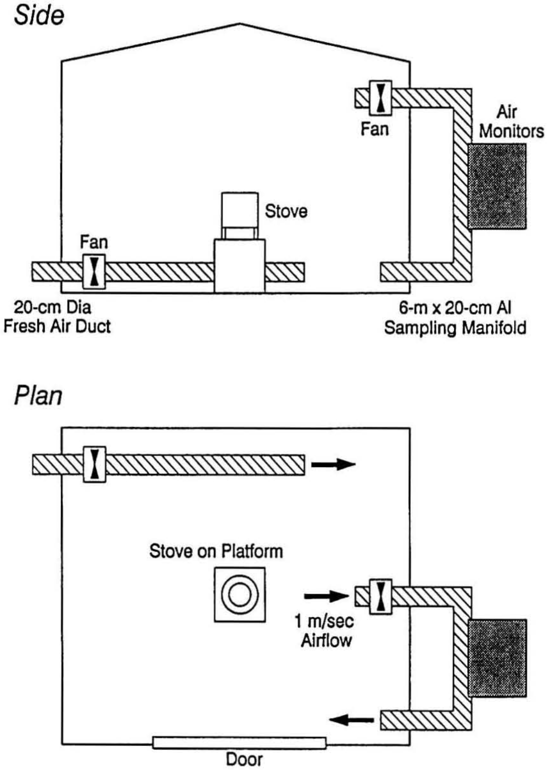

Fig. 1. Schematics of shed, air ventilation, and air circulation.

Table 1. Formulations of coal briquettes.

Briquette	Component	Weight Composition
Coal A	Lakhra Coal	64.5%
	Slaked Lime	24.5%
	Clay	10.0%
	Potassium Nitrate	1.0%
Coal B	Lakhra Coal	54.8%
	Slaked Lime	20.8%
	Clay	8.5%
	Potassium Nitrate	0.8%
	Coke Dust	15.0%
Coal C	Sor-Range Coal	83.3%
	Slaked Lime	5.7%
	Clay	10.0%
	Potassium Nitrate	1.0%
Coal D	Lakhra Coal	100%

Table 2. Proximate analysis of Sor-Range and Lakhra coals.

	Sor-Range Coal	Lakhra Coal
Moisture	9.14	12.06
Ash	8.28	23.55
Volatile Matter	40.66	33.83
Fixed Carbon	41.92	30.56
Sulfur (total)*	1.53	3.84
Calorific Value Btu/lb.	10,595	7,500

*Pakistani coals typically have sulfur in organic (50%) and inorganics (50%) forms.

Smoke reduction

In order to study the quantities of smoke emitted by the different coal briquettes, a separate furnace and emission product collection system was employed. A briquette was burned in a combustion tube furnace at 800°C and the emissions collected in a train of traps at ice and liquid nitrogen temperature. After collection, the condensates were extracted with benzene, the benzene extract dried, and the residue weighed. The smoke/tar emissions were reduced by as much as 86% in an optimum briquette formulation compared to a raw coal briquette; this optimum formulation was similar to the composition of Coal A briquettes. A small amount of oxidant (1% by weight of potassium nitrate) was found to futher reduce smoke and improve the ease with which the briquettes burned.

Calculations

Combustion data reported are averaged for replicate analyses. Variability between burns arises due to variations in ignition and evenness of combustion, unburned fuel falling through the grate of the Angethi stove, and differences in stacking of the charge. The following calculations were made:

Combustion Efficiency: [1-A/W]·100%
Respirable Particles: $[\delta W_f \cdot V]/[W \cdot F \cdot T]$
Relative Emission Factor: $\int C/W$

where A is the ash weight (kg), W is the weight of fuel (kg), W_f is the weight of particles on a filter (mg), V is the chamber volume (m^3), F is the sampling rate of sampler (m^3/min), T is the sampling interval (min), and $\int C$ is the integrated concentration of a pollutant (g/m^3).

Combustion efficiency

The percentage of fuel mass lost, defined here as combustion efficiency, varied substantially between different types of fuel. Average values and ranges for combustion efficiency are shown in Table 3. The traditional fuels provided the most complete combustion, burned readily, and left little residue. The dung produced a very fine, flocculent ash; complete collection of this ash for weighing was impossible,

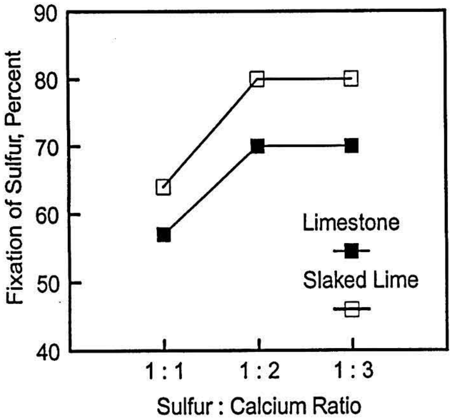

Fig. 2. Fixation of sulfur during combustion at 800°C vs. lime or limestone contents of Sor-Range coal briquettes.

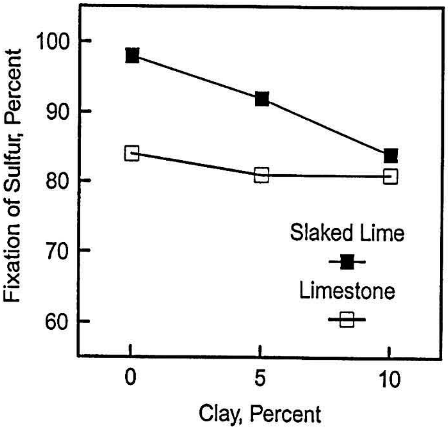

Fig. 3. Fixation of sulfur vs. clay content of Lakhra coal briquettes containing lime or limestone at a 1:2 sulfur-to-calcium molar ratio.

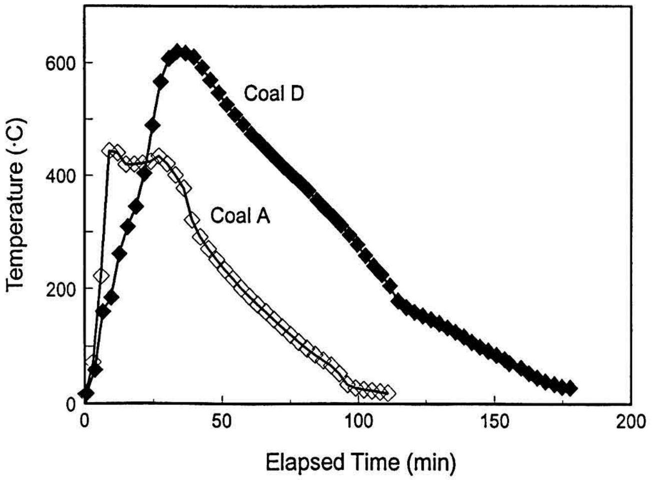

Fig. 4. Typical temperature profiles in 200 g charges burning raw (D) and amended (A) Lakhra coal briquettes.

Table 3. Measured and anticipated mass loss during combustion.

Sample	Combustion Efficiency (%)			Ash Description
	----------Measured----------		Calculated*	
	Average	Range		
Coal A	54.4 ± 5.1	61.3-49.0	56.4	Hard, large-grained cinders
Coal B#	40.8 ± 8.5	52.2-32.0	-	"
Coal C	77.0 ± 3.9	81.6-71.1	78.8	Small-grained cinders
Coal D	80.5 ± 3.2	83.7-77.3	76.4	Fine-grained cinders
Wood	92.6	-	-	"
Charcoal	96.1 ± 0.4	95.7-96.5	-	"
Dung	>95	-	-	Flocculent ash

*Calculation assumes conversion of slaked lime to quicklime and no weight loss from the clay.
#Contains 15% coke dust of unknown combustion efficiency.

which negated accurate estimate of combustion efficiency. Among the coal briquettes, the unamended Coal D furnished the most complete combustion, which was about 20% less than the traditional fuels. Coal C burned slightly less completely than Coal D, and produced a somewhat coarser ash. The amended Lakhra Coals A and B burned the least efficiently, and produced hard, cinder-like ash. Furthermore, briquettes of Coals A and B frequently left small partially unburned cores, which adds a small error to

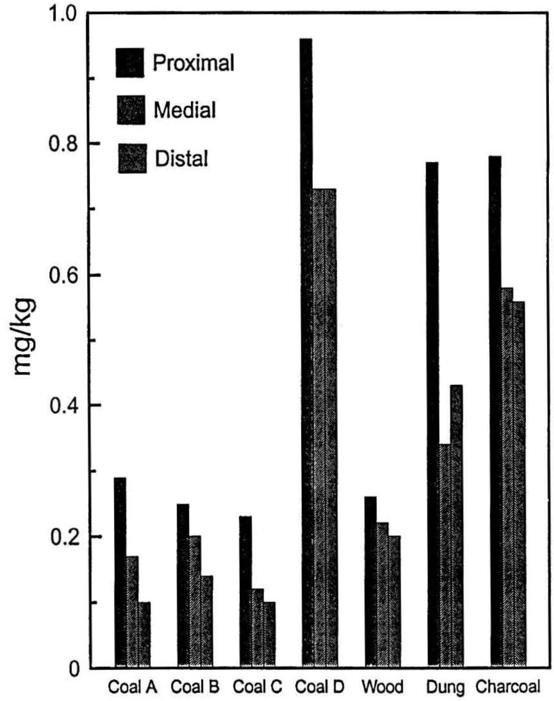

Fig. 5. Respirable sized particles emitted during burning of 200 g charges of coal briquettes and traditional fuels.

Table 4. Total respirable particle emmissions, mg/kg fuel combusted.

Sample	Inorganic		
	Proximal	*Medial*	*Distal*
Coal A	0.292 ± 0.120	0.172 ± 0.120	0.095 ± 0.120
Coal B	0.249 ± 0.034	0.198 ± 0.069	0.138 ± 0.034
Coal C	0.232 ± 0.138	0.120 ± 0.103	0.095 ± 0.112
Coal D	0.955 ± 0.421	0.731 ± 0.353	0.731 ± 0.327
Wood	0.258	0.215	0.198
Charcoal	0.783 ± 0.447	0.585 ± 0.387	0.559 ± 0.387
Dung	0.774 ± 0.413	0.344 ± 0.069	0.430 ± 0.146

the calculation of their combustion efficiencies. Temperatures at the center of the fuel pile were measured with a K-type thermocouple. Temporal temperature profiles are shown in Fig. 4 for Coals A and D. There is some variation in temperature between repeat burns. The maximum temperature for burning Coal A varied between 400-500°C during four different burns.

Respirable particles

Respirable inorganic particle emissions are summarized in Table 4. Particles were collected at three locations: *Proximal*, at a lateral distance of 25 cm from the Angethi stove; *Medial*, at a distance of 50 cm; and *Distal*, 100 cm. Each of the sampler inlets was at an elevation 25 cm above the top of the stove. The gravimetric data are compared graphically in Fig. 5.

Results of analyzing the particulate matter for toxic heavy elements are summarized in Table 5.

Carbon monoxide, sulfur dioxide, and nitrogen oxides

Results from the monitoring of carbon monoxide, sulfur dioxide, and nitrogen oxides are provided in Table 6, and Figs. 6, 7, and 8. Emissions are generally greatest soon after ignition and decrease upon tran-

Table 5. Analyses of inorganic particles, by ICP/MS, reporting µg detected. Std. coal represents the mean concentration (µL/L) in 101 coals [3]. nd=not detected.

	Std Coal	Dung	Wood	Coal A	Coal B	Coal C	Coal D
Weight Collected, µg		7.0, 13.4	3.0	10.1, 10.4	2.9, 3.0	3.4	11.3, 11.0
No. Trials	101	2	1	2	2	1	2
As	14.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Be	1.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cd	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	13.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	34.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sb	13	n.d.	n.d.	n.d.	n.d.	n.d.	2.2 ± 2.9
Se	2.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	272.3	n.d.	1.2	3.0 ± 0.28	n.d.	1.2	1.8 ± 0.5

Table 6. Peak concentrations [Pk], (mg/m^{3}), times [t], (hours) to reach peak and relative emission factors [EF], (g/kg) for inorganic oxides.

	CO			NO_x			SO_2		
	[Pk]	t	EF	[Pk]	t	EF	[Pk]	t	EF
Coal A	92	0.30	26	2.2	0.18	0.32	14.6	0.32	2.2
Coal B	277	0.22	42	6.2	0.17	0.58	15.1	0.20	1.7
Coal C	138	1.18	50	0.7	0.28	0.19	13.8	0.25	3.5
Coal D	179	0.33	54	1.8	0.27	0.34	18.2	1.18	7.2
Wood	239	0.20	34	1.9	0.22	0.31	11.2	0.33	2.0
Dung	203	0.53	41	8.4	0.15	0.57	15.4	0.32	2.5
Char	313	0.57	66	2.5	0.60	0.63	6.8	0.57	1.4

sition to the later phase of char burning. Emission produced solely by operating the propane torch was measured separately and found to be insignificant. Oxide emission profiles are compared in Fig. 9. This figure allows comparisons of peak and integrated emission factors between all fuels that were studied.

DISCUSSION

Comparison of briquettes

First, the compositional characteristics of the coal briquettes are considered and whether further improvements might be made. Balancing the proportions of coal, slaked lime, or limestone, clay and oxidant was intended to effect an optimum compromise between the mechanical strength, ease of combustion, fixation of sulfur in the ash, and minimization of smoke and offensive odors.

Slaked lime, rather than crushed limestone, is the choice for maximizing sulfur fixation at the relatively low temperatures prevailing in the Angethi stove, as indicated in Figs. 1 and 2. The reason for slaked lime being a particularly effective desulphurizer lies with its relatively high initial specific surface (up to 20 m^2 g^{-1} is common for slaked limes) and its decomposition at 400-500°C to produce an even more active, higher specific surface quicklime (CaO) (Glasson 1963). The slaked lime used in the Pakistani briquettes was 7.67 m^2 g^{-1}. Most SO_2 adsorption and reaction with CaO occurs between 400-500°C as organic sulfur and iron pyrites are being oxidized to SO_2; the last pyritic sulfur, however, requires 700°C for its release (Glasson and O'Neill 1980). In contrast to lime, crushed limestone is difficult to produce with specific surface exceeding 2 m^2 g^{-1} (Gammage et al. 1977) and in air it decomposes to CaO at a significant rate only above 600°C. For higher temperature desulphurization, above 700°C, limestone rather than slaked lime is expected to become the preferred reactant (Glasson and O'Neill 1979). The temperatures developed in the Angethi stove for 200 g charges of coal briquettes do not exceed 700° (Fig. 4), confirming that slaked lime is the appropriate sulfur fixant to use.

Although slaked lime by itself can bring about up to 97% fixation of the sulfur in Lakhra coal briquettes, its effect in reducing emissions of smoke is limited. Clays have strong protonic donor properties and are used as catalysts in petroleum cracking. In our work, bentonite clay was evaluated as an adsorbent for pyrolysis and catalytic cracking of heavier molecular weight organics and concomitant reduction of smoke. The most effective compromise quantity of clay proved to be 10 weight %; in conjunction with a sulfur:lime molar ratio of 1:2, smoke and tar emission was reduced by about 86% while sulfur fixation still exceeded

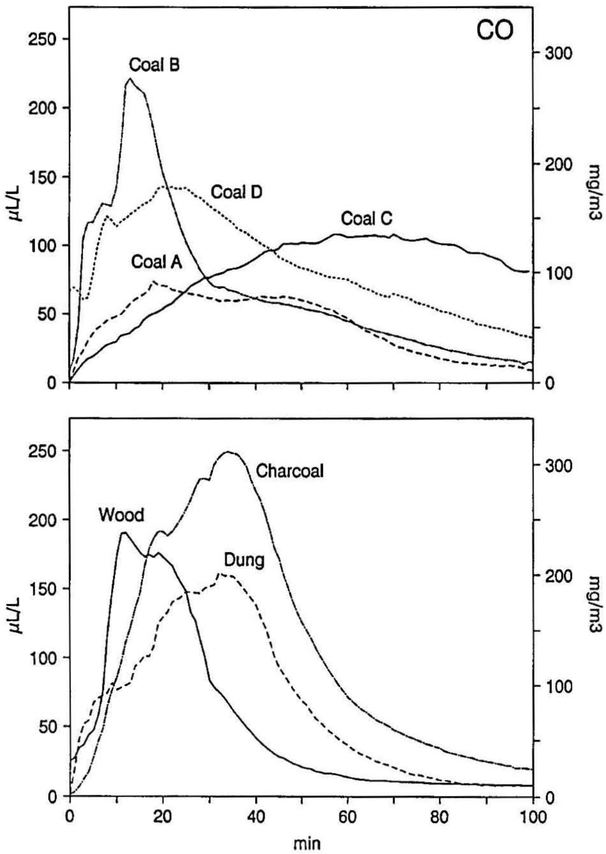

Fig. 6. Emission profiles of CO.

80% in the combustion tube experiments. Larger amounts of clay adversely affected the mechanical strength and calorific value of the briquettes. The addition of a small amount of oxidant, potassium nitrate, was found to improve the combustion characteristics, and assist in further smoke reduction.

Further improvements to the briquettes might be made by using a slaked lime of higher specific surface than that currently employed (7.7 m^2 g^{-1}). It would not be economically feasible to use calcium carbonates of high specific surface, which can be formed via precipitation from solution or else thermal decomposition of a parent salt such as oxalate, formate or acetate (Glasson 1958). Precipitated calcite would be a prohibitively expensive substitute for natural crushed limestone. There may be benefit to examining the effectiveness of alternative clays, such as kaolinite or Fullers Earth, as well as to evaluate a given type of clay as a function of its specific surface.

The measured combustion efficiencies of three of the coal types (A, C, and D) agrees within a few percent with the combustion efficiencies calculated from the proximate analyses of the coals and the briquette compositions. The close correspondence implies that we are usually managing to burn the briquettes to near completion as well as collect nearly all of the ash for weighing.

Comparative emissions

The RSP data (Fig. 4) show a clear pattern that is relatively easy to interpret. The raw Lakhra coal, which has a high 24% ash content and produces a heavy smoke, produces the highest RSP loadings. The lime and clay amended coals (A, B, and C), each emit about one-fifth as much RSP. The slagging ef-

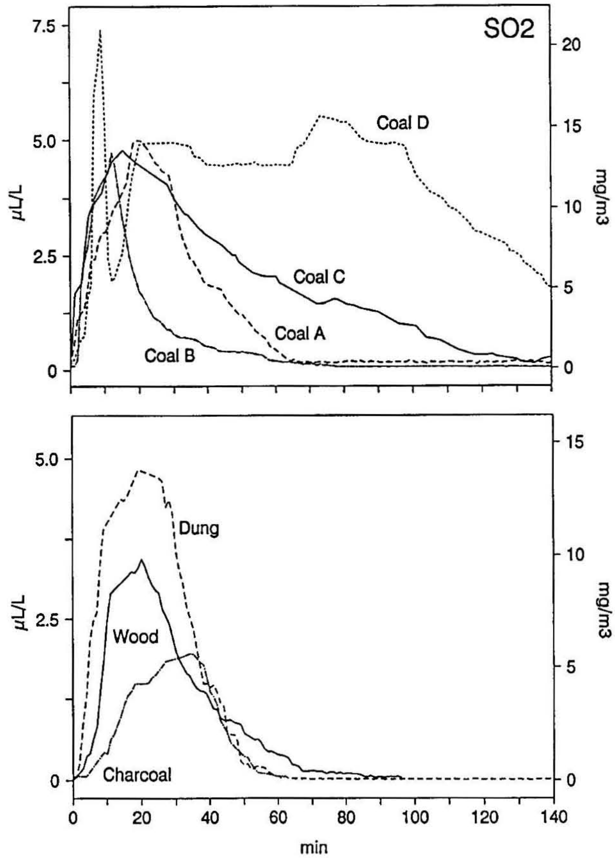

Fig. 7. Emission profiles of SO_2.

fect of the burnt lime and clay serve to bind the noncombustible mineral content of the coal and minimize its release in fine particulate form. Organic particles are reduced by any catalytic-cracking effect exerted by the clay. The respiratory particle hazard posed by burning the raw coal is, therefore, reduced severalfold if one substitutes the lime-clay coal briquettes. By coincidence, the burning of these amended coal briquettes produces RSP in amounts almost similar to the RSP from the firewood. Dung and charcoal emit considerable more RSP.

Comparing the amended coal briquettes to the traditional Pakistani fuels, it can be said that the RSP loadings from burning briquettes are generally significantly less and in no case worse.

The analyses of RSP for eight toxic heavy metals leads to the conclusion that a health hazard does not exist (Table 4). Only Sb and Zn were occasionally detected and then only slightly above the 1-μg limit of detection. In comparison to health hazards posed by other types of inorganic emission, the heavy element threat is insignificant.

Emissions of sulfur dioxide are of particular concern because of the high sulfur content of low-rank Pakistani coals. Although the combustion tube experiments at 800°C indicated sulfur fixation of better than 80% (Fig. 7), the firing of each type of amended coal briquette in the Angethi stove produces high peak SO_2 concentrations of about 5 μL/L after 10-20 min; the SO_2 emissions then decline significantly. Coals A and B cause little sulfur dioxide air pollution during the char-burning phase, when the lime/clay is acting as an efficient fixing agent for the releasing SO_2. We visualize both a physical and a chemical process to explain the sequence of SO_2 emissions. In the early stages, burning is restricted to the skin of

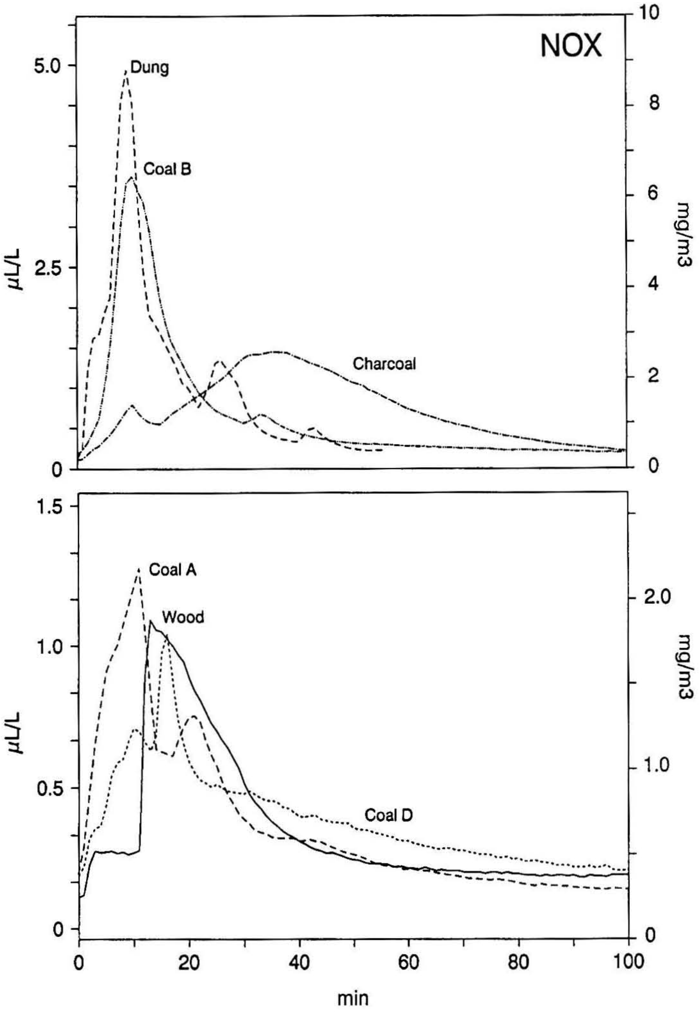

Fig. 8. Emission profiles of NO_x.

individual briquettes. The SO_2 produced in the briquette surface has maximum possibility for escape before it can react with any lime or quicklime. As burning proceeds into the interior of the briquette, the SO_2 produced has to pass through a thickening layer of quicklime and has an increasing likelihood of becoming fixed rather than escaping. The time of peaking of SO_2 emissions from amended coal briquettes coincides approximately with the time that temperatures reach 400°C (10-20 min). At this time and temperature the lime begins transforming rapidly to active CaO that reacts more efficiently with SO_2. Such a scenario offers a plausible explanation for the early peaking of SO_2 emissions and near complete retention in the latter stages of combustion.

The full sulfur-fixation potential (80% or more) of the amended coal briquettes is, however, clearly not being reached under the burning conditions we chose to operate the Angethi stove. Reference to Fig. 6 shows that the amended Lakhra coals (coals A and B) are reducing SO_2 emissions by 60-80% compared to SO_2 emissions from the raw Lakhra coal briquettes (coal D). Differences in temperatures developed in the Angethi stove and the combustion tube are likely responsible for the different efficiencies of sulfur fixation.

The raw Lakhra coal has the unpleasant characteristic of sustained emission of 5 μL/L SO_2 over the entire period that the briquette is burning. It is reported by the FRC that about 50% of the total sulfur

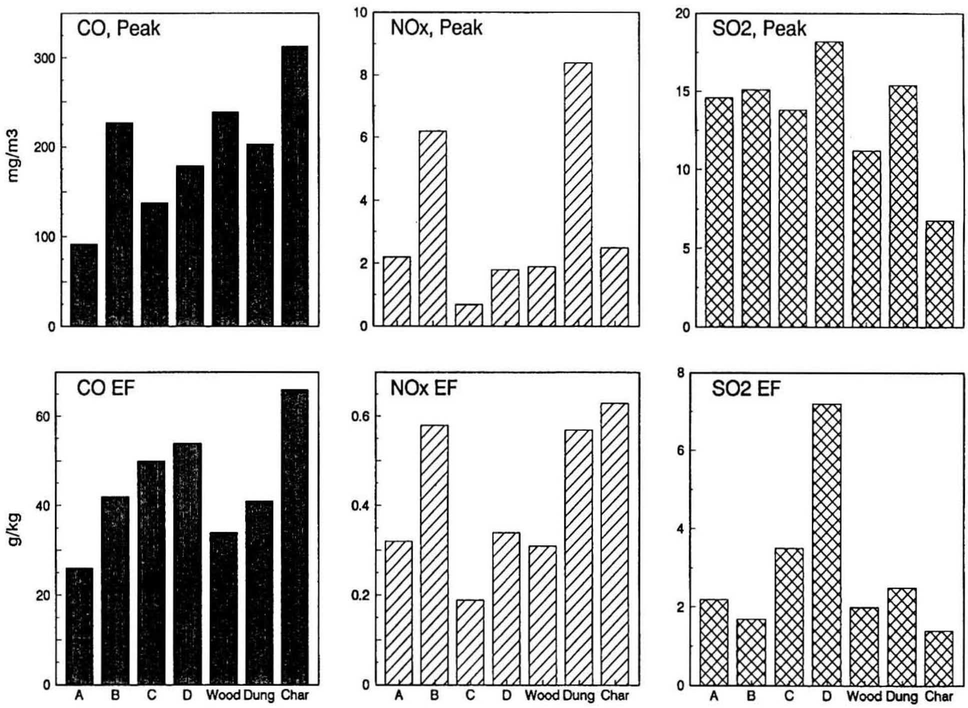

Fig. 9. Peak concentrations and emission factors of major inorganic oxide pollutants.

in Pakistani coals is organic sulfur, which presumably devolatilizes at about the same rate as other volatile matter and accounts for much of the early emission of SO_2. The remaining sulfur is mostly iron pyrites whose oxidation occurs mainly between 400-500° with the last traces of sulfur requiring a temperature in excess of 700° for its release (Chakrakarti et al. 1981). The last stages of decomposition of iron pyrites are likely responsible for the SO_2 releases from the raw coal during the latter occurring char-burning phase.

The traditional fuels, with their sulfur content in organic form, also release SO_2 in the early stages of combustion. Peak SO_2 concentrations occurring after 20 min are several μL/L in each instance, with dung producing the highest peak concentration of 5 μL/L. On a comparative basis, the SO_2 emissions from amended coals and traditional fuels are quite similar, both in peak and integrated SO_2 emissions.

The peak emissions of CO from the coal briquettes and traditional fuels range from a minimum of 100 μL/L for coal A to 300 μL/L for charcoal (Table 6). Integrated emission factors (EF) vary by twofold; coal A produces the least amount (26g/kg) and wood charcoal the greatest amount (66 g/kg) of carbon monoxide. If, however, the EF values are normalized by factoring in the noncombustible, non-CO producing constituents, the EF values are much closer (63 and 67 g/kg for coal A and wood charcoal, respectively). Of course, there is no *a priori* reason why EF factors should be the same for the different types of fuel. Production of CO is principally linked to availability of oxygen. One might reasonably expect the loose fibrous dung to receive a better oxygen supply than the burning coal briquettes, where firmly compacted particles, and subsequently formed coarse grained slag, would restrict access to oxygen. Corrected EF values for CO are 63-120 g/kg and 42 g/kg for different types of coal briquettes and dung, respectively. These results suggest that the physical structure of the fuels and the ability of air to access the burning regions are the prime determinants in carbon monoxide formation.

There have been few measurements of NO_x from burning of domestic fuels in underdeveloped countries. In our study, peak concentrations of 1-5 μL/L NO_x were measured. Dung gave the highest peak of 5 μL/L. The coal briquettes produced lesser peaks of NO_x emission. The additives in the amended coal briquettes do not appear to reduce either peak or

EF values of NO_x compared to NO_x emission from raw coal briquettes. It is worthwhile noting that the 1-5 µL/L levels of NO_x are in the range of threshold-weighed-average and short-term exposure limits set for the practice of industrial hygiene (ACGIH 1992).

Comparisons with other studies

It is not possible to compare directly our peak concentrations with peak concentrations from other studies. Peak concentrations are a function of fuel loading, room volume, air exchange rate, and rate of combustion. The first two factors can be controlled or held constant. Air exchange rate, however, is not usually controlled, or even monitored, although there are a few exceptions (Ahuja et al. 1987). Combustion rate is more difficult to control since it depends on fuel types, size and shape, air flow patterns, air velocities, and even the extent of the initial sample ignition. Peak concentrations are best used for relative comparisons among different fuels under the experimental conditions chosen by a given investigator. This approach was used in this study. Nevertheless, one is interested to know if the experimental conditions we employed are producing emissions that fall within the range of concentrations reported in real life for the burning of traditional fuels. Mean CO indoor concentrations during cooking with traditional unflued stoves are reported to range from 64-360 µL/L (Reid et al. 1986). Our own mean CO levels during Angethi stove operation are about 100-150 µL/L (Fig. 6), which gives us some confidence that our simulations are reasonably close to conditions actually being used during domestic cooking.

RECOMMENDATIONS

The principal purpose of the study was to determine whether quantities of potentially hazardous emissions from the coal briquettes with lime and clay additives were more or less than those from cooking fuels traditionally used in Pakistan. In broad terms, one can state that substitutions of the amended coal briquettes for firewood or dung will not worsen indoor air quality with respect to CO, SO_2, NO_x, and RSP. Given the favorable economics of coal briquettes and the possibility for a lessened rate of deforestation, their promotion as an alternative fuel source should be encouraged.

The greatest emissions of pollutants occur shortly after light-up of the fuel when burning is restricted to the outer surfaces of the briquettes. The operator of the Angethi stove would be advised to start a burn outdoors and if necessary carry the stove indoors after smoke emissions subside. Such a *modus operandi* would significantly reduce indoor air pollution that otherwise is much in excess of currently adopted standards and guidelines for indoor air quality in developed countries.

Acknowledgment — The research was sponsored by the U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., and supported by the Pakistan Mission of the United States Agency for International Developmemnt (USAID) under an interagency agreement between US-AID and the United States Department of Energy (US-DOE). The authors wish to thank Dr. E.L. Fuller, Jr. for measuring the specific surface of the slaked lime and to Dr. D.R. Glasson for his technical advice with regard to scavenging of sulfur dioxide by lime and lime-related materials.

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Environment International, Vol. 19, pp. 147-154, 1993
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0160-4120/93 $6.00 +.00

SIZE DISTRIBUTIONS OF SUBMICROMETER AEROSOLS FROM COOKING

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EI 9208-177 M (Received 10 August 1992; accepted 18 November 1992)

Although gas stove usage varies from country to country, it is still one of the major indoor combustion sources. In order to assess the health effects of using gas stoves, the physical characteristics of the particle emissions from cooking were conducted in a first-floor apartment in the Taipei area. The particle size distributions from scrambling eggs, frying chicken, and cooking soup were measured in the kitchen by a high resolution particle sizer, which could measure the particles in the size range of 0.01 µm to 1 µm. The concentrations of the submicrometer particles increased significantly from 15 000 cm^{-3} to 150 000 cm^{-3} during cooking. Additionally, the ultrafine particles constituted 60%-70% of the total submicron aerosols. The changes in the size distributions and the concentrations of the submicrometer aerosols before, during, and after the aerosol generations were compared. On the average, the median diameters of scrambling eggs, frying chicken, cooking soup, and of the background conditions were 40 nm, 50 nm, 30 nm, and 70 nm, respectively. Regarding the surface area-weighted size distributions, the surface median diameters of the four situations were 180 nm, 300 nm, 150 nm, and 220 nm, respectively. Furthermore, the volume median diameters in the conditions mentioned above were almost similar, namely 300-350 nm.

INTRODUCTION

Indoor air quality has become an important issue in recent years. Most people spend more than 80% of their time indoors (NRC 1981). The major sources of indoor air pollutants include combustion sources, building materials, and consumer products. For indoor combustion sources, many investigations were conducted to evaluate the characteristics of air pollutants from smoking, gas ranges, unvented gas space heaters, kerosene space heaters, wood stoves, coal stoves, and forced air furnace systems (Tucker 1987; Moschandreas et al. 1987; Traynor 1987). Because of the warm climate, none of these heaters are used in Taiwan. Cooking is an important indoor combustion source, because more than 95% of the households use gas stoves in Taiwan. The primary targets exposed to the particulate emissions from cooking are women, elderly persons, and children.

It is suggested that the food heating process might emit carcinogens, such as polycyclic aromatic hydrocarbon (PAH). There have been more than twenty kinds of PAHs identified from these food heating processes. Among those identified PAHs, more than ten chemicals were considered possible causative agents of human cancers (Claxton et al. 1987). Cooking is a combustion process which emits highly concentrated smaller particles with a subsequent coagulation. Several field measurements (Stout et al. 1984; Tu and Knutson 1988; Strong 1988) have been performed to evaluate the size characteristics of the particulate emissions from cooking. It was indicated that cooking had led to particle concentrations one or two orders of magnitude higher than the background conditions. However, the median diameters (MD) of the cooking aerosols were still quite different from the three studies mentioned above. These discrepancies might result from the different instruments used in the field measurements and the cooking method. Despite the availability of a number of investigations, no comprehensive comparison of size distributions is possible. The reason is a lack of accurate data on background conditions, different cooking methods, and the environmental conditions after cooking.

For the health evaluation of cooking by physical aspects, the aerodynamic diameter of the generated aerosol is the most important parameter to determine the deposition site and the amount in the respiratory tract. The objective of this field investigation was to evaluate the characteristics of submicron aerosols (smaller than 1μm) and ultrafine aerosols (smaller than 0.1 μm) of scrambling eggs, frying chicken, and cooking soup in the kitchen. Submicrometer aerosols have a larger deposition efficiency in the respiratory tract, especially the alveolar region (Phalen et al. 1991; James et al. 1991). For example, the bronchial and alveolar deposition fractions of 0.06-μm aerosols are approximately 0.10 and 0.34, respectively. For 2-μm aerosols, the bronchial and alveolar deposition fractions are 0.04 and 0.19, respectively. The variations of particle size distributions and the concentrations of the submicrometer aerosols and ultrafine aerosols produced before, during, and after cooking were evaluated. Furthermore, the median diameter (MD), the surface median diameter (SMD), and the volume median diameter (VMD) of each condition in the kitchen were discussed.

METHODS

The field measurements were conducted mainly in a kitchen and the outside of a first floor apartment with a living room, two bedrooms, a kitchen, and a bathroom in Taipei in April 1992. The dimensions of the kitchen are 5 m × 1.5 m × 3 m. The particle sizer is a high resolution electrical mobility aerosol spectrometer, including a differential mobility particle sizer (DMPS TSI 3932) and a condensation particle counter (CNC TSI 3022). This particle detector is capable of measuring the concentrations of the aerosols within the size range of 0.017 - 0.886 μm (divided into 33 channels) at the sampling flow rate of 3 Lm^{-1}. The median diameters of each channel are presented in Table 1. The DMPS/CNC instrument was used with a bipolar charger to charge aerosols to a known Botlzman distribution. Then, the aerosols were classified by their ability to traverse an electric field and counted by an optical detector after a supersaturated vapor condense onto particles, causing them to grow into larger droplets. The surface and volume concentrations of the submicrometer particles as well as the median diameters with a standard deviation of the particle aerodynamic size distributions were determined before, during, and after cooking. The DMPS/CNC instrument was installed 3 m away from the gas stove in the kitchen. The outside measure-

Table 1. The mean median diameters of the 33 channels for the DMPS/CNC.

Mobility Channel	Median Diameter (μm)
1	0.017
2	0.018
3	0.021
4	0.023
5	0.025
6	0.028
7	0.031
8	0.035
9	0.038
10	0.043
11	0.048
12	0.053
13	0.059
14	0.066
15	0.074
16	0.083
17	0.093
18	0.104
19	0.117
20	0.132
21	0.150
22	0.170
23	0.193
24	0.221
25	0.253
26	0.291
27	0.337
28	0.391
29	0.457
30	0.535
31	0.631
32	0.746
33	0.886

ments were conducted in front of the entrance of the apartment for a 24-h continuous sampling.

During all of the indoor field measurements, the doors and windows of the apartment were closed. A 5-min air sampling of DMPS/CNC was used to measure the submicrometer aerosols. In order to examine the changes of the size distributions and of the concentrations of submicrometer aerosols and ultrafine aerosols before, during, and after the aerosol generations, the time sequences of particle generation and measurement were as follows. Before any particle generation, several sets of the measurements were made as background conditions without cooking. The time period for scrambling eggs, frying chicken, and cooking soup was 15 min in order to obtain two or three measurements during these aerosol generation periods. The following measurements were made for 2 h after the combustion activities ceased for the purpose of evaluating the decay behavior of the generated particles. Each measurement sequence of the combustion sources was repeated three times Each kind of the particles was produced again and the time evolution of the particle size distributions was again measured.

RESULTS AND DISCUSSION

The particle size distributions of cooking as well as the outdoor aerosols were measured in the kitchen and outside. When the kitchen was not used for any purpose, the concentrations of the ultrafine and submicrometer aerosols were found to be in the range of 8 400 - 15 000 cm^{-3} (average 13 200 cm^{-3}), and 12 000 - 20 000 cm^{-3} (average 22 100 cm^{-3}), respectively. The ultrafine aerosols were found to constitute approximately 50% - 70% of the submicrometer aerosols. On the average, the MD, SMD, and VMD were 70 nm, 220 nm, and 330 nm, respectively, with an average geometric standard deviation of 2. The median diameters of these background conditions were found to be similar with those observed indoors from several investigations (Stout et al. 1984; Tu and Knutson 1988; Strong 1988). Outdoors, the field measurements were conducted continously in the front of the entrance of the apartment for 24 h, so the variations of the characteristics of the outdoor aerosols could be assessed. It was shown that the concentrations of the ultrafine and submicrometer aerosols ranged from 7 500 to 34 800 cm^{-3} (average 15 600 cm^{-3}) and from 10 000 to 43 500 cm^{-3} (average 19 400 cm^{-3}), respectively. The results demonstrated that the concentrations of the outdoor aerosols strongly depended on the traffic conditions, for instance, the number of automobiles and motorcycles passing during the daytime. The peaks of the outdoor aerosol concentrations occurred during two different time periods—between 7 and 8 a.m. and 4 and 6 p.m. On the other hand, the lowest outdoor aerosol concentrations were observed during the early morning (from 12 p.m. to 6 a.m.). The relationship between the aerosol characteristics and the traffic conditions was not conducted in this study, but this issue needs more investigation. Moreover, the ratios of ultrafine aerosols to submicrometer aerosols ranged from 0.60 to 0.89 with an average value of 0.80, which were much higher than those observed in the indoor environment. It was indicated that the ultrafine aerosol was the dominant fraction of the detected particles. In addition, the MD was measured to be in the range of 50 nm-68 nm with an average of 54 nm, which was much smaller than that found indoors.

The aerosols in the kitchen were generated from scrambling eggs, frying chicken, and cooking soup. Each measurement sequence for each type of aerosol was repeated three times. The particle concentrations, particle size distributions, surface and volume median diameters of the background conditions before, during, and after cooking were determined. The condensation nuclei counted as a function of time during and after scrambling eggs, frying chicken, and cooking soup for all three times are shown in Figs. 1, 2, and 3, respectively. In addition, the number-weighted particle size distributions of scrambling eggs, frying chicken, and cooking soup in the following situations—before (background), during (aerosol start, aerosol, and aerosol end with a 5-min time interval), and after the aerosol generation (recovery, 30 min, and 60 min) are presented in Figs. 4, 5, and 6, respectively. Meanwhile, the MD, SMD, and VMD with GSD of each case are detailed in Table 2. Therefore, the decay behavior of the generated aerosols could be evaluated by three conditions: 5 min after the end of the aerosol generation (recovery); 30 min after the end of the aerosol generation (30 min); and 60 min after the end of the aerosol generation (60 min).

In regard to scrambling eggs, the submicrometer particle number concentrations could reach 112 000 cm^{-3} and 180 000 cm^{-3}. In comparison, the concentrations of the ultrafine particles were in the range of 90 000 cm^{-3} to 150 000 cm^{-3}. Furthermore, the average concentration ratio of the ultrafine aerosols to submicrometer aerosols was approximately 0.85. During the active aerosol generation, the MD, SMD, and VMD were in the range of 33 - 47 nm, 180 - 270 nm, and 330 - 430 nm, respectively. The results of scrambling eggs were similar to those observed (MD = 54 nm) for frying food without specifically

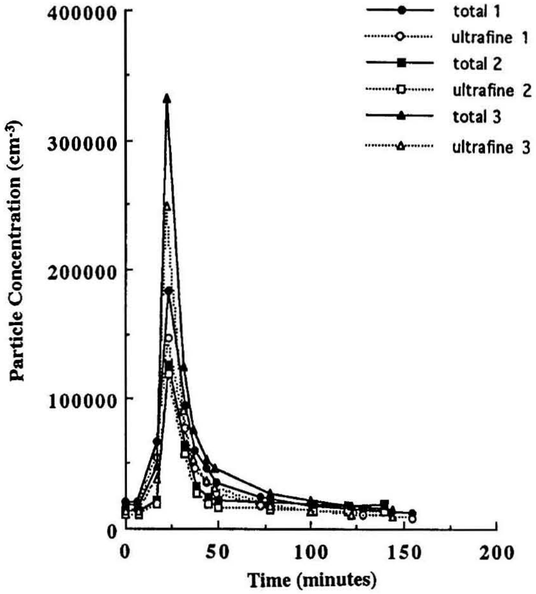

Fig. 1. Condensation nuclei measurements (including submicrometer and ultrafine aerosols) made during and after particle generation by scrambling eggs (three times).

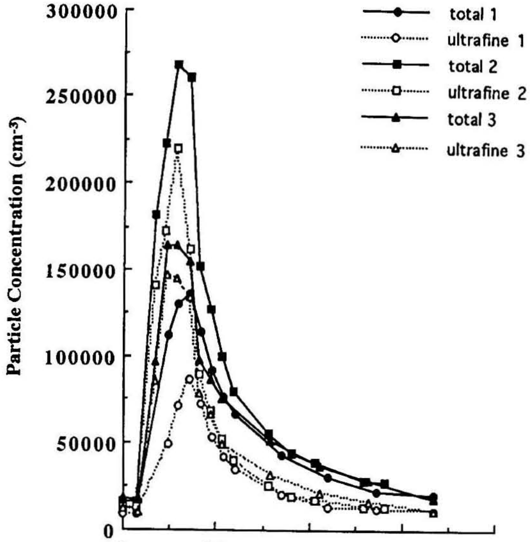

Fig. 2. Condensation nuclei measurements (including submicrometer and ultrafine aerosols) made during and after particle generation by frying chicken (three times).

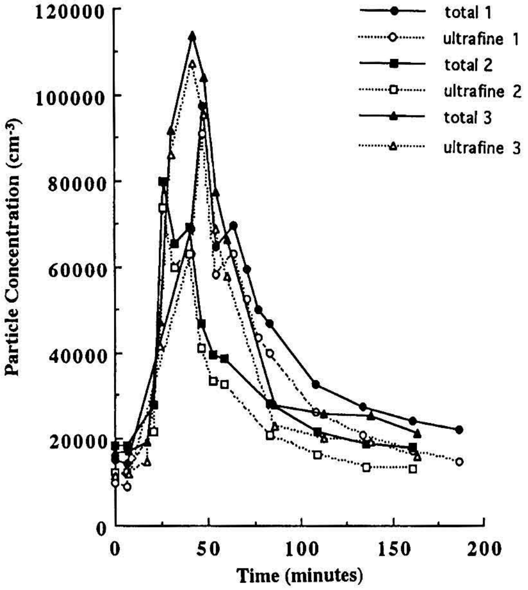

Fig. 3. Condensation nuclei measurements (including submicrometer and ultrafine aerosols) made during and after particle generation by cooking soup (three times).

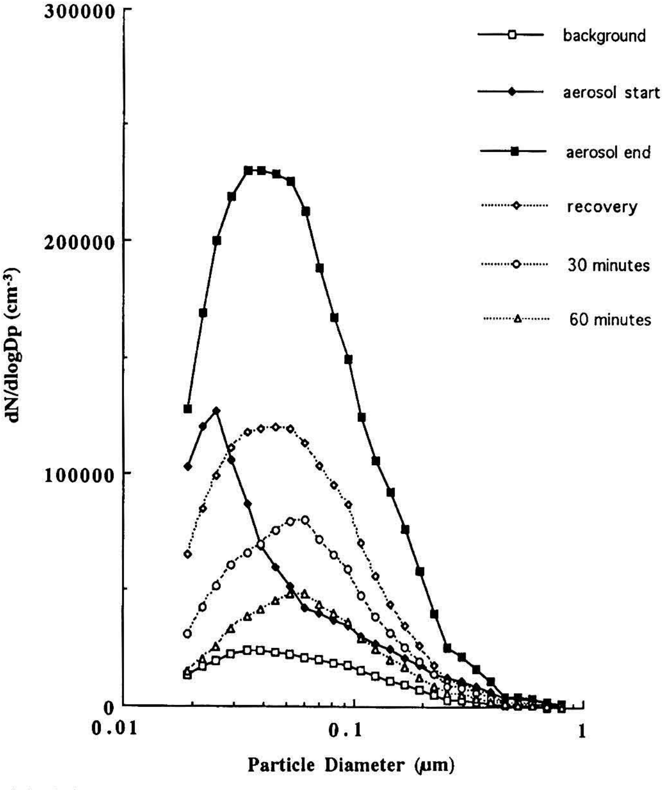

Fig. 4. The number-weighted size distributions of the submicrometer aerosols before, during, and after particle generation by scrambling eggs.

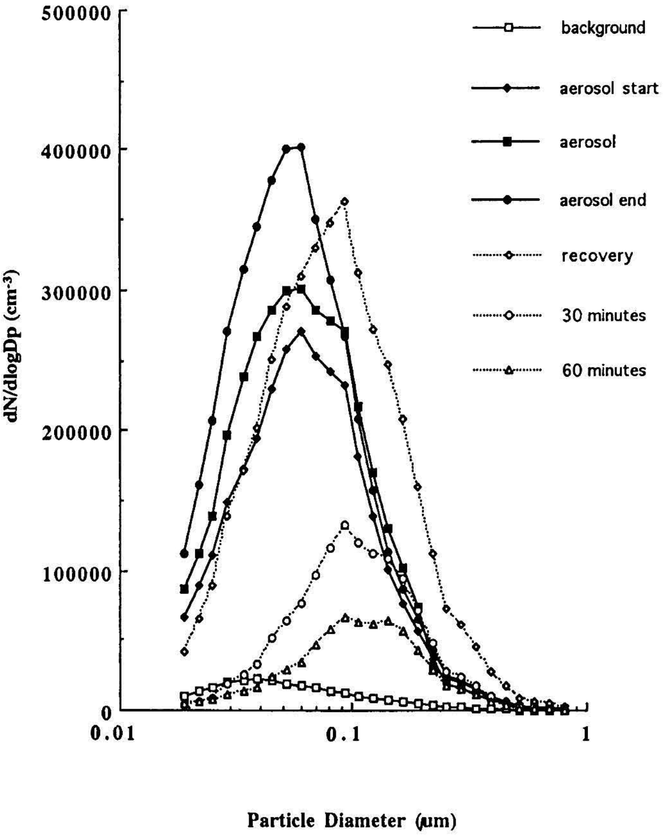

Fig. 5. The number-weighted size distributions of the submicrometer aerosols before, during, and after particle generation by frying chicken.

indicating what kind of cooked food (Tu and Knutson 1988). Regarding frying chicken, the submicrometer aerosol number concentrations ranged from 120 000 cm^{-3} to 260 000 cm^{-3} with the average ratio of ultrafine to submicrometer aerosols of 0.80. While the aerosols were produced, the MD, SMD, and VMD were found to be 60 nm, 160 nm, and 270 nm, respectively. Moreover, the size characteristics of frying chicken were the same as those measured with cooking in the kitchen by Stoute et al. (1984). It is suggested that the disappearance of small aerosols, generated from gas combustion, from the particles measured during scrambling eggs and frying chicken might be related to the coagulation effects. During cooking, the presence of the higher humidity and emitted organic vapors tends to induce the smaller aerosols to disappear by coagulation.

Regarding cooking the vegetable soup for 15 min, aerosols produced from gas combustion with a MD of 30 nm, and the number concentrations increased to 80 000 cm^{-3}. One particular note is that the ultrafine aerosols constituted 90% of the total submicrometer aerosols by number. In addition, during cooking soup, the SMD and VMD were found to be 150 nm and 300 nm, respectively. These results demonstrated that the MD was close to that found in the kitchen by a diffusion battery by Strong (1988). However, Strong gave no specific information about the cooking process or what kind of food was cooked. From Tu and Knutson's investigations (1988), the MD of cooking soup was 14 nm, which is much smaller than those measured by our group and Strong (1988). One of the major reasons might be that the sampling instruments used in our field evaluations only detect the aerosols in the size range of

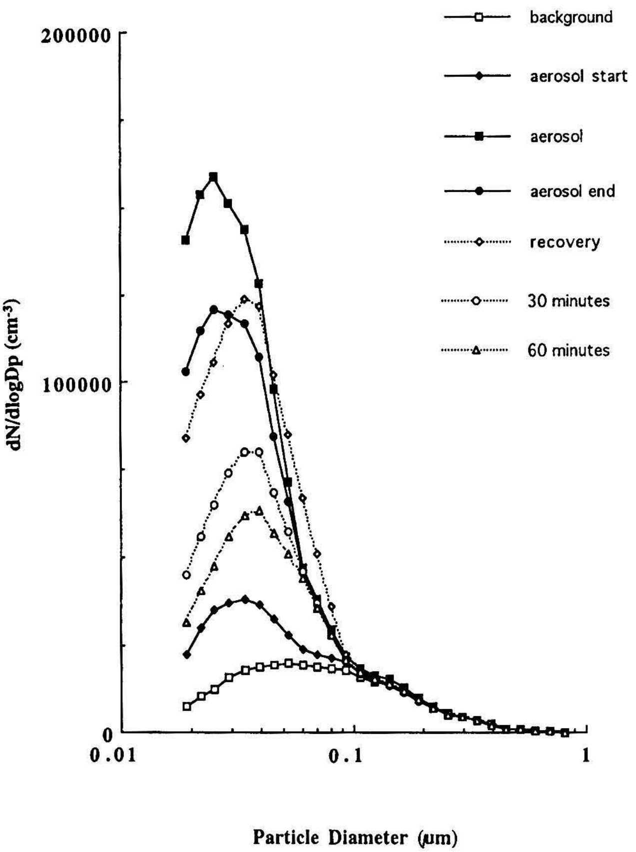

Fig. 6. The number-weighted size distributions of the submicrometer aerosols before, during, and after particle generation by cooking soup.

0.017 μm-0.886 μm. This 14 nm mode of cooking soup might appear, but the instruments used in this investigation could not detect it. Therefore, it is worthwhile conducting further field measurements to characterize the size range of the cooking aerosols smaller than 0.017 μm (the smallest size detected in this study). In summary, in the case of these three types of aerosols mentioned above, the larger particles stayed airborne longer and would remain in the similar particle size distributions for a longer period of time, such as scrambling eggs and frying chicken (as shown in Figs. 4 and 5). The smaller particles produced by cooking in the kitchen would deposit (diffusion) on the surface and or coagulate to the larger particles (shift to the larger size ranges), as for example in cooking soup (Fig. 6).

CONCLUSIONS

Cooking was found to be a main source of submicrometer and ultrafine aerosols from gas combustion in the stove, from scrambling eggs, frying chicken, and cooking soup. The concentrations of the submicrometer particles during the cooking periods significantly increased from 40 000 cm^{-3} to 100 000 cm^{-3}. On the average, the MD, SMD, and VMD of cooking were found to be approximately 40 nm, 200 nm, and 325 nm, respectively. In addition, a much higher aerosol deposition of the submicrometer aerosols, especially ultrafine particles, was observed in the respiratory tracts. Cooking should be considered as one of the important particulate sources in the domestic environments.

Table 2. Summary of the measurements of concentrations of submicrometer and ultrafine aerosols (Ct and Cu), MD, SMD, VMS, and GSDs of each cooking.

	Ct (10^3 cm^{-3})	Cu (10^3 cm^{-3})	MD (μm)	GSDn	SMD (μm)	GSDs	VMD (μm)	GSDv
Scrambling eggs								
background	20	15.4	0.050	2.054	0.203	2.167	0.338	1.908
aerosol start	66.5	54.7	0.034	2.217	0.272	2.257	0.432	1.741
aerosol	184	147.2	0.047	2.008	0.194	2.224	0.335	1.942
recovery	95.3	77.1	0.048	1.972	0.186	2.246	0.329	1.979
30 min	32.6	23	0.059	1.984	0.201	2.150	0.338	1.924
60 min	21.2	15	0.059	2.019	0.216	2.157	0.358	1.895
Frying chicken								
background	16.2	12.8	0.047	2.044	0.207	2.194	0.346	1.885
aerosol start	182.6	141.5	0.058	1.856	0.157	2.058	0.264	2.019
aerosol	223	172.6	0.058	1.882	0.161	2.074	0.272	2.015
aerosol end	264	219.7	0.051	1.853	0.161	2.202	0.291	2.060
recovery	260	162.3	0.075	1.948	0.208	1.971	0.319	1.854
30 min	79.6	39.4	0.094	1.821	0.212	1.861	0.309	1.822
60 min	43.4	19.8	0.099	1.884	0.222	1.836	0.318	1.791
Cooking soup								
background	14.4	9.1	0.071	2.131	0.230	1.980	0.346	1.802
aerosol start	69	63.4	0.032	1.816	0.164	2.585	0.333	2.027
aerosol	97.4	91	0.034	1.745	0.140	2.585	0.304	2.150
aerosol end	65	58.6	0.036	1.835	0.165	2.469	0.322	2.030
recovery	69.7	63.3	0.037	1.810	0.157	2.486	0.316	2.075
30 min	40.9	33.9	0.048	1.851	0.178	2.337	0.328	2.015
60 min	28.8	23.3	0.054	1.847	0.197	2.315	0.335	2.033

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Environment International, Vol. 19, pp. 155-166, 1993
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0160-4120/93 $6.00 +.00

CATCHMENT-SCALE DEPOSITION AND REDISTRIBUTION OF CHERNOBYL RADIOCAESIUM IN UPLAND BRITAIN

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EI 9208-175 M (Received 7 August 1992; accepted 20 December 1992)

Fallout from the Chernobyl nuclear accident in April 1986 resulted in a significant increase in the inventory of radiocaesium in many areas of upland Britain. Caesium-137 derived from nuclear weapons testing in the 1950s and 1960s has been widely used as a sediment tracer to monitor soil erosion. The presence of Chernobyl fallout provides an opportunity to examine the short-term, post-input behaviour of radiocaesium in upland soils and assess its potential for investigating sediment transfer in upland systems. Sampling undertaken in the catchment of Lake Vyrnwy, North Wales considered the vertical distribution of radiocaesium in different soil types, the catchment-wide variation in Chernobyl fallout deposition, and the radiocaesium content of sediment from a variety of slope and fluvial environments. Whilst uncertainty surrounding the estimation of baseline inventories limits the detailed interpretation of short-term sediment dynamics, it is apparent that the sediment-associated redistribution of Chernobyl radioactivity may result in its accumulation in certain parts of the catchment over longer timescales.

INTRODUCTION

The caesium radioisotopes ^{134}Cs and ^{137}Cs provide a distinctive set of tracer properties which can be used to investigate the erosion, transport and deposition of sediment within the landscape. Caesium-137, a fallout product of the atmospheric testing of nuclear weapons in the 1950s and 1960s, has a half-life of 30.1 y and on reaching the earth's surface is in most environments strongly adsorbed by fine grained particulate matter in the surface horizons of the soil (Tamura 1964; Frissel and Pennders 1983). The subsequent redistribution of ^{137}Cs is therefore primarily associated with the erosional transport of sediment particles. Measurements of the ^{137}Cs inventory at different locations compared with an estimate of the baseline fallout to the area, provide a means of assembling information on the rates and patterns of soil loss which has been mainly applied to examine soil erosion on arable land (de Jong et al. 1983; Walling and Quine 1990; Sutherland et al. 1991).

The accident at the Chernobyl nuclear power plant on 26 April 1986 resulted in an estimated 5% increase to the global inventory of ^{137}Cs (Cambray et al. 1987). In addition to ^{137}Cs, the shorter-lived radioisotope ^{134}Cs ($T_{0.5}$ = 2.2 y), which was not present in nuclear weapons fallout, was also deposited. In the UK the majority of Chernobyl-derived radiocaesium was deposited between May 2 and May 4 of 1986 (Smith and Clark 1989). This fallout resulted, on average, in an estimated 40% increase in the national inventory of ^{137}Cs (Cambray et al. 1987) although the non-uniform distribution of rainfall coincident with the plume caused wide variations in fallout. Relatively high levels of Chernobyl fallout occurred in North Wales, Cumbria and southern Scotland, yet within these upland regions local variations in rainfall produced a wide variation in fallout deposition over relatively small spatial scales.

The presence of Chernobyl fallout enables two main lines of research to be pursued.

1) It provides an opportunity to examine the short-term, post-input behaviour of radiocaesium in soils helping to reassess and refine the use of bomb-test ^{137}Cs in sediment tracing investigations.

2) Investigation of the potential for using Chernobyl fallout (^{134}Cs and ^{137}Cs) as a tracer of sediment movement in its own right to supplement bomb-test ^{137}Cs.

These two aims have been addressed in the catchment of Lake Vyrnwy, North Wales. In addition, a subsidiary aim of evaluating the viability of using ^{137}Cs tracing techniques in upland areas is examined. Whilst the use of bomb-test ^{137}Cs measurements has been extended from arable areas to estimate erosion on rangeland (Lance et al. 1986; Loughran et al. 1990), its application in upland areas has been limited (Bonnett et al. 1989).

STUDY AREA

The catchment of Lake Vyrnwy covers an area of 94.8 km^2 in the headwaters of the Severn Basin. It was selected for study since it lies within the main axis of Chernobyl fallout affecting Wales (Fig. 1a) and comprises part of a wider study of the transport of radionuclides in the Severn (Walling et al. 1989). The topography, soils, and land use are typical of the region and of upland Britain in general. The altitudinal range is between 251 m and 666 m with extensive areas of upland plateau, dissected by steep-sided valleys. The geology consists mainly of mudstones of the Ordovician Arenig beds and the Silurian Wenlock beds with superficial deposits. Mean annual rainfall ranges from 1600 mm in the east to 2400 mm in the higher western side of the catchment. Soils are typical of the wet conditions, with peats of the Crowdy Series on the upland plateau, stagnopodzols and podzolic soils on the valley slopes, and stagnogleys in the lower parts of the catchment (Fig. 1b).

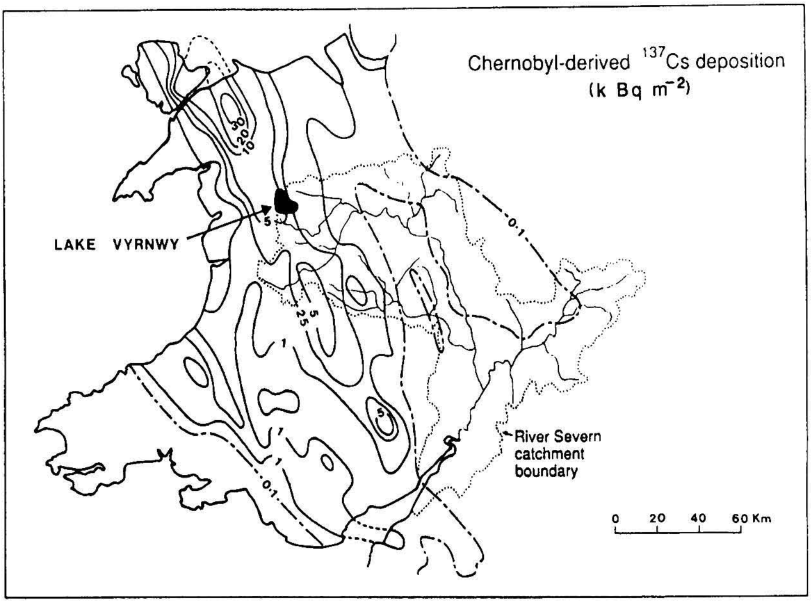

Fig. 1a. Location of the Lake Vyrnwy catchment in relation to Chernobyl fallout across Wales.

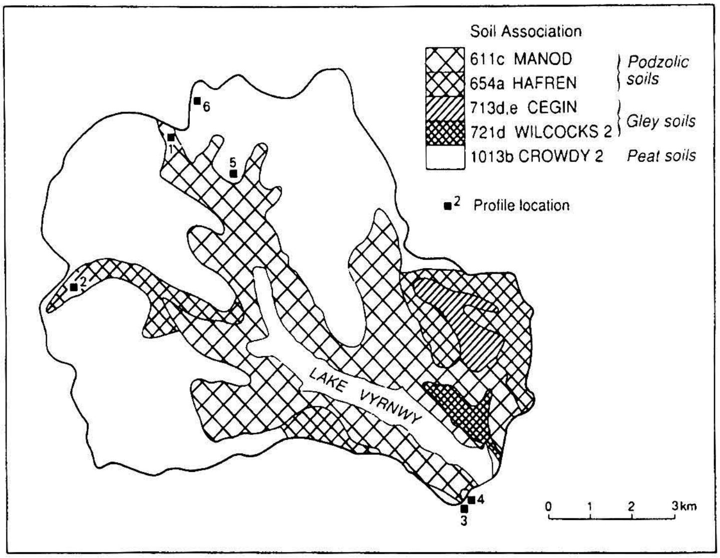

Fig. 1b. Soil map of the catchment.

Reservoir construction was completed in 1882 to supply water to Liverpool and the reservoir has subsequently developed a variety of recreational uses. Within the catchment, the upland moors area is used for rough grazing. Many of the valley sides are used for forestry, a number of which have been subject to clear felling in recent years and may represent an important sediment source.

METHODS

In order to examine the redistribution of the Chernobyl radiocaesium within the catchment, four phases of fieldwork were initiated in November 1987. The first component was an investigation of the nature of radiocaesium retention in the various soil types of the catchment. For radiocaeisum to be used as a sediment tracer, it is important that fallout is retained near the soil surface. Sectioned soil profiles were obtained using the method described by Campbell et al. (1988) whereby a bevelled metal plate is used to excavate successive 1- or 2-cm increments from an area defined by a steel sampling frame of 200 × 400 mm. Six profiles were obtained from each of the principal soil types of the catchment (locations are given in Fig. 1b).

The second phase consisted of a sampling programme to investigate the spatial variability of Chernobyl radiocaesium deposition across the catchment. Soil samples were collected from 79 locations on gently sloping, undisturbed land along interfluve ridges so that the total Chernobyl input could be assessed. The distance between each sampling location was between 500 and 1000 m to provide adequate coverage of the whole catchment. At each location, five soil cores (47 mm Ø) were taken to a depth of 10 cm. The results of the sampling undertaken in the first phase had shown that >90% of Chernobyl-derived radiocaesium was contained above this depth. Samples were also collected along a series of slope transects to investigate whether there was any evidence of aspect control on the distribution of Chernobyl fallout deposition.

The third aspect of the investigation involved the sampling of different erosional and sedimentary environments across the slopes of the catchment in order to evaluate the usefulness of using Chernobyl radiocaesium to study sediment transfer within upland environments and to identify areas of marked radiocaesium accumulation or depletion. Soil cores of equivalent size to the fallout survey were collected from a variety of sites which included clear-cut forestry plantations, burnt moorland, colluvial footslopes and channel sediment. The final component of the project considered the incorporation and accumulation of radiocaesium in deltaic and reservoir sediments and is reported in more detail by Rowan et al. (1993).

All soil and sediment samples were transported back to the laboratory, oven dried at 50°C, disaggregated and passed through a 2-mm sieve before being packed into Marinelli beakers for gamma spectrometry measurement using an Ortec HPGe coaxial detector. The activities of ^{134}Cs and ^{137}Cs were calculated from the photopeaks produced at 605 and 662 keV, respectively, having calibrated the detector with standards of known activity and similar geometry to the samples. Count times were between 10000 and 25000 sec. All activities have been corrected for decay to 2 May 1986 and can be expressed as either concentrations (Bq kg^{-1}) or inventories (Bq m^{-2}). Gamma spectrometry involves a statistical counting procedure and individual measurements accordingly embody some error. This analytical precision was typically ±5% for ^{137}Cs and ±10% for ^{134}Cs at the 95% confidence level. A few samples were recounted but no measurement discrepancies were encountered. Further details of the sample preparation and counting procedures are reported elsewhere (Walling and Quine 1990).

RADIOCAESIUM RETENTION IN SOILS

The activity concentration profiles for the six sampling locations are shown in Fig. 2. The strong adsorption of caesium has been widely demonstrated in lowland agricultural soils but it may be more weakly retained by acidic upland soils with low clay and potassium contents and high organic content (Livens and Loveland 1988). The exponential distribution of all the profiles indicates that most of the radiocaesium has been adsorbed near the soil surface. The proportion of the total inventory above certain depths is shown in Table 1. The combined bomb-test and Chernobyl ^{137}Cs inventory is contained within the upper 30 cm, with more than 90% within the upper 20 cm and more than 75% in the upper 10 cm. The ^{134}Cs is retained closer to the surface, suggesting that the bomb-test fallout has been subject to some degree of downward movement subsequent to its accumulation in the soil. Bonnett et al. (1989) observed that Chernobyl fallout was restricted to the upper 5 cm of soils of the nearby Plynlimon experimental catchments. However, the Vyrnwy profile data indicate that only 60 to 80% of Chernobyl fallout has been retained in this layer, but in all cases more than 90% of the ^{134}Cs inventory is retained within the upper 10 cm.

Small perturbations occur in the exponential profiles which may relate to recycling through the vegetation. In lowland agricultural soils, caesium transfer to the vegetation, though potentially important in terms of concentration, represents a minimal loss of the total inventory amounting to less than 1% (Coughtrey and Thorne 1983). However, the contamination of hill pastures and moorland in some areas of upland Britain has persisted longer than expected. This is because many of the soils of upland areas, such as the study

Table 1. Radiocaesium depth distributions in Vyrnwy input cores.

	Podzolic soils		*Gley soils*		*Peat soils*	
	1	2	3	4	5	6
^{137}Cs						
Total (Bq m^{-2})	8772	8894	4839	6154	6969	8340
% above 5cm	54.8	42.0	49.9	42.6	59.6	65.7
% above 10cm	81.3	88.3	81.6	81.6	78.3	76.6
% above 20cm	94.8	100	99.8	98.0	96.9	96.0
^{134}Cs						
Total (Bq m^{-2})	2279	2061	1626	2194	1411	2484
% above 5cm	71.6	76.9	76.0	61.5	71.6	80.7
% above 10cm	96.9	97.2	93.9	96.6	96.3	94.9

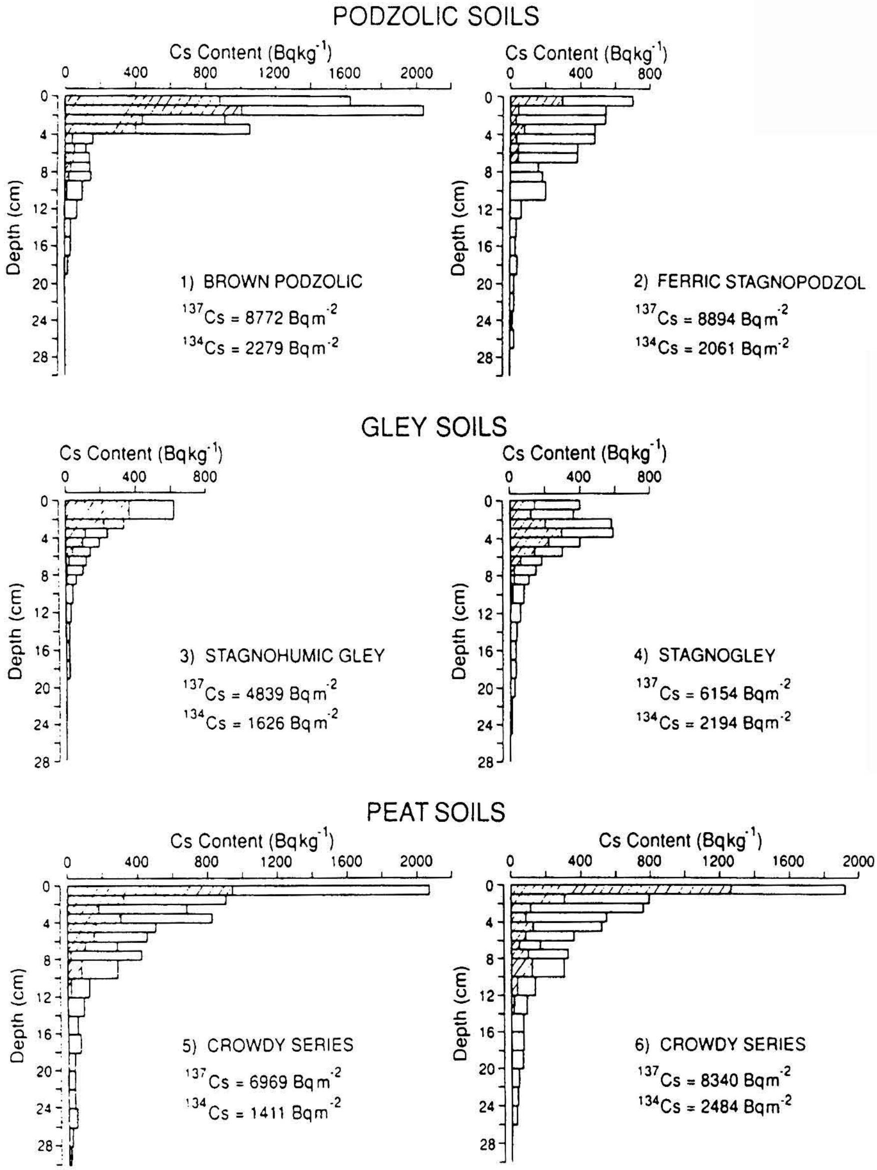

Fig. 2. Vertical distribution of radiocaesium concentrations in soil profiles.

area, are acidic, peaty, and low in micaceous clays, so that caesium in these soils has continued to be exchanged between the soil and the vegetation. It is also possible that a more substantial proportion of the radiocaesium inventory could be stored temporarily within the vegetation at any sampling site (Kirk and Staunton 1989). Vegetation samples have not been analysed in this study. Nevertheless, the soil profile data show no evidence of extensive down-profile migration of radiocaesium, suggesting that measurements of radiocaesium inventories could be used in soil redistribution studies.

SPATIAL VARIABILITY OF RADIOCAESIUM FALLOUT

The inventories of Chernobyl-derived radiocaesium obtained from the core sampling programme demonstrate considerable variability and a complex spatial pattern. Similar findings were reported by Bonnett et al. (1989) for the adjacent Plynlimon area. The mean ^{137}Cs activity in the upper 10 cm determined in the 76 input samples (corrected for decay to 3 May 1986) is 5323 Bq m^{-2} with a coefficient of variation of 44.5%. Inventories range from 1715 ±178 to 12 189 ± 492 Bq m^{-2}. The mean ^{134}Cs inventory is 1447 Bq m^{-2} with a coefficient of variation of 58.4% and individual inventories ranging between 226 ±97 and 4293 ± 485 Bq m^{-2}.

The use of ^{137}Cs measurements in erosion studies has been based on the simple premise that locations with less ^{137}Cs than the baseline inventory have undergone topsoil erosion whereas sites with higher levels of ^{137}Cs than the baseline indicate areas of soil or sediment deposition. If the initial distribution of fallout deposition is highly variable, the uncertainties associated with the estimation of the baseline inventory will be large and will constrain the viability of the technique. In this case, the high coefficients of variation for both ^{134}Cs and ^{137}Cs inventories suggest that a high level of radiocaesium depletion would be needed before it could be demonstrated with statistical confidence that the inventory at a particular site is significantly less than the baseline inventory. In other words, the technique will only be recognise extremely high rates of erosion or deposition. However, the coefficients of variation of the inventories take no account of the spatial dependency of the data. Preliminary investigation of the data indicated a highly variable spatial pattern of fallout, but some form of trend was apparent with the highest inventories found in the central and northern parts of the catchment and with lower values in the eastern and western extremities. There is no apparent coincidence between the pattern of Chernobyl fallout and the distribution of different soil types. The existence of this trend in the distribution of fallout implied that a regionalised estimate of baseline fallout with much smaller associated uncertainties might be made for different parts of the catchment and this was explored geostatistically using kriging.

Kriging is a geostatistical technique which permits quantitative analysis of the spatial variability of the distribution of a parameter and provides unbiased estimates with minimum variance (Oliver et al. 1989). Two stages are required in the kriging process; the first involving the production of experimental semivariograms and the second the application of the resultant parameters to interpolate the spatial distribution of the data. Since the estimation variances can also be quantified, the technique can be used to estimate values with a known level of confidence.

Semivariograms for the inventory data were best approximated by a spherical bounded model and were fitted using a least squares regression procedure (Fig. 3). The larger degree of spatial dependence is exhibited by the ^{134}Cs data set, where a range of 2.4 km was estimated. This suggests that the ^{134}Cs inventories can be interpolated within this range. The range of the ^{137}Cs data is, by contrast, much shorter at 0.8 km, indicating that the local variability of ^{137}Cs data is greater. This might be considered unexpected in view of the general assumption that the baseline bomb-test fallout across an area is relatively even. The higher degree of spatial dependency in the ^{137}Cs data appears to be due to the variability of Chernobyl-derived ^{137}Cs deposition superimposed upon a distribution of ^{137}Cs inventories which may have already exhibited some local variability, and because the samples were only collected to a depth of 10 cm.

Parameters derived from the semivariograms have been used to produce kriged interpolation maps of the distribution of radiocaesium fallout across the catchment and of the standard errors of the interpolation (Fig. 4). The map of ^{134}Cs inventory clearly depicts a ribbon of high fallout levels running across the catchment from the central southern watershed to the northwestern corner of the catchment. This linear feature is consistent with the strongly orientated pattern of Chernobyl fallout across the Severn catchment (Fig. 1a) and the expected distribution of fallout across the U.K. predicted from rainfall data by Smith and Clark (1989).

These fallout maps can be used in conjunction with the maps of standard errors to estimate the baseline ^{134}Cs and total ^{137}Cs inventories with known confidence intervals for any location within the catchment, although it should be noted that the kriging analysis does not take the analytical precision of individual input samples into account. This permits meaningful comparison between the estimated baseline and actual radiocaesium inventory for any point to determine whether there has been significant radiocaesium depletion or accumulation.

The radiocaesium inventories of samples along slope transects in two separate valleys were also measured to examine whether aspect influenced the deposition of Chernobyl fallout. Analysis of variance for the north-, south-, and east-facing slopes of Cwm

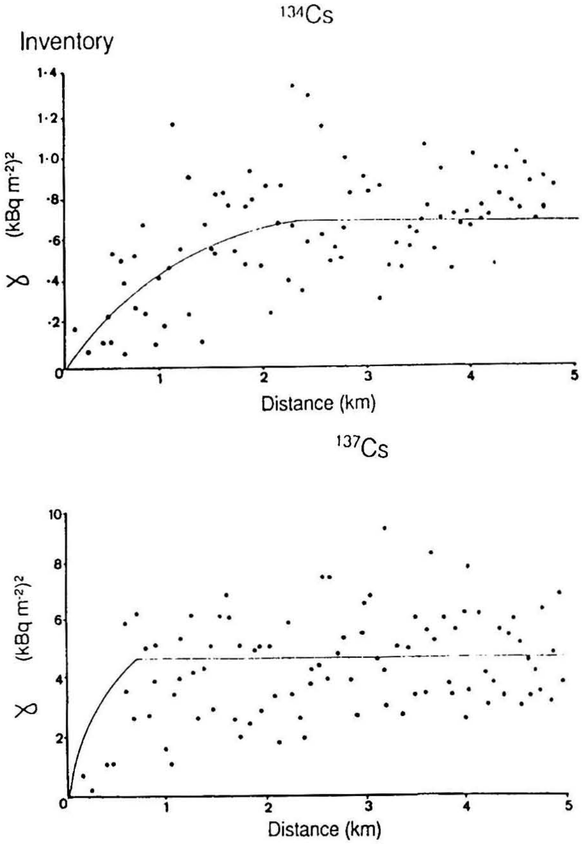

Fig. 3. Semivariograms for radiocaesium inventory data.

yr Hafod produced no significant variation in mean fallout (α=0.05). Similarly, there is no significant variation between the north- and south-facing slopes of the Afon Nadroedd valley.

RADIOCAESIUM REDISTRIBUTION ON CATCHMENT SLOPES

A number of samples were collected from hillslopes thought to be subject to soil redistribution. These included additional slope transects in areas of forestry disturbance and burnt moorland, whose locations are shown in Fig. 5.

Although the transects described in the previous section provided no evidence of aspect-induced variations in mean fallout, the values of individual points along these transects displayed some variation, which may indicate redistribution of radiocaesium associated with soil erosion. In Fig. 6, the ^{134}Cs and ^{137}Cs inventories of samples collected along each of the Cwm yr Hafod transects have been plotted against relative relief and compared with the 95% confidence interval for baseline fallout at the transect location, determined from the interpolated maps. Individual points plotting outside the range can be considered to have significantly different radiocaesium inventories from the estimated baseline fallout, with those plotting below the range considered as locations subject to erosion and those above as depositional sites. A number of samples did plot outside the reference envelope, but no general pattern of depletion was found. However, elevated levels of radiocaesium are observed at the base of three of the five transects and these may reflect accumulation of top soil transported from upslope areas or some limited degree

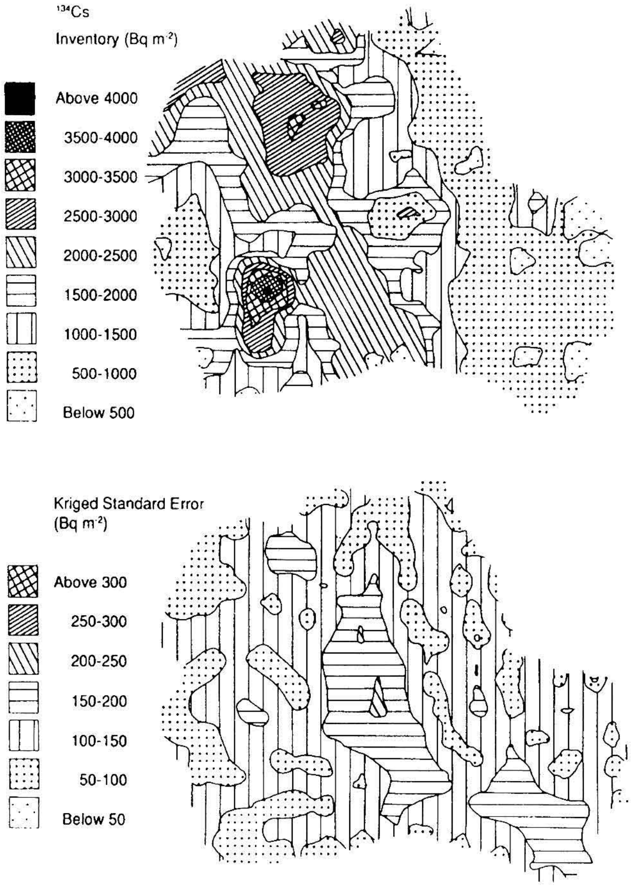

Fig. 4. Interpolated maps of the distribution of radiocaesium inventories.

of downslope transfer of the radiocaesium input in runoff prior to adsorption. Samples were also collected from additional transects on slopes that had been subject to recent disturbance. Three samples were taken from a south-facing slope in the Dolau Gwynion subcatchment where *Calluna* vegetation had been burnt in the summer of 1986. The estimated baseline ^{137}Cs inventory was 4000 ± 600 Bq m^{-2} (95% C.I.) and the midslope sample from this transect contained more than 6000 Bq m^{-2}, suggesting that some soil eroded from upslope was redeposited at this location. Samples collected from parallel transects showed no significant difference in mean ^{137}Cs inventories between mature coniferous plantation (5999 Bq m^{-2}) and a recently clear-cut site (5231 Bq m^{-2}). Samples from a plantation site in the Nadroedd subcatchment, which was clear-cut before the Chernobyl accident, provided clear evidence of the redistribution of radiocaesium. The estimated baseline inventories for this site were 8500 ± 1400 Bq m^{-2} for ^{137}Cs and 2700 ± 300 Bq m^{-2} for ^{134}Cs. A sample from the upper slope contained less than 5000 Bq m^{-2} ^{137}Cs and less than 700 Bq m^{-2} ^{134}Cs, whereas a footslope site adjacent to a drainage ditch, which had visible signs of recent sediment accretion, contained more than 23 000 Bq m^{-2} ^{137}Cs and more than 6000 Bq m^{-2} ^{134}Cs. These results highlight the environmental mobility of Chernobyl fallout and the need to pay attention to the prospect of longer term redistribution at all scales.

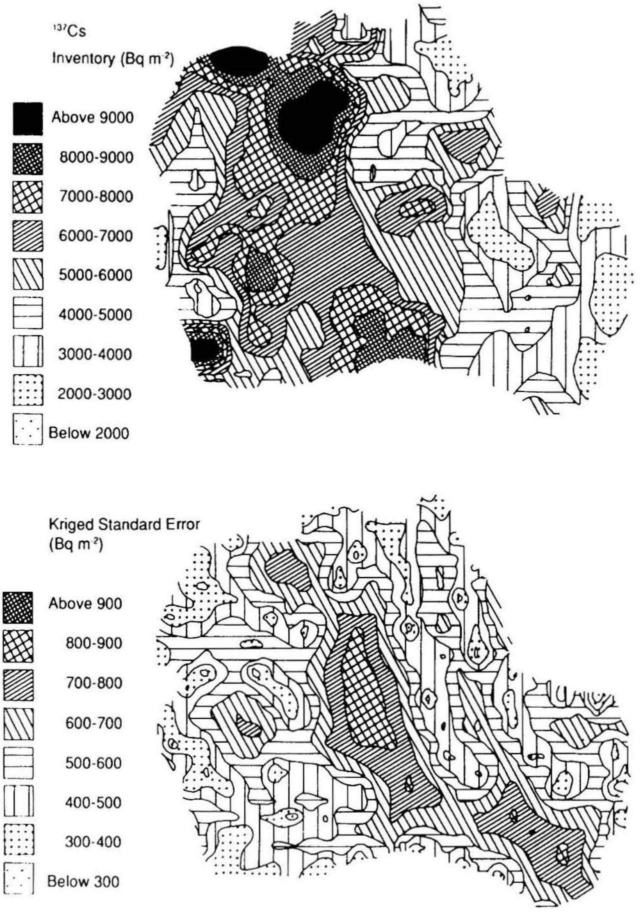

Fig. 4. Continued.

FLUVIAL REDISTRIBUTION AND ACCUMULATION OF CHERNOBYL RADIOCAESIUM

Sediment samples were also collected from a variety of fluvial environments and the activity concentrations of these samples are presented in Table 2. A considerable degree of variation is apparent, some of which relates to the pattern of Chernobyl fallout across the catchment. However, the link between the activity concentration of Chernobyl-derived radiocaesium in catchment soils and in sediments stored within channels or transported in suspension is further complicated by the extent to which particle size sorting has enriched or diluted the activity concentration of the fluvial sediments. If the degree of enrichment can be estimated, measurements of radiocaesium concentrations of undisturbed surface soil and channel bank samples can be used to "fingerprint" the source of suspended sediment (Peart and Walling 1986). The high radiocaesium concentration of sediment trapped behind an organic dam in the Nadroedd plantation suggests that its major source may be eroded topsoil rather than bank material, but further data would clearly be needed to identify source areas with any confidence.

The highest radiocaesium concentrations were found in deltaic sediments, both at the head of Lake Vyrnwy and in the delta of a small retention pond in the Dolau Gwynion subcatchment. Deltas represent major sinks for the accumulation of transported sediment and associated contaminants and the significant

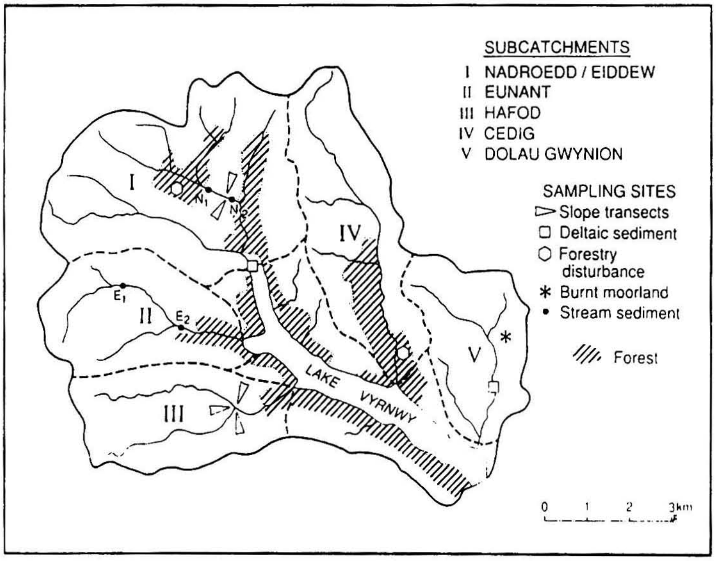

Fig. 5. Location of the Vyrnwy sampling sites.

		^{137}Cs (Bq kg^{-1})	^{134}Cs (Bq kg^{-1})
INPUT SITES			
Mean		389	114
Minimum		108	18
Maximum		1203	603
NADROEDD SUBCATCHMENT			
Clear cut plantation site			
Bank material		20	4
Undisturbed soil		251	61
Sediment trapped by organic dam		300	98
Stream sediments	N1	361	94
	N2	539	147
EUNANT SUBCATCHMENT			
Stream sediment	E1	1048	232
	E2	497	148
Roadside bank		274	96
Storm suspended sediment		350	192
DELTAIC SEDIMENTS			
Main lake (max)		1403	563
Dolau Gwynion lake		1061	231

Table 2. Activity concentrations of Vyrnwy soil an sediment samples from selected sites.

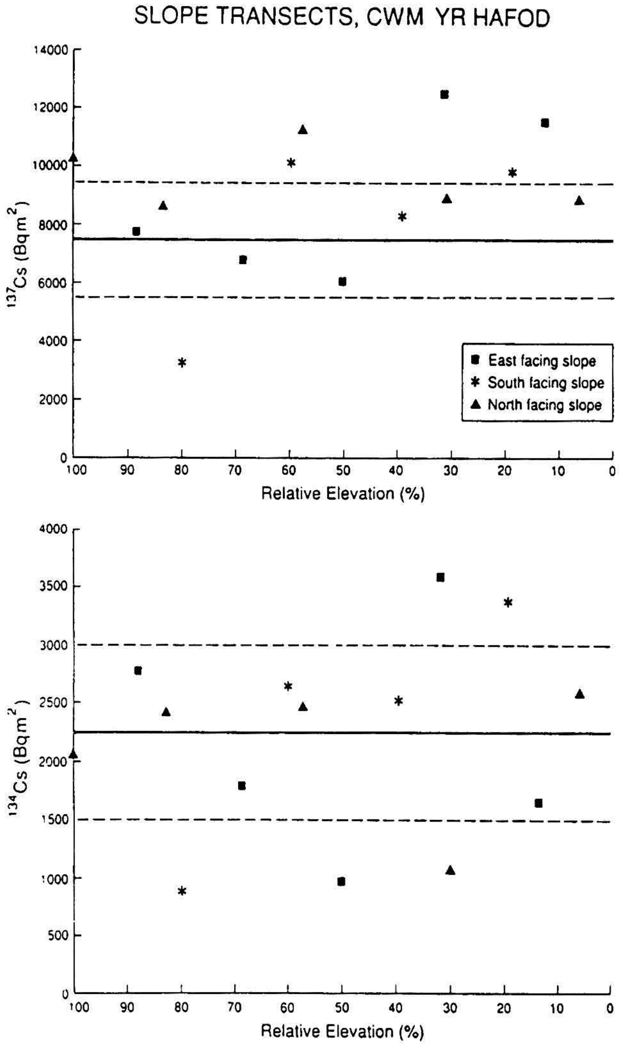

Fig. 6. Distribution of radiocaesium inventories on selected slope transects.

accumulations of Chernobyl-derived radiocaesium in the Vyrnwy deltas provide indirect evidence of substantial sediment transport since 1986. The ^{134}Cs inventory for the Dolau Gwynion delta, for example, is ten times more than the baseline fallout to that part of the catchment. In the main delta of Lake Vynrwy, samples from low lying locations adjacent to the channel have accumulated up to three times the estimated baseline ^{134}Cs inventory. The incorporation of Chernobyl radiocaesium into deltaic and reservoir sediment sequences is reported in greater detail elsewhere (Rowan et al. 1993).

Since the half-life of ^{134}Cs is only 2.2 y, at most sites the accumulation of ^{134}Cs from Chernobyl fallout by sediment-associated transport is counterbalanced by its radioactive decay. However, by virtue of its longer half-life (30.1 y) the fluvial transport of Chernobyl-derived ^{137}Cs may produce enhanced accumulation of radioactivity in sediment sinks and represents a longer term problem.

DISCUSSION

The measurements undertaken across the Lake Vyrnwy catchment reveal that radiocaesium inventories are highly variable and spatially complex, although the evidence suggests that the bulk of Chernobyl-derived fallout has been retained close to the soil surface. In terms of the study aims, the results suggest that the post-input behaviour of radiocaesium in this environment does not inhibit its application as a sediment tracer, but that the spatial variability of Chernobyl fallout imposes severe constraints on application of ^{137}Cs tracing techniques. Nevertheless, geostatistical interpretation of the data demonstrated that regionalised estimates of baseline fallout with smaller confidence intervals can be produced, which provide a statistical basis for identifying sample locations with radiocaesium inventories significantly higher or lower than the baseline.

These limitations of the technique for using radiocaesium measurements to provide erosion estimates suggest that in upland areas affected by Chernobyl fallout, it is unlikely that radiocaesium inventories at specific sites can be used to estimate erosion rates using the methods developed for arable land. However, the large radiocaesium inventories in the sediments of the delta allude to considerable sediment transfer within the catchment. High levels of radiocaesium redistribution in the Dolau Gwynion catchment where preparations for forestry operations had been undertaken and in the Nadroedd clear-cut site suggest that forestry operations have contributed substantially to this flux.

The interpolation maps developed in this study indicate the parts of the catchment which appear to have the received the highest radiocaesium input and permit the total loading of the catchment or subcatchments to be estimated. Since the redistribution of radiocaesium is associated with the erosion, transport and deposition of sediment it follows that landuse changes in upland areas affected by Chernobyl fallout which result in increased erosion may liberate large quantities of radionuclides into the fluvial system.

Acknowledgment — This work was undertaken during the tenure of two Natural Environment Research Council postgraduate studentships in the Department of Geography, University of Exeter. We thank Severn Trent Water Authority for permitting access to the catchment.

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Environment International, Vol. 19, pp. 167-178, 1993
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0160-4120/93 $6.00 +.00

ARSENIC—A CLASSIC EXAMPLE OF CHEMOPHOBIA

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EI 9202-107 M (Received 10 February 1992; accepted 5 September 1992)

This review examines the evidence which has served as the basis for the classification of arsenic as a carcinogen. The difficulties encountered in examining multivariant systems and choosing a single variant (in this case arsenic) as the causative agent are discussed. The inability to induce tumors in animal systems by the administration of arsenicals and the nonoccurrence of excess cancer deaths in a number of locations in the united states where arsenic-rich drinking waters are consumed are noted. Finally, the question is raised whether epidemiological data, alone, with no demonstration of experimental carcinogenesis, should serve as the basis for the classification of a substance as a carcinogen.

INTRODUCTION

The purpose of this review is to examine experimental evidence which shows that arsenic compounds are relatively innocuous. The major categories examined are arsenic in drinking water, the carcinogenicity of arsenic compounds, and the role of subjective judgments in the classification of certain chemical compounds as hazardous substances.

The mere mention of the word arsenic evokes the response, poison. An evil reputation has shadowed this element for hundreds of years. In plays, novels, movies, and television dramas, homicide by way of arsenic has been, and continues to be, a favorite theme. The strong psychodynamic role which the word arsenic plays is starkly illustrated by its use in the play by Kesselring, "Arsenic and Old Lace". The mystique surrounding this word succeeded in attracting a large audience to the play and subsequent film. However, the Brewster sisters were much more judicious in their selection of poisons. Instead of arsenicals, which are relatively weak poisons, they dispatched their elderly gentlemen guests with cyanide and strychnine, two poisons which dwarf arsenicals in their efficacy. That arsenophobia still plays a powerful role is demonstrated by the recent exhumation of the remains of our former president, Zachary Taylor. The symptoms which accompanied his death received wide national exposure and publicity with the claim that Zachary had been a victim of arsenic poisoning. Following exhumation and laboratory analysis, no evidence of arsenic poisoning was found.

At the present time, inorganic arsenic (primarily As_2O_3, but also As_2O_5 and $AsCl_3$) is referred to as a cancer hazard (OSHA 1990). Also, in drinking waters, the United States Environmental Protection Agency (EPA) has established an upper limit of 0.05 mg/L (Southwick et al. 1982; USEPA 1991). To conclude that inorganic arsenic represents a cancer hazard, evidence supporting this point of view has been cited by those panels or individuals authorized to make such decisions. Obviously, the same reasoning applies to the upper limits decided upon for arsenic concentration in public drinking water, viz., that evidence exists which suggests that higher levels can be harmful. This review will deal almost exclusively with the presentation of scientific studies. It should be noted that the decisions taken with respect to arsenic have resulted in the complete shutdown in the production of basic industrial arsenic (As_2O_3) in the United States. All arsenic trioxide, the basic material for the subsequent synthesis of industrial arsenicals, is now imported into the United States.

The literature dealing with the subject is voluminous. Before proceeding to the subjects, a brief discussion of the chemistry, occurrence, and uses of this element will be given.

OCCURRENCE AND CHEMISTRY

Cullen and Reimer (1989) refer to a number of sources which cover the chemistry of this element in detail.

Arsenic is an element widely distributed in nature. It occurs with minerals in rivers, lakes, and oceans. It is found in all living organisms—botanical, marine, animal. Of particular importance is its occurrence with nonferrous metal sulfides, especially copper. During the roasting of sulfidic ores which contain arsenic, the element is converted to the trioxide, As_2O_3. This white crystalline solid melts at 315°. Its relatively low melting point means that it has an appreciable vapor pressure at temperatures involved in smelting operations. Consequently, the vapors condense on the surfaces of the cool flue ducts. It is from the surfaces of such ducts that arsenic trioxide is scraped and made available for commercial use. The oxide can be resublimed to a high level of purity. Arsenic trioxide represents the single most important raw material for the commercial use of this element, and it is the principal reagent for the synthesis of other arsenicals. The exposure of workers in the nonferrous smelting industries to arsenic (and to all of the other substances involved in the industry) has furnished the greatest incentives for the introduction of stringent limits on exposure to inorganic arsenic.

Pyrites frequently contain arsenic in solid solutions at concentrations generally in the range of 0.2 to 5 g/kg. However, concentrations as high as 50 g/kg have been reported. Arsenic concentrations in igneous and sedimentary rocks are in the range of 0.1-3000 mg/kg. The high values, 2-3 g/kg occur with some sedimentary iron ores and a few coals. Arsenic is found in all lakes and rivers. The range is wide, often less than 1 $\mu g/L$ (ppb), but concentrations as high as 200 mg/kg (Searles Lake, CA), 0.5-1.6 mg/kg (Cordoba, Argentina) have been measured. Mammalian tissues contain arsenic in the range of 0.3 mg/kg. Freshwater fish generally exhibit concentrations less than 1 mg/kg. Marine fish have the ability to concentrate arsenic in their tissues and some extraordinarily high volumes have been reported. In the case of shrimp, levels in the range of 3.8-128 mg/kg on a dry-weight basis have been reported (Coulson et al. 1935). In the case of canned seafoods, unusually high concentrations have been measured (Dick and Pugsley 1950): clams, 15.9 mg/kg; oysters, 16.0 mg/kg; smoked oysters, 45.8 mg/kg; lobsters, 22.1 mg/kg; and shrimp, 19.9 mg/kg. If EPA drinking water limits were applied to seafood on a weight-by-weight basis, all seafood would be deemed unfit for human consumption. The arsenic in marine organisms has been shown, in most cases, to be present primarily as arsenobetaine, $^{-}O(O)C\text{-}CH_2As^{+}(CH_3)_3$. When administered to mice orally (Vahter et al. 1983) at a dose of 400 mg As kg^{-1} body weight, no toxic effects were noted.

The element is the third member of the nitrogen group and is a typical metalloid. Being a member of group Va (group 13), it has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$. Factors which characterize its chemistry are the predominance of the +3 and +5 oxidation states and the ability of its trivalent compounds to act as sigma election donors (Lewis base) via the $4s^2$ election pair and concurrently as π electron acceptors utilizing their empty 4d orbitals. The latter is currently an area of great interest in the field of transition metal chemistry.

Arsenic trioxide, As_2O_3, readily dissolves in alkali to form solutions of arsenite, AsO_2-. These solutions undergo reaction with the lower alkyl halides to form alkylarsenic bonds. This is a basic reaction for the synthesis of carbon-arsenic bonds and is know as the Meyer reaction. Alkylarsonates, $RAs(O_2)^{-}$, the products of the Meyer reaction undergo reduction in SO_2/HCl to the alkylarsinedihalides, $RAsCl_2$. These dihalides can be redissolved in alkali and with a low molecular weight alkyl halide, add a second alkyl group. Hydrolysis and mild oxidation give arsenic acids, $R_2As(O)OH$, the most important of which is dimethyl-arsinic acid $(CH_3)_2As(O)OH$, commercially known as cacodylic acid. The organic chemistry of arsenic is extensive (Doak and Freedman 1970).

One remarkable and unexplained aspect of arsenic chemistry is the hydrolytic stability of arsenic halides. All of the other elements of group Va form halides which hydrolyze rapidly. Thus, arsenic halides can be prepared out of aqueous solutions. The slow rate of hydrolysis of the arsenic-chlorine bond undoubtedly accounts for the damaging effects of Lewisite, $ClCH=CHAsCl_2$, 2-chlorovinyldichloroarsine. All arsenic halides rapidly penetrate the skin and the mucous membranes. This is followed by slow hydrolysis with the release of hydrochloric acid. The result is the formation of deep burns and slow-healing, painful blisters. Arsenic halides should be handled with care and penetration through the skin and inhalation should be meticulously avoided.

Arsenic pentoxide, As_2O_5, the anhydride of *o*-arsenic acid, H_3AsO_4 cannot be prepared from the elements, but is formed when arsenic trioxide is dissolved in concentrated nitric acid and the solution is evaporated. The crystalline solid $H_3AsO_4 \cdot 1/2\ H_2O$ first separates, and on dehydration, yields white hygroscopic crystals of As_2O_5.

Arsine, AsH_3, is a toxic gas primarily because it is a powerful reducing agent. Methylarsine, CH_3AsH_2; dimethylarsine, $(CH_3)_2AsH$ and trimethylarsine, $(CH_3)_3As$ are important because methylated arsenic compounds are widely distributed in nature and are widely encountered metabolites of arsenic in organisms ranging from microbes to mammals.

This review is not intended to be comprehensive; the interested reader is referred to the review by Cullen and Reimer (1989).

PRODUCTION AND USES

As_2O_3 is produced as a byproduct of the smelting of ores, primarily those of copper, silver, gold, lead, and zinc. Total consumption in the United States has remained fairly constant, ranging from 18-30 Gg metric tons (20 000-30 000 tons) per year (as As_2O_3). At the present time, none of this compound is produced in the United States. Sweden has been the world's largest producer. Other major producers are the former Soviet Union, France, Southwest Africa, the Philippines, and Mexico. The resurgence of copper mining in Chile during recent years may have served to make that nation a major arsenic producer.

Most commercial applications, about 80%, has gone into agricultural chemicals. The single most widely used agricultural arsenical is arsenic acid, H_3AsO_4. The chemical is important in connection with the mechanical harvesting of cotton. It serves as a desiccant to reduce crop moisture which otherwise would seriously interfere with the mechanical cotton-harvesting machines. Furthermore, the desiccation with arsenic acid has been claimed to bring about earlier stalk destruction (by reducing both insect buildup and overwintering populations). This reduces disease losses and cuts down weed problems. The desiccation of the cotton plants enables the farmer to harvest the cotton crop at an earlier time then would otherwise be possible by waiting for an extended dry fall season. The earlier harvesting makes possible land preparation further in advance of the winter season. This increases soil retention of moisture which reduces later irrigation and pumping needs. These are especially important factors in Texas and Oklahoma where extended dry periods are frequently encountered. In these two states, about 2 000 000 acres (8 000 km^2) annually are treated with arsenic acid. Spraying with arsenic acid is also claimed to control the boll weevil by removing the food supply of this overwintering insect. This results in fewer weevils during the following crop season and a reduction in the subsequent use of insecticides.

Livestock are not allowed to graze areas treated with H_3AsO_4, and cotton gin mills are not allowed to use treated plants or gin trash for animal feed or forage. Soils which have accumulated arsenate can be treated with gypsum or lime. This converts the arsenic to relatively insoluble calcium arsenate so that there is essentially no runoff of arsenate (Richardson et al. 1978).

Cacodylic acid, $(H_3C)_2As(O)OH$, and the sodium salts of methanearsonic acid, $(H_3C)As(O)(OH)_2$, whose acronyms are DSMA (disodium methane arsonate) and MSMA (monsodium methanearsonate) are effective for the control of weeds and crabgrass. Solutions of these compounds are easily available in the gardening sections of most garden supply and hardware stores. They are relatively nontoxic materials; the LD_{50}'s in rats are 830 mg/kg (cacodylic acid); 1.8 g/kg (DSMA); and 1.8 g/kg (MSMA).

The use of metal arsenates, viz., lead arsenate, calcium arsenate, and magnesium arsenate, was once fairly widespread for the control of insects in orchards and vegetables. The use of these metal arsenates has virtually disappeared during recent years. They have been displaced by organic insecticides.

The glass industry is the second largest consumer of arsenic compounds. About 17% of the arsenic used in the United States goes into glass compositions. It is difficult to obtain details as to exactly where and how arsenic is used in the glass industry. Personal inquiries to a major glass manufacturer indicated that microscope slides contained 30-50 g/kg arsenic. The fact that a compound formulated as As_2Se (Oak Ridge National Laboratory 1976) is used in glass formulations suggests strongly that the role of this compound is to decrease the intensity of the green color due to the presence of iron in container glasses.

Hence, agricultural chemicals, primarily H_3AsO_4, $(CH_3)_2As(O)OH$ and $(CH_3)_2As(O)(OH)_2$ together with glass compositions which utilize As_2O_3, As_2Se, and As_2O_5, account for 95-97% of the total industrial consumption of arsenic in the United states. The remainder finds use in medicinal, veterinary, and electronic applications.

Arsenicals have been used in medicine for centuries. Particularly worthy of mention because of its widespread use for a whole spectrum of illnesses over a long period of time is Fowler's solution. This is a 1% aqueous solution of arsenic trioxide. It was widely prescribed for the treatment of a wide variety of ailments, including skin conditions such as psoriasis and eczema, as well as epilepsy and asthma. There seems to be little doubt that the continued application of arsenite to the skin does result in a statistically meaningful increase in keratoses and skin pigmentations. Although the medicinal use of Fowler's solution has been almost abandoned, especially in the United States, some use persists. When its use was popular, Fowler's solution was frequently taken internally. Often, some patients overdid their use of the medication. This resulted in a number of unpleasant side effects including vomiting, abdominal pains, diarrhea, erythema, and a number of additional and unpleasant symptoms. The use and abuse of Fowler's solution are discussed at greater length elsewhere (NRC 1977).

Chemotherapy had its origins with the research of the renowned chemist, Paul Ehrlich. The first widely recognized and highly renowned chemotherapeutic agent was Salvarsan, popularly known as the magic bullet and arsphenamine. This is a derivative of *o*-aminophenol with arsenic in the 4-position (*o*-to the hydroxyl group and *m*-to the amino group). It has been named chemically as 3,3'-diamino-4,4'-dihydroxyarsenobenzene. This terminology is questionable in that it implies an arsenic-arsenic double bond, which is incorrect. For many years, this compound and its analogues were the drugs of choice for the treatment of syphilis, other venereal diseases, and tropical parasitic diseases. When syphilis was treated with Salvarsan and related arsenicals, amounts of the order of 0.5 g and more were administered intravenously over extended periods of time with no apparent ill effect, and the treatment was considered to be effective (Peoples 1974). Penicillin and other antibiotics have replaced arsenicals in the treatment of venereal diseases.

A number of organoarsenic compounds still find important and useful applications. Caparsolate, *bis* (carboxymethylmercapto)(*o*-carbamoylphenyl)arsine, in the form of the sodium salt, has found important veterinary application in the treatment of filariasis (heartworm) and lungworm infections in dogs. Derivatives of phenylarsonic acid such as the 4-nitrophenyl and *p*-aminophenyl compounds are used as additives in livestock feeds and poultry feeds primarily as coccidiostatic agents. These compounds are rapidly excreted in the urine in both livestock and poultry. From 50-75% is excreted during the first 24 h, and the remaining 25% is excreted over a period of 8-10 d. Feeds containing these additives are withdrawn at least 5 d before slaughter. FDA tolerances for arsenic are set at 2.0 ppm (mg/kg) for uncooked swine and liver tissues and 0.5 ppm (mg/kg) for uncooked pork muscle, edible chicken, turkey, and eggs.

On a small scale, some arsenicals still find use in human and veterinary medicine. Most of the diseases tested are related to tropical parasites. Glycobiarsol, a bismuth salt of N-glycoloylarsanilate is used for the treatment of amebiasis, trichomoniasis, and moniliasis. Carbarsone, *p*-carbamoylaminophenylarsonic acid is used for the treatment of human intestinal amebiasis and blackhead disease in poultry. Melarsopropol therapy is utilized for the treatment of trypanosomiasis, filariasis, and encephalitis. Other arsenicals still in use in medicine include Tryparsamide, Neoarsphenamine, Melarsonyl, and lead arsenate.

In the wood preservation industry, several inorganic arsenates play a certain role. The compound called chromated copper arsenate, which appears to be a mixture of cupric and chromic arsenates, is an extremely effective treatment for the protection of wood products against rotting by microbial and fungal action. Another important fungicide which contains arsenic is 10,10'-bis(phenoxarsine) oxide. It is known commercially as Vinyzene and is incorporated into polyvinyl plastic compositions to inhibit the growth of fungi and microorganisms.

In the area of electronics, the binary compound, gallium arsenide (GaAs) is considered to be a critical player in the field of high-speed computing machines. Gallium arsenide films can be prepared by chemical vapor deposition (CVD) and by the thermal decomposition of compounds containing gallium and arsenic. Among the gaseous arsenic compounds that are involved in this industry are highly toxic arsines, both arsine, AsH_3 and organoarsines, such as ethyl arsine, $(C_2H_5)AsH_2$. These substances are not only toxic, but extremely flammable.

Finally, mention should be made of arsenic triselenide As_2Se_3. Arsenic triselenide is one compound which is molded into optical components such as lenses and prisms, where infrared transmission is required. Of more widespread use is arsenic triselenide in the receptors of electrostatic photocopying machines. It is not unusual for arsenic to be present up to levels of 150 mg/kg in the selenium receptor drums which form an essential part of many electrostatic photocopying machines. The arsenic undergoes reaction with the selenium and is present in the form of arsenic triselenide. In a recent report (Murphy 1991), it is claimed that the compound was found to be nontoxic in a variety of standard test procedures.

ARSENIC INGESTION AND PRACTICAL PHYSIOLOGICAL EFFECTS

Numerous studies are concerned with the internal intake of dissolved arsenic compounds and their physiological effects. It is these studies which have guided the decisions taken by those health assessment groups authorized to make decisions which directly affect the public, such as maximum allowable concentrations of various chemicals in drinking water. This discussion will only deal with exposure of the public at large.

Fowler's solution (about a 10 g/L aqueous solution of As_2O_3) finds only limited use at the present time; however, because of its widespread use for many years, physiological effects merit some discussion. Its application was primarily to the skin, but internal prescription was not unusual. One aspect concerning the actual preparation of Fowler's solution should be considered. The solubility of arsenic trioxide is given as 12 g/L of water. It dissolves slowly in water, but rapidly in alkali. If a significant number of solutions were prepared using sodium hydroxide solutions, such data are of critical importance in evaluating the effects of different variables. Solutions of relatively high or relatively low pH's could, simply because of their hydrogen ion concentrations, exhibit significant physiological effects. Note that the arsenic was in the +3 volume state, as arsenite, and that it was common to use Fowler's solution over extended periods of time. Conventionally accepted treatment for ailments such as epilepsy and asthma often involved the internal consumption of aqueous arsenite for periods of months or years. The same is true of external application for eczema, psoriasis, and recurring skin eruptions. As pointed out by Holland (1904), the dosage was determined by an initial dosage of five drops, diluted with water, after meals, three times a day. This amounts to more than 20 mg of arsenic. This dosage was increased by one drop daily until the disease was considered to be under control or until the eyelids swelled and diarrhea occurred. When the latter symptoms were noted, the dosage was lowered.

The consequences of arsenic administration for extended periods of time were found to be palmar and plantar keratoses. Keratoses are characterized by tissues which are hardened, often described as horny. Other characteristics of extended periods of arsenite exposure are the appearance of skin pigmentation and skin lesions. An extensive review of this subject has been published (Neubauer 1947). Neubauer who claimed to have identified 143 cases of arsenical cancer. However, Frost (1967) reported that several of these cancers were attributed to individuals who had never received any arsenicals.

Northernmost Chile is one of the worlds's driest areas. Some regions have no record of any recorded rainfall. The surface and landscape have been likened to that of the moon and waters in desert areas tend to have high concentrations of dissolved salts. Antofagasta, a city in northern Chile, was served by a water supply which contained appreciable concentrations of arsenic (0.8 mg/L). In 1971, Borgono and Greiber (1971) related an unusually high occurrence of ailments, viz., bronchopneumonia, bronchiectasis, abnormal skin color, and hyperkeratosis to the high levels of arsenic in the drinking water. A number of other reports from South America, mostly from Chile and Argentina (notably from the city of Cordoba), have related the occurrence of disease to high concentrations of arsenic in drinking water. These studies are described elsewhere (USEPA 1988). These studies vary with respect to the quality of the statistics reported. Among the criticisms made are small sample size, symptoms not specified according to dose, selection bias, and limited analysis of data. One criticism was the potential presence of other dissolved species. The presence of trace quantities of beryllium, boron, cesium, rubidium, and any other number of other trace metals or dissolved organic compounds cannot be excluded. Indeed, a statistical analysis based on a single variable when any other number of contributing variables existed is highly suspect.

In its special report on ingested inorganic arsenic (USEPA 1988), the risk assessment forum relied heavily on several studies conducted in Taiwan (Tseng et al. 1968; Tseng 1977). The Taiwan studies showed an apparent relationship between arsenic ingestion and the occurrence of skin cancer. The population which consumed this water also displayed an unusually high incidence of an illness which as been termed Blackfoot disease. The latter is described in the following way (Lu et al. in press), "This disease resembles so-called arteriosclerosis obliterans or thromboangiitis obliterans in the consequences of ulcer and gangrene caused by the clinical features of numbness and coldness sensation of distal extremities, chest pain, intermittent claudication, etc., and by the pathological evidence of peripheral vessels obliteration." Blackfoot disease is not considered to be a malignancy. The name stems from the darkening and discoloration of the feet that accompany the disease.

The Taiwanese studies were selected as the most suitable for the quantitative estimate of (arsenic) risk by the EPA risk assessment group because it was considered to represent the largest study and comparison populations. Also, these studies claimed to have identified a large number of skin cancer cases and reported response by 12 dose and age groups. EPA concluded that the MLE (maximum likelihood estimate) of cancer risk for a 70-kg person who consumes 2 L of water daily containing 1 μg/L of arsenic ranges from 3×10^{-5} (females) to 7×10^{-5} (males). Assuming an intake of 1 μg/kg·d of arsenic the MLE ranges from 1×10^{-3} to 2×10^{-3}. The authors of the EPA report considered the fact that the water contained bacteria and ergot alkaloids, but discounted these as causative carcinogens making the statement that "neither bacteria nor ergot alkaloids are known to be associated with skin cancer." The EPA risk assessment report appeared in July of 1988. The paper of Lu et al. did not appear until 1990.

The fact that artesian wellwater in Taiwan contains, in addition to what are considered too high levels of arsenic, a number of organic contaminants has been and continues to be a subject for investigation (Lu et al. 1977). The absolute identification of all of the organic compounds and their relative concentrations is not certain, but some have been identified as ergot alkaloids, organic acids, possibly lysergic acid, and compound(s) related to ergotamines.

The interesting aspect of the more recent paper (Lu et al. 1990) is fluorescence intensity, a measure of the concentration of organic compounds and arsenic concentration. They conclude that "arsenic in well water can combine with fluorescent compound to become a complex". They state further "both arsenic and fluorescent compound reveals direct relationship with the epidemical degrees of blackfoot disease".

A considerable number of studies have appeared which show that no unusual health effects are observed among populations which consume drinking waters that are considered to be unusually high with respect to dissolved arsenic. Well water in a residential area near Fairbanks, Alaska, was found to contain unusually high levels of arsenic, up to 10 mg/L. This is 200 times the recommended EPA standard. A group of 211 area residents completed questionnaires related to their water consumption histories. Physical examinations were conducted, and urine, hair, nail, and wellwater samples were analyzed for arsenic content (Harrington et al. 1978). What are considered to be above normal levels of arsenic were measured in the urine and hair of subjects who had been consuming arsenic-rich wellwater. They concluded that no clinically evident symptoms or signs of arsenicalism were seen in the most heavily exposed subjects. They speculated that in contrast to Chilean or Taiwanese, the Alaskan population is exceptionally well nourished and of high socioeconomic status. However, they indicated that other contaminants could account for the clinical abnormalities encountered in other populations.

Millard County, Utah, is another region of the United States where the public drinking water contains arsenic at concentrations of 0.18 mg/L to 0.21 mg/L. In this case, 145 residents who had regularly consumed this arsenic-rich water were compared with a control group in a nearby community where the drinking water contained arsenic concentration of 0.02 mg/L, within the prescribed EPA standard. Controls were selected by random number selection from within the age categories to match age and sex distribution of the exposed group. According to Southwick et al. (1982), no excess cancer was found in the exposed population. Morton et al. (1976) reported that no relationship between arsenic levels in drinking water and the incidence of skin cancer could be found in studies conducted between 1968 and 1974 in Lane County, Oregon, where the water supply is also classified as arsenic-rich. Also of interest is the observation that persons drinking wellwater with an average of 0.016 mg/L of arsenic had a lower incidence of cancer than an urban population consuming water the arsenic concentration of which is 0.005 mg/L (Berg and Burbank 1972).

An additional report of research undertaken in a similar manner (Goldsmith et al.1972) involves a California study in which the arsenic levels in the drinking water were 0.5 mg/L. In this study, no direct correlations could be found between accumulated arsenic levels in the body and prevalent illnesses in the community.

CARCINOGENICITY OF ARSENIC

To designate an element, rather than a chemical compound, as carcinogenic is intrinsically incorrect. A number of polyaromatic hydrocarbon such as benzypyrene are known to cause tumors, but we do not classify carbon as carcinogenic. β-naphthylamine, a nitrogen-containing compound is considered to be a carcinogen, but nitrogen is not carcinogenic. In the case of arsenic, the compound that has been indicted is arsenic trioxide. Arsenites have also been implicated, but the evidence is less convincing. The evidence for labelling arsenic as a carcinogen is exclusively epidemiologic and primarily based on statistical studies of workers engaged in the nonferrous smelting industries.

Studies are mentioned which correlate arsenic concentrations in drinking water to skin cancers. Because Fowler's solution was introduced in 1786 and used widely to treat millions of patients, observations relating to the occurrence of symptoms among this group should be statistically meaningful. Also, treatment with Fowler's solution often continued for many years. It has been reported (Wildenberg 1978; Vallee et al. 1960) that few epitheliomas were reported among this large group of people. A truly carcinogenic substance applied both externally and internally by so many people over so many years should have resulted in the occurrence of tens of thousands of cancers. Also, exposure to ultraviolet light from the sun is responsible for a fraction of skin cancers, and this variable has not been factored into these studies.

The use of arsenical pesticides has been reduced dramatically, arsenic sprays and dusts were widely used in german wine-growing districts from 1925 to 1942. These were probably copper acetoarsenite and calcium arsenate. However, at some time during this period, copper sulfate and nicotine were also added to the spray mixture. In addition, sulfur dusting was also used for the control of some pests. Also, fillers for these dusts included lime, talc, and gypsum. As expected, vineyard workers were quite heavily exposed to these arsenic compounds. The wine prepared from these grapes was reported to contain 0.2-8.9 mg/L. Moselle vineyard workers were reported to consume rather large quantities of wine, of several liter per day. The sources of the foregoing and subsequent information is cited in the reference section (Roth 1958, Roth 1957; Stellwag 1928; Denk et al. 1969; Frohn 1938).

In view of the exposure to pesticides together with the reported intake of wine having high arsenic concentrations, it would be expected that this group should display symptoms caused by the intake of these substances. Roth reported an unusually high number of cancers of the liver, lung, bile duct, and the esophagus. These were observed in 47 autopsies performed on this cohort. Note that actual cause of death was not necessarily a malignancy. Roth also persists in labelling cirrhosis, which was highly prevalent in the autopsied subjects as arsenical cirrhosis, yet, the unusually high wine consumption among this group has been pointed out. There seems to be no question that the health of these vineyard workers suffered from exposure to the chemicals they used. However, in addition to arsenic, these workers were exposed to sulfur, copper, lead, nicotine, lime, talc, gypsum, and aniline dyes (magenta, used to impart a purple color to calcium arsenate). They were also victimized by poor hygiene which gave them little opportunity to cleanse themselves after exposure, and they were generally known to be heavy smokers and heavy drinkers.

A statistically significant increase of 27% was claimed for respiratory cancer among orchardists in the state of Washington (Milham 1974). Epidemiologist Radford (1975) pointed out that other possibilities could yield the same results. In the subsequent open literature publication of his findings Milham (1975) concluded that Washington State orchardists exhibited an overall cancer mortality rate nearly equal to that of all other occupations.

NIOSH carried out a further cancer mortality study in the Wenatchee Valley where the orchards are located. The cancer mortality rates were compared with those for the states as a whole. They claimed a 7% excess cancer death rate for the three areas made up of Chelan, Douglas, and Okanogan counties. They further concluded that Chelan county accounted for all of the excess cancer mortality. Interestingly, a 28% deficit was reported for Okanogan county. An EPA study (Nelson et al. 1973) came to somewhat different conclusions. They considered the fact that two-thirds of the population resided in one county, Chelan, and concluded that there were no excess cancer deaths. Another report (Sauer 1976) corroborated the EPA conclusion. Sauer agreed that Chelan County did not have an unusually high incidence of cancer. He concluded that in those counties in which the apple orchards were located, the cancer incidence, for all types of tumors including lung cancer, for white males, age-adjusted, was lower than the rate either for the United States or the state of Washington.

It has been mentioned that inorganic arsenic has been classified as a cancer hazard (OSHA 1990). The primary evidence cited in support of this decision is that which relates to epidemiological studies involving cancer death rates among workers in the nonferrous metal smelting industry. Although the literature here is extensive, this discussion will be limited to those studies which have played the principal roles in the official decisions which have resulted in the classification of inorganic arsenic as a cancer hazard. The use of lead arsenate was terminated in 1948, but it found extensive use as an orchard spray from 1910 through 1946. In the apple growing district of Wenatchee alone, consumption of lead arsenate reached 7 342 000 pounds in 1937. In order to properly evaluate the occupational hazards encountered by this group, the exposure of these workers were should be examined. In the commercial preparation of lead arsenate, a slurry of lead oxide in water was first prepared. To this slurry was added arsenic acid, H_3AsO_4. The manner of arsenic acid synthesis was considered proprietary, but it is likely that it occurred by the reaction between arsenic trioxide and concentrated nitric acid. Another procedure which has been described in the literature involves the reaction between arsenic trioxide and chlorine to produce arsenic trichloride. Oxidation of arsenic trichloride with excess chlorine, in an aqueous medium, yields arsenic acid. Note that the oxidation of arsenic trioxide by nitric acid is accompanied by the release of copious amounts of oxides of nitrogen. Exposure to fillers, such as talc, asbestos (which was widely used to insulate steam pipes), and sulfur (frequently added as an additive for additional insect control) are likely additional possibilities.

One study has received considerable attention (Ott et al. 1974). These investigators studied the mortality of workers at a chemical plant operated by the Dow Chemical Company which manufactured lead arsenate, calcium arsenate, copper acetoarsenite and magnesium arsenate. The plant employed as few as 30 people in 1928 and up to 100 in 1948. Turnover in the plant was high. In fact, less than 25% of the labor force remained with a unit for more than a year. Essentially, the study was intended to determine whether there existed a statistical relationship between the cause of death and the exposure to arsenic.

The collected data were adjusted for age and year of death and differences in proportionate mortality between the group under study and the controls were compared. Respiratory cancer was responsible for 16.2% of the deaths in the exposed group compared with 5.7% in the controls. A significant increase in deaths from lymphatic and hematopoietic cancers was also claimed. These same data were further detailed (Blejer and Wagner 1976). This report establishes that of the 173 deaths in the study by Ott et al., 138 had occurred among workers with less than one year of exposure and 16 of these were due to respiratory cancer.

Similar studies were carried out using statistics based on the mortality of workers who had been employed in a pesticide plant operated by the Allied Chemical Co. (Baetjer et al. 1974; American Wood Preservers Institute 1979). The salient conclusions drawn from these studies are as follows: incidence of death among the retirees in the age-specific death rate analysis was 3.5 times that among the controls; exposure to some chemicals in the plant resulted in increased cancer risk; the excess mortality was concentrated in cancer-caused deaths; these were found primarily in three job categories: Operators in the arsenic trioxide plant, operators and packers in the insecticide plant and warehouse workers who were responsible for charging arsenic acid reaction kettles.

Attention will be turned to statistics related to workers in the nonferrous smelting industries. One of the most widely cited among these studies involves workers at the Anaconda Copper Smelter, in Montana, from 1938 to 1956 (Lee and Fraumeni 1969). The results reported by these investigators are as follows: heavy and medium exposures (to ambient arsenic) resulted in significant increases in SMR (standardized mortality ratios) for respiratory cancer; the SMR was highest among that group of workers which had been employed at the smelter for more than 15 y prior to 1938, but decreased to 263 among workers with 1-14 y of work at the smelter. Among that group having less than one year of exposure, the SMR was 286.

The study, although useful, suffered from the following weaknesses (USEPA 1984). The arithmetic means used by the authors should be viewed as rough estimates; smoking histories were not recorded; and a positive relationship also existed between exposure to sulfur dioxide and respiratory cancer.

The mortality of workers in a smelter in Magna, Utah (Rencher et al. 1977) has also been statistically evaluated. The proportionate mortality for smelter workers was compared with that for mine workers, construction workers, refinery workers, office workers and for the over-20-y population of Utah. Among the smelter workers, 7% of the deaths were attributed to respiratory cancer. This is to be compared with that of other factory employees which ranged from 0 to 2.2%, to that for the state as a whole, 2.7%. These studies mentioned the death rate from lung cancer was no higher among smelter workers who did not smoke than for mine and construction workers who did smoke. Of significance was the observation that exposure to sulfur dioxide, sulfates, lead, and copper was also higher among those whose deaths were attributed to lung cancer.

A sample of 1 800 workers at the Anaconda smelter (Welch et al. 1982) was also analyzed statistically. The group was made up of all that category designated by Lee and Fraumeni as having had heavy exposure, together with a random sampling (20%) of the remaining known workers. Smoking histories were obtained by direct questioning or through the use of questionnaires. Both the white male populations of Montana and the United States were used to establish SMR's.

The departments in which the group worked fell into one of four categories, low, medium, high, and very high arsenic exposure. Each worker was assigned to one of these four categories. Together with knowledge of the time spent in each department, a time weighted arsenic exposure level was calculated. Following statistical analysis of the date, the authors concluded that death from respiratory cancer was strongly related to arsenic exposure. Exposure to arsenic appeared to be the principal factor in the observed increased death rate for respiratory cancer.

A number of other epidemiological studies relating cancer incidence to (arsenic) exposure in smelters have been reported (Tokudome and Kuratsume 1976; Axelson et al. 1978). These studies tend to corroborate the observation that workers in the nonferrous smelting industries display an above-normal death rate from malignancies. Another study (Pershagen 1985) which has been widely cited in recent years will be discussed subsequently.

CARCINOGENICITY STUDIES IN ANIMALS

Despite concerted and repeated efforts to do so, experiments designed to induce tumors in laboratory animals are noteworthy for the negative results they have yielded. One review (Frost 1975) cites 40 separate animal experiments performed with arsenicals which attempted to show an arsenic-cancer relationship, but all failed to do so. In one report (USEPA 1986), it is noted that most attempts to induce tumors in laboratory animals following oral exposure to arsenic (nature of the arsenic compounds not stated) have been inconclusive or negative and that the reasons for this inability to observe a clear carcinogenic response in animals are not known. In the report issued by the subcommittee on arsenic of the National Academy of Sciences (NRC 1977), one can find the following statements: "In general, animal studies have not shown carcinogenicity for arsenic compounds, even when administered at near maximally tolerated dosage for long periods. The fact that there is no established method for producing cancer by treatment with any form of arsenic in an animal model system is an enigma."

One example of the extraordinary attempts made to induce tumors in animals with arsenicals will be described (Ishiniski et al. 1976). In this study, a finely divided copper ore containing 4.0% arsenic and flu dusts containing 11.0% arsenic (presumably in the form of arsenic trioxide) were tested for carcinogenicity and co-carcinogenicity with benzo(α)pyrene. The method of administration was by intratracheal instillation directly into the lung once a week for about four months. The animals were allowed to die spontaneously. The results indicated that to confirm carcinogenicity of arsenic to the lung could not be established. Furthermore, squamous cell carcinoma of the lung in Wistar-King rats could not be induced by intratracheal instillation of arsenical substances.

Also illustrative of the inability to induce cancers in animals through the administration of arsenicals is one involving dogs (Byron et al. 1967) and another, Long-Evans rats (Schroeder et al. 1968). The subject of the first experiment was a group of beagle dogs. The animals were fed arsenate or arsenite up to levels as high as 125 mg/kg. The animals were autopsied at death. No carcinogenic effect could be detected from the feeding of the two arsenicals.

In the experiments of Schroeder and co-workers, the diet fed to Long-Evans rats contained 0.46 mg As/kg wet-weight and sodium arsenite was fed in the drinking water at a level of 5 mg As/L. The diet was continued until the animals died of natural death. No specific disorders were noted in either the control or experimental groups, nor was there a carcinogenic or tumorigenic effect. There are several studies claiming a positive correlation between exposure to arsenic and a carcinogenic or tumorigenic effect.

For example, a 10% occurrence of hepatomas has been reported in trout fed a synthetic diet containing carbarsone at 4.8 g/kg of diet. Of 50 trout exposed to carbarsone, five developed hepatomas. A control group fed the same diet without carbarsone developed no hepatomas. This study was reviewed (Kraybill and Shimkin 1964) and the suggestion made that contamination of the diet by aflatoxin could have biased the experiment. It should also be noted that carbarsone is a ureidophenylarsonic which could easily be contaminated with or hydrolyzed to aniline or an aniline derivative.

In earlier experiments (Leitch and Kennaway 1922), it was claimed that in a group of 100 mice receiving 86 applications of alcoholic 1.2 g/L potassium arsenite twice daily to shaved skin, one developed a metastasizing squamous epithelioma. Repetition of this experiment (Leitch 1923) led to negative results.

A large increase in leukemia was reported in both mothers and offspring of Swiss mice by the subcutaneous injection of sodium arsenate solution (Osswald and Goerttler 1971). During pregnancy, each pregnant mouse received a daily injection, each containing arsenic, in the form of sodium arsenate, equivalent to 0.5 mg/kg. Some groups of offspring received an additional 20 subcutaneous injections at weekly intervals at the same concentration levels. These were the offspring of the arsenic-treated females. Leukemia was reported to occur in 11 of 24 mothers. Among the offspring, 6 of 37 females and 7 of 34 males developed leukemia. Among the offspring receiving the additional 20 injections, 17 of 41 males and 24 of 50 females were reported to develop leukemia. The exact reason for the occurrence of such a high level of leukemia is unknown.

DISCUSSION

It has already been mentioned that reports, which reflect a higher incidence of cancer, especially lung cancer among workers employed in the nonferrous smelting industries, are taken as the strongest evidence for the labelling of inorganic arsenic as a carcinogen. Several aspects of these studies merit further discussion.

Pinto et al. (1977) published a survey of workers in the copper smelting industry and noted that 70% of the adult males were smokers and somewhat over a third were classified as heavy smokers. This fraction is considerably higher that the national average. Furthermore, the arsenic-exposed group consisted of a high percentage of foreign-born workers compared with the control group. This, for example, would be especially true in copper smelters located in Texas or Arizona. Also the average age of smelter workers who died of lung cancer was about 72 y (Pinto et al. 1977). Hence, the increased death rates attribute to arsenic exposure could also be explained in terms of increased age at death, large proportion of foreign born, and high smoking rates.

Some studies claim that they are adjusted for smoking. The smoking data are usually obtained by interviews with or questionnaires completed by survivors of the deceased. However, it is difficult to give an accurate assessment as to how much the workers smoked.

Perera et al. (1991) refer to a recent statistical study (Pershagen 1985) to support the theory of arsenically induced cancer. Careful study of the paper cited shows that the investigator concedes the following: Other metals emitted to the air in large amounts include copper, lead, and zinc. The duration of the main occupation was at least 5 y for all such subjects. Although the control of these potential confounding factors was crude in some instances, it is unlikely that they explain the excess risk. It is not unlikely that the smelter emissions may have been of importance; the emissions to air from the smelter contain a number of carcinogenic agents. If lung cancer risk is related to smelter emissions, it is difficult to determine the responsible agent or agents; exposure to air pollutants may have been of importance for the increased lung cancer risk. Substantial air emissions from the smelter, e.g., of arsenic, may have played a role. No firm conclusions can be drawn especially in view of the inadequate exposure data.

It is obvious that a double standard is being applied to arsenic. If one examines a container of saccharin (as well as many other consumer products), the statement "...warning this substance has been found to cause cancer in laboratory animals" will be found. It seems to be most unusual, and it is certainly extremely difficult to explain why arsenicals should demonstrate carcinogenicity only in humans and not in any other experimental animal.

The proper assessment of a human toxicant consists of two steps. In the first step, the causation must be established. This step usually requires experimental animals. Humans are rarely exposed to one toxicant at sufficiently high levels to exclude effects of other toxicants. Exceptions are acute effects such as the effect of methylisocyanate as a consequence of the Bhopal Accident. In the second step, the dose response function is appropriately established by epidemiological evidence. This is particularly true for arsenic (Reeves 1975).

Population groups in several western communities in the United States have been exposed to high levels of arsenic in their drinking water with no ill effects. No arsenical has ever been shown to be tumorigenic in a large number of animal experiments. Epidemiological studies which claim to show an arsenic-cancer relationship are subject to extreme complexities and difficulties with respect to isolation of the etiologic agent. Thus, it seems that the evidence does not justify the conclusion that arsenic should be labelled as a cancer hazard. It does appear that bias and subjectivity played a role in the decision of the jury. This bias also resulted in the expenditure of large amounts of time and money in dealing with an environmental problem which is, relatively speaking, minor. Problems of great magnitude which affect a large segment of the population should be given priority. Exposure to arsenicals does not fall into this category. The following citation supports the contention that the decisions of scientific panels can, and are influenced by prejudicial and preconceived judgements, "...the arsenic problem is not viewed by investigators with a critical enough eye. The idea that arsenic is a carcinogen remains uppermost. Hence, the prevailing attitude seems to be that all data must tend to prove it. This myth has now plagued scientific research on arsenic for 150 years" (White 1978).

Acknowledgment —The financial support made available by the Robert A. Welch Foundation of Houston, TX, during the preparation of this manuscript is acknowledged.

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Environment International, Vol. 19, pp. 179-191, 1993
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0160-4120/93 $6.00 +.00

THE EFFECT OF FARMING PRACTICES ON REDUCING EXCESS NITROGEN FERTILIZER USE

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EI 9112-192 M (Received 28 December 1991; accepted 26 December 1992)

This paper studies the effects of crop rotation and a limitation on the application of nitrogen fertilizer on the reduction of excess nitrogen available for potential leaching into the ground water. For a farmer initially planting corn continuously, the adoption of a soybean-corn rotation will have a smaller compliance cost, but it will not eliminate the excess application of nitrogen fertilizer under a relatively low nitrogen fertilizer to corn price ratio. An explicit limitation on nitrogen fertilizer use would be needed to achieve this objective. Limiting nitrogen fertilizer use on cropland susceptible to a high potential for leaching will have a smaller compliance cost than on cropland with a moderate potential for leaching.

INTRODUCTION

Nitrogen is an essential plant nutrient required to produce food and fiber. While the increased use of nitrogen fertilizer has contributed to increased food and fiber production in the United States in recent years, it has also been identified as a major contributor to the elevated concentration levels of nitrates in ground water in some regions of the country (Office of Technology Assessment 1984; Nielsen and Lee 1897; USEPA 1990). The U.S. Environmental Protection Agency's (EPA's) recent Pesticide Survey (1990) further indicates that many community water systems and rural wells, where extensive application of nitrogen is found, contain nitrates over the Maximum Contaminant Level.

High concentration levels of nitrates in drinking water supplied from ground water have become a public concern because of their real and suspected risks to human health (Freshwater Foundation 1988). The presence of nitrates in drinking water can cause potentially fatal infant methemoglobinemia (blue baby syndrome). Nitrates are also linked to nitrosamine, a potent carcinogen affecting a wide range of organs in many animal species (Cantor 1988).

Targeting vulnerable areas to reduce nitrate leaching associated with nitrogen fertilizer use into the ground water is a plausible national environmental policy. The targeting approach recognizes the dif-

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*The views expressed are those of the authors and do not necessarily represent the policies of the U.S. Department of Agriculture or the views of other U.S. Department of Agriculture staff members.

ferences in the vulnerability of various types of soils to leaching and, correspondingly, prescribes different policies to minimize (or at least mitigate) nitrate leaching. Additionally, the targeting approach is an effective tool if the objective is to minimize the social cost of the program (Tietenberg 1978; Baumol and Oates 1988).

In order to reduce the nitrogen fertilizer use that is a threat to the groundwater under the targeted cropland, a variety of methods is available. One approach is to adopt a fertilizer-reducing farming practice, such as a crop rotation in which a legume crop (e.g., soybeans) is rotated with a nonlegume crop (e.g., corn). The legume crop is used to provide fixed-nitrogen as a substitute for fertilizer-nitrogen. Adoption of this sort of crop rotation can reduce the residual (excessive) nitrogen (this will be discussed below) in the soil through a reduction in the frequency and amount of nitrogen fertilizer applications on a field and through the more efficient use of the nitrogen fertilizer applied because of more conducive soil conditions in which to grow a crop. The benefits and costs associated with this approach are the focus of this paper. It is possible that planting soybeans can increase nitrogen loss because of increased loss of topsoil from the soybean planting. However, research results indicate most cropland highly vulnerable to chemical leaching is not vulnerable to soil erosion (Huang et al. 1990). For those highly vulnerable cropland acres, the loss of nitrogen from soil erosion can be insignificant as compared with the leaching loss. Furthermore, one of the most beneficial aspects of a soybeans-corn rotation is its ability to reduce soil insect species such as corn rootworm, corn root aphids, wireworm species, and maize billbug (Fairchild 1980; Smith and Pimentel 1978). Reduction of insect population in the soil, resulting from a soybeans-corn rotation, can improve plant health and increase nitrogen uptake efficiency.

Adoption of a crop rotation and the limitation on nitrogen fertilizer use are two compliance options that can be used to reduce excess nitrogen. (A formal definition of excess nitrogen is provided below.) While the adoption of a crop rotation is an effective way to reduce nitrogen fertilizer (and, hence, nitrogen) use, explicitly limiting nitrogen fertilizer use might be required to reduce excess nitrogen (Huang and Lantin 1990). Much past research related to water quality protection from nitrate contamination has assumed arbitrary levels for reducing the nitrogen fertilizer application rate (Taylor and Swanson 1978). Little research has used a nitrogen balance relationship to determine the approximate level to which nitrogen fertilizer application should be reduced. One exception is Walker and Swanson (1986).

In what follows, the concept of excess nitrogen will be discussed. Alternative options designed to reduce the excess application rate of nitrogen fertilizer which leads to the presence of excess nitrogen available for potential leaching into the ground water will be delineated. A dynamic model for the evaluation of policy options is described. Finally, an Iowa case study is used to estimate the relative costs to a farmer of reducing the excess nitrogen fertilizer application rate under each alternative on cropland with a moderate and a high potential for leaching.

THE DEFINITION OF EXCESS NITROGEN

An accurate estimate of the excess nitrogen available for leaching is difficult to obtain (Blackmer 1987). For the purpose of this study, the amount of excess nitrogen, n_e, available for potential leaching associated with farming activities is defined as the difference between the amount of nitrogen applied from all sources on one acre of cropland and the amount of nitrogen present in both crop (grain) harvested and plant residues removed, n_p, at the end of the growing season. The amount of nitrogen applied includes that from nitrogen fertilizer, n_f, nitrogen credited from previous legume crops, n_s, and nitrogen from manure application, n_m. The excess nitrogen available for potential leaching over a continuous time interval, t, is thus computed as

$$n_e(t) = n_f(t) + n_s(t) + n_m(t) - n_p(t) \qquad (1)$$

Note that this definition is concerned with the excess nitrogen caused only by human farming activities at time, t. It assumes that, for a given acre, the nitrogen available for plant uptake from other sources is negligible. The nitrogen from other sources is the amount of nitrogen from atmospheric nitrogen absorbed by the soil and nitrogen from the organic matter in the soil after subtracting nitrogen losses attributable to other factors. These other factors include nitrogen losses due to denitrification, volatilization, water run-off, and soil erosion. For a productive cropland, the nitrogen from other sources can be significant. It is frequently referred to as inherent nitrogen. The inherent nitrogen of a specific field is the nitrogen in harvested crop based on long-term yields from the field without application of nitrogen fertilizer (Voss and Shrader 1988). Any of the assumptions above can be removed and a different estimate of the excess nitrogen can be calculated. For instance, for a particular cropland site encountering significant soil erosion, the nitrogen loss due to soil erosion can be estimated and subtracted from the right-hand side of Equation 1.

As defined, the concept of excess nitrogen has considerable practical appeal. Using the notion, a farmer can estimate the amount of nitrogen added and the amount of nitrogen removed from a field in order to calculate the residual nitrogen in the soil. A farmer using this relationship can apply the right amount of nitrogen fertilizer to minimize the excess application of nitrogen, if he or she is concerned with nitrogen contamination in groundwater. A farmer can also use it to approximate the amount of nitrogen available for potential leaching in areas where soil conditions favor water infiltration. In these areas, reducing the excess nitrogen that is available for potential leaching is tantamount to reducing excess nitrogen leaching into the ground water. In what follows, the n_e can be used as a yardstick to quantify the excess nitrogen from crop production.

OPTIONS TO REDUCE NITROGEN FERTILIZER USE

As noted above, rotating crops is one way a farmer can reduce his or her application of nitrogen fertilizer. This approach will be considered here. Several common crop rotations will be evaluated to provide information on the relative costs of adopting alternative farming practices designed to reduce the nitrogen fertilizer application rate. The cost to a farmer of the rotations will vary from one option to another. The farm-level performance of various crop rotations under four different options is considered. The alternatives are enumerated below.

No restriction

Under this option, cropland targeted for a reduction in the nitrogen fertilizer application rate is in the farm program (as detailed in Glaser 1986). Key components of the farm program include price and income support for program participants. Nonrecourse loans provide price support, while target prices and deficiency payments provide income support. Nonrecourse loans are loans to farmers enabling them to hold their crops for sale later in the marketing year. The loans are nonrecourse in that farmers can forfeit without penalty the loan collateral (the commodity) to the government as settlement of the loan. The target price is the legislatively mandated price of the crop. If the market price falls below the target price, an amount equal to the difference is paid to the farmer who participates in the program. This difference is referred to as the deficiency payment. Also, this difference cannot exceed the difference between the target price and the price-support loan levels. In order to take advantage of the program's provisions, the farmer agrees to remove 5% (for corn for the 1992/1993 crop year) of his or her base acreage from production. Note that for the 1992/1993 crop year, the target price for corn is $2.75 per bushel, the loan rate is $2.01 per bushel, and the deficiency payment is expected to be $0.48 per bushel (Economic Research Service 1992). Under the farm program, no restriction on the nitrogen fertilizer application rate is imposed on a crop rotation and no nitrogen credits are considered for growing legume crops prior to planting corn. This option is used as the reference for comparing the impacts of different crop rotation patterns when a restriction on nitrogen fertilizer use is imposed.

Continuous planting of corn with a restriction on the nitrogen fertilizer application rate

This option emulates the no fertilizer use restriction option except that the farmer is required to reduce the nitrogen fertilizer application rate. This requirement is implemented by assuming that no excess nitrogen is available for potential leaching (as defined by relationship 1). To compute the nitrogen fertilizer application rate to achieve zero excess nitrogen available for potential leaching for a specific crop requires knowledge of the crop production function. From this, the relationship between the nitrogen application rate and the amount of nitrogen in grains and plant residues can be established. Using Equation 1, a proper application rate can be computed. The purpose of enforcing a no excess nitrogen available for potential leaching constraint is to compute the compliance cost of the constraint which, in turn, could be used for an assessment of the comparable rental cost under the Conservation Reserve Program (CRP).

Soybean-corn rotation with a restriction on nitrogen fertilizer use

The conditions under this option are identical to the no fertilizer use restriction option except that the farmer will be required to reduce the nitrogen fertilizer application rate so that the excess nitrogen available for potential leaching (as defined by relationship 1) is equal to or less than zero. There will be a credit for nitrogen fixed by soybeans.

Meadow-corn rotation with a restriction on nitrogen fertilizer use

Under this option, all of the contingencies of the no fertilizer use restriction option apply. In addition, however, the farmer will be required to reduce the nitrogen fertilizer application rate so that the excess nitrogen available for potential leaching will be equal to or less than zero. There will be a credit for nitrogen fixed by meadow.

The dynamic optimization model

Different options can have different impacts on a farmer's decision with regard to the application rate of nitrogen fertilizer. In order to formalize the farmer's decision process, consider the following. For an initial level of nitrogen in the soil, n_0, a farmer is confronted with selecting an optimal crop rotation subject to several constraints and physical relationships. Assume that the farmer is confronted with a set of viable crop rotations, $\{r_q, q=1, 2, ..., Q\}$, and has as his or her objective the maximization of the discounted net per acre return, Z. This is accomplished by choosing the optimal crop rotation, r^*. The decision process is therefore defined by

$$Z(n_0, r^*) = \text{Maximize } [z(n_0, r_q), q=1, 2, ..., Q] \quad (2)$$

where

$$z(n_o, r_q) = \sum_t [(p_m^{i(r_q)}(t)\, y_c^{i(r_q)}(t) - w\, n_f^{i(r_q)}(t) - c^{i(r_q)}) + (p_t^{i(r_q)} - \max(p_m^{i(r_q)}, p_l^{i(r_q)}\, y_p^{i(r_q)}))]\, (1-b_i)\, (1+s)^{-t} \quad (3)$$

where $p_m i$, $p_t i$, and $p_l i$ are, respectively, the market price, target price and loan rate for crop i, at time t; $y_c i$ and $y_p i$ are, respectively, the per area yield of crop i harvested, and the program yield (a constant) at time t; w is the price of nitrogen fertilizer; n_f is the nitrogen fertilizer application rate for crop i, at time t; c^i is the per area production cost excluding the cost of nitrogen fertilizer at time t; b_i is the percent of base acreage set-aside; and s is the rate of discount. The $i(r_q)$ indicates that a specific crop is grown at each time period but that this might change depending on the sequence of the rotation being considered. Note that the analysis ignores any change in net income due to risk in production and market prices. Note that the discount rate is assumed to equal 4% throughout the analysis. See Dervis et al. (1982) for a discussion of the reasonableness of this value.

The decision process will be subject to a series of constraints and physical relationships (exclusive of any constraints imposed in order to limit nitrogen fertilizer use):

(a) The amount of nitrogen available for plant uptake, $n_a(t)$, is limited by the per area nitrogen fertilizer application rate, $n_f(t)$, and the residual nitrogenavailable from the previous periods for use at time t, $n_z(t)$:

$$n_a(t) = n_f(t) + n_z(t). \quad (4a)$$

(b) The residual nitrogen at time t, $n_z(t)$, is a function of the excess nitrogen available for potential leaching, $n_e(t\text{-}1)$, and the residual nitrogen carried over from the previous period, $n_z(t\text{-}1)$:

$$n_z(t) = f[n_e(t-1), n_z(t-1)] \quad (4b)$$

where $n_e(t\text{-}1)$ is defined in relationship (1).

(c) There is an initial amount of (residual) nitrogen in the soil:

$$n_z(0) = n_0. \quad (4c)$$

(d) Nitrogen uptake by crop i (for the plant and grain) at time t, $n^1{}_p(t)$, is a linear function of the crop yield:

$$n^i{}_p(t) = a^i\, y^{i(r_q)}(t) \quad (4d)$$

where a^i is a constant and the other terms are as previously defined. For the analysis in this paper, it is assumed that a=0.9 for corn grain. That is, there are 0.9 lbs (0.41 kg) of nitrogen contained in one bushel of corn (Fertilizer Institute 1976). Only corn grain is removed from the field.

(e) Crop yield at time t, $y^{i(r_q)}(t)$, is assumed to be a function of the nitrogen available for plant uptake at time t, $n_a(t)$:

$$y^{i(r_q)}(t) = g^{i(r_q)}[n_a(t)]. \quad (4e)$$

Finally, it is assumed that no manure is applied by the farmer. That is, throughout the subsequent analysis, it is assumed that $n_m = 0$.

In order to empirically implement the model, it is necessary to have explicit representations for two sets of functions—the residual nitrogen transformation functions,

$$n_z(t) = f[n_e(t-1), n_z(t-1)]$$

and the crop yield function,

$$y^{i(r_q)}(t) = g^{i(r_q)}[n_a(t)].$$

These will be discussed next.

FUNCTIONAL REPRESENTATIONS

Residual nitrogen transformation functions—the continuous planting of corn

The amount of available residual nitrogen in the soil, $n_z(t)$, at time t under the continuous planting of corn at time t is given as

$$n_z(t) = n_z(t-1) + n_f(t-1) - n_p(t-1) \qquad (5)$$

where $n_z(t-1)$ is the residual nitrogen available for crop use at time t-1. If the excess nitrogen available for potential leaching is greater than zero, it is assumed that k amount of it is leached. Note that $0 \leq k \leq 1$. The amount of nitrogen, $n_l(t)$, leached at time t is

$$n_l(t) = k\,[n_a(t) - n_p(t)]. \qquad (6)$$

Given this relationship, relationship (5) can be rewritten as

$$n_z(t+1) = (1-k)\,[n_a(t) - n_p(t)]. \qquad (7)$$

Note that should $n_a(t) = n_p(t)$, then no nitrogen will be leached. This, however, is only one of a large number of possibilities and it is subsumed in the analysis.

An exact determination of a value for k is difficult to make. The value can be approximated, however, using the procedure suggested by Schaffer et al. (1990)

Schaffer et al. suggest the use of the following relationship to determine an appropriate value for k:

$$k(t) = 1 - e^{-1.2\ wal(t)/por} \qquad (8)$$

where wal(t) is the water available for leaching at time t and por is the porosity of the soil in the root zone. The variable wal(t) is computed as

$$wal(t) = pe(t) - et(t) - [awhc - wr(t)] \qquad (9)$$

where pe(t) is the effective precipitation at time t, et(t) is the potential evapotranspiration at time t, awhc is the water holding capacity of the soil, and wr(t) is the water content of the soil at time, t.

In implementing equation (7), an average value for k(t) across time periods is assumed. In areas where the ground water is extremely vulnerable to nitrogen contamination due to leaching, the value of k will approach 1 while for areas where leaching is very unlikely, the value of k approaches 0. In this study, a value of k=1 will be used for areas considered to have a high potential for leaching while a value of k=0.5 will be used for areas where the leaching potential is only moderate.

Residual nitrogen transformation functions: the legume-corn rotation

The amount of residual nitrogen in the soil which is available for corn use at time t when a legume crop (either soybeans or meadow) is grown at time t-1 is given as

$$n_z(t) = n_s(t-1) \qquad (10)$$

where $n_s(t)$ is the net legume-fixed nitrogen that can be used for growing corn. When a legume crop is grown in rotation with corn, it is assumed that the legume crop fixes nitrogen for plant use ($n_p(t-1) = 0$), that no fertilizer is applied to the legume crop ($n_f(t-1) = 0$), and that the residual nitrogen from the previous corn crop is absorbed by the legume crop at the beginning of the growing season. These assumptions are consistent with those made by Schaffer et al. 1990. Also it is assumed that the amount of nitrogen fixed by the legume crop and then leached out of the root zone during the legume growing period is negligible.

Yield functions

Before discussing the yield functions, it is necessary to comment on the data used in the estimation since the data define the nature of these functions. The yield data (relating yield and nitrogen fertilizer use) were obtained from an Iowa State University research farm study at Kanawha, Iowa (Iowa State Experiment Station 1986). This study examined the effects of nitrogen fertilizer application rates and crop rotation patterns on crop yields. In the study, only the nitrogen fertilizer application rate and the sequence of crop rotations varied. All other factors were held constant. These data are used to estimate the yield functions for specific crop rotations. These estimated yield functions are an integral part of the analysis. The crop rotations considered are soybean-corn (BC) and meadow-corn (MC) in addition to the continuous planting of corn. These rotations are common in the Corn Belt region of the United States (Gill and Daberkow 1991). The fertilizer-nitrogen application rate for corn production varies among rotations. In each rotation, only corn production receives nitrogen fertilizer. Soybeans and meadow yield levels are kept constant, regardless of the amount of nitrogen fertilizer applied on corn in the preceding year in the rotation sequence. Experimental

Table 1. Estimated coefficients for yield response to nitrogen fertilizer application rates for different preceding crops[1].

Rotations	A(i,j)	B(i,j)	C(i,j)	R^2
Corn after Corn	65.64 (4.31)	0.730 (0.088)	-0.0017 (0.0004)	0.94
		Sample size - 16		
Corn after Soybeans	107.0 (5.1)	0.521 (0.105)	-0.0012 (0.0004)	0.94
		Sample Size - 8		
Corn after Meadow	149.9 (3.17)	0.165 (0.066)	-0.0004 (0.0003)	0.79
		Sample Size - 8		

[1] The yield function is specified as y(i,j) - A(i,j) + B(i,j)(n_a(i,j)) + C(i,j)((n_a(i,j))**2, where y(i,j) denotes the yield for crop i preceded by crop j, n_a(i,j) is the nitrogen fertilizer application rate for crop i when preceded by crop j, and A(i,j), B(i,j) and C(i,j) are coefficients to be estimated. In the field experiments, only corn received nitrogen fertilizer applications.

Note that the values in parentheses are standard errors of the estimates. R^2 is the coefficient of determination.

data substantiate the integrity of this assumption (Voss and Shrader 1988).

The estimated yield functions for the three different crop sequences are given in Table 1. The functions were estimated via ordinary least squares (Draper and Smith 1966). The intercept term of the yield function for the continuous planting of corn is used as the measure of the inherent productivity of the soil. The intercept is the annual corn yield that would be realized from the soil without the application of any nitrogen fertilizer and is an indication of the initial nitrogen level, n_0, in the soil. The difference between the intercepts of the yield functions when corn is continuously planted and when one of the legume-corn rotation sequences is planted is the yield response attributable to the legume-fixed nitrogen used subsequently by corn.

POLICY OPTION CONSTRAINTS

The options that are considered are those designed to limit the use of nitrogen fertilizer. The objective is to reduce the excess nitrogen available for potential leaching to zero on the targeted cropland with a high and a moderate potential for nitrogen leaching. This requires introducing two additional constraints into the problem formulation. The first additional constraint is for the continuous planting of corn. It requires that the residual nitrogen carried over from one period to the next, $n_z(t)$, plus the nitrogen fertilizer applied, n_f, must be less than or equal to the nitrogen removed from the field through plant uptake and removal of the harvested crop. That is,

$$n_z(t) + n_f\,(t)\;0.9\;y^{i(r_q)}(t). \qquad (11)$$

Recall from the above discussion that it is assumed that 0.9 lbs (0.41 kg) of nitrogen are contained in one bushel of corn.

The second additional constraint is for the legume-corn rotation. It requires that the nitrogen fixed by a legume crop, $n_s(t)$, plus the inherent nitrogen, $n_i(t)$, plus the nitrogen fertilizer applied, $n_f(t)$, must be less than or equal to the nitrogen removed from the field. That is,

$$n_s(t) + n_f\,(t)\;0.9\;y^{\,i(r_q)}\,(t). \tag{12}$$

Cost of production data are from Duffy and Chase (1988). The cost data represent average production costs for farms in Iowa (Iowa State University 1986). The commodity price data are from the Economic Research Service (19..). The December 1989 nitrogen fertilizer price of $0.15/lb ($0.33/kg) is assumed to prevail initially although a sensitivity analysis is conducted in order to examine the effects of variations in the price of nitrogen fertilizer on the results.

SIMULATION RESULTS

Each planting pattern under each of the policy options is examined for two types of cropland. Note that given the nature of the crop rotation decision variable, it is necessary to specify the rotations to be considered and then solve the optimization problem. A comparison of the various rotations will then suggest which one is optimal in the context of the problem under consideration. For cropland with a high potential for leaching, it is assumed that for each time period, t, any unused nitrogen will be lost and hence cannot be used for future (i.e., t+1, t+2, ...) crop production. For cropland with a moderate leaching potential, it is assumed that 50% (i.e., k=0.5) of the residual nitrogen is carried over from one period to the next. The model defined by equations (2) to (10) is used for the analysis of the no fertilizer restriction option. The initial level of nitrogen in the soil, n_0, is calculated by assuming the farmer is continuously planting corn before a policy option is implemented. The Generalized Algebraic Modeling System (GAMS) is used to solve the model (Kendrick and Meeraus 1985). GAMS is a mathematical programming package for solving linear, nonlinear, and mixed integer optimization problems. The convergence criterion was specified so that when the change in the value of the objective function was less than 0.01, an equilibrium was reached.

No fertilizer use restriction

Regardless of the leaching potential of the cropland, switching from the continuous planting of corn to one of the legume-corn rotations, while imposing no fertilizer use restriction, will reduce the excess nitrogen available for potential leaching and it will increase net farm income. It will not, however, eliminate the excess nitrogen (as defined by equation (1)) on cropland with either a high or moderate leaching potential. A relatively large amount of nitrogen fertilizer is required for the production of corn. Nitrogen fixed by a legume crop alone will not be sufficient to produce corn so that the maximum net farm income will be realized. For example, the meadow-corn rotation needs an additional 116 lbs (52.62 kg) of nitrogen fertilizer per acre to grow corn (optimally) in addition to the nitrogen fixed by the meadow. This result is contingent on the relatively low ratio of the price of nitrogen fertilizer to the price of corn ($0.15/$2.10=0.071). If the nitrogen applied in the form of fertilizer and that fixed by the legume crop are considered in concert, both the soybean-corn and meadow-corn rotations exhibit excess nitrogen available for potential leaching on cropland susceptible to high as well as moderate leaching.

Furthermore, switching from the continuous planting of corn to a soybean-corn rotation will cause a larger reduction in nitrogen fertilizer (and, hence, excess nitrogen) use and a large increase in net farm income on cropland with a high leaching potential relative to cropland with a moderate leaching potential. Thus, for example, the reduction in the nitrogen fertilizer use is 144 lbs (65.32 kg) on cropland with a high leaching potential compared to a reduction of 6 lbs (2.72 kg) on cropland with a moderate leaching. The increase in net farm income is $29 per acre ($ 71.63 per hectare) on cropland with a high leaching potential relative to $8 per acre (19.76 per hectare) for cropland with a moderate leaching potential over a six year rotation cycle. These results clearly indicate that a policy aimed at reducing excess nitrogen would be most effective if it is targeted at cropland with a high leaching potential.

Limiting fertilizer use

Next, consider the impact on a farmer when nitrogen fertilizer use is constrained as defined by relationships (11) and (12). While the price of corn is assumed to be $2.10 per bushel (as before), it is now assumed that the price of nitrogen fertilizer ranges between $0.05 and $0.45 per lb ($0.11 and $0.99 per kg) in $0.10 increments. (This assumption allows for a study of how sensitive the results are to the price

Table 2a. Nitrogen fertilizer application rate (kg per hectare in parentheses) when nitrogen fertilizer use is constrained in Iowa.

	Nitrogen Fertilizer Price				
Crop Rotation	$0.05	$0.15	$0.25	$0.35	$0.45
	Nitrogen Fertilizer Application Rate				
	-------- Pounds per acre per year --------				
Continuous Planting of Corn with No Fertilizer Use Restriction					
-On Cropland with a High Potential for Leaching	207 (232)	193 (216)	180 (202)	165 (184)	151 (169)
-On Cropland with a Moderate Potential for Leaching	170 (190)	166 (185)	162 (181)	157 (176)	146 (163)
Continuous Planting of Corn with a Restriction on Fertilizer Use					
-On Cropland with a High Potential for Leaching	114 (128)	114 (128)	114 (128)	114 (128)	114 (128)
-On Cropland with a Moderate Potential for Leaching	114 (128)	114 (128)	114 (128)	114 (128)	114 (128)
Soybean-Corn Rotation with a Restriction on Fertilizer Use					
-On Cropland with a High Potential for Leaching	93 (104)	93 (104)	93 (104)	93 (104)	93 (104)
-On Cropland with a Moderate Potential for Leaching	93 (104)	93 (104)	93 (104)	93 (104)	93 (104)
Meadow-Corn Rotation with a Restriction on Fertilizer Use					
-On Cropland with a High Potential for Leaching	67 (75)	67 (75)	57 (64)	0 (0)	0 (0)
-On Cropland with a Moderate Potential for Leaching	67 (75)	67 (75)	57 (64)	0 (0)	0 (0)

Table 2b. Net farm income per acre (per hectare in parentheses) when nitrogen fertilizer use is constrained in Iowa.

	Nitrogen Fertilizer Price				
Crop Rotation	$0.05	$0.15	$0.25	$0.35	$0.45
	Net Farm Income				
	-------- Dollars per acre over six years --------				
Continuous Planting of Corn with No Fertilizer Use Restriction					
-On Cropland with a High Potential for Leaching	855 (2112)	760 (1877)	672 (1660)	590 (1457)	515 (1272)
-On Cropland with a Moderate Potential for Leaching	864 (2134)	781 (1929)	689 (1702)	617 (1524)	540 (1334)
Continuous Planting of Corn with a Restriction on Fertilizer Use					
-On Cropland with a High Potential for Leaching	707 (1746)	653 (1613)	599 (1480)	545 (1346)	492 (1215)
-On Cropland with a Moderate Potential for Leaching	707 (1746)	653 (1613)	599 (1480)	545 (1346)	492 (1215)
Soybean-Corn Rotation with a Restriction on Fertilizer Use					
-On Cropland with a High Potential for Leaching	759 (1875)	738 (1823)	716 (1769)	694 (1714)	673 (1662)
-On Cropland with a Moderate Potential for Leaching	759 (1875)	738 (1823)	716 (1769)	694 (1714)	673 (1662)
Meadow-Corn Rotation with a Restriction on Fertilizer Use					
-On Cropland with a High Potential for Leaching	665 (1643)	650 (1606)	635 (1568)	628 (1551)	628 (1551)
-On Cropland with a Moderate Potential for Leaching	665 (1643)	650 (1606)	635 (1568)	628 (1551)	628 (1551)

of nitrogen fertilizer.) As before, each rotation is examined based on cropland with either a high or moderate leaching potential. The effects on fertilizer application rates and net farm income of limiting fertilizer use are shown in Table 2a and Table 2b, respectively. The results show no difference in the nitrogen fertilizer application rate and net farm income between the two types of cropland. This result is not surprising because imposing a constraint on fertilizer use forces excess nitrogen to equal zero at each time period. The bottom line is that in order to have zero excess nitrogen available for potential leaching, a significant reduction in the nitrogen fertilizer application rate is required for each of the planting options considered (i.e., the continuous planting of corn, a soybean-corn rotation, and a meadow-corn rotation). Although both soybeans and meadow fix nitrogen that is available for the subsequent production of corn, the nitrogen fertilizer application rate for both the soybean-corn and the meadow-corn rota-

Table 3a. Reduction in net farm income per acre (hectare in parentheses) when switching from continuous planting of corn without nitrogen fertilizer restriction to crop rotations with nitrogen fertilizer restriction in Iowa.

	Nitrogen Fertilizer Price				
Crop Rotation	$0.05	$0.15	$0.25	$0.35	$0.45
	Net Farm Income				
	--------- Dollars per acre --------				
-On Cropland with a High Leaching Potential					
Continuous Planting of Corn	25 (62)	18 (44)	12 (30)	8 (20)	4 (10)
Soybean-Corn Rotation	16 (40)	4 (10)	-7 (-17)	-17 (-42)	-26 (-64)
Meadow-Corn Rotation	32 (79)	18 (44)	6 (15)	-6 (-15)	-18 (-44)
-On Cropland with a Moderate Leaching Potential					
Continuous Planting of Corn	26 (64)	22 (54)	15 (37)	12 (30)	9 (22)
Soybean-Corn Rotation	18 (44)	8 (20)	-5 (-12)	-13 (-32)	-21 (-52)
Meadow-Corn Rotation	33 (82)	22 (54)	9 (22)	-2 (-5)	-13 (-32)

Note that it is assumed that the price of corn is $2.10/bu ($0.95/kg).

tions is constrained (i.e., constraint (12) is binding). This result is a consequence of the relatively low price of nitrogen fertilizer at \$0.15/lb (\$0.33/kg). When nitrogen fertilizer prices are greater than \$0.35/lb (\$0.77/kg), the fertilizer application rate on the meadow-corn rotation is reduced to zero. Utilizing the residual nitrogen in the soil, $n_z(t)$, will reduce the excess nitrogen available for potential leaching at the same time resulting in an increase in net farm income. This reduction (in excess nitrogen) and gain (in net farm income), however, are mitigated as the price of nitrogen fertilizer increases. Further, under the limiting fertilizer use option, the soybean-corn rotation will provide the highest net income when the nitrogen fertilizer price rises above \$0.35/lb (\$0.77/kg).

Table 3b. Reduction in average net farm income per pound (kg in parentheses) reduction in r excess nitrogen fertilizer use when switching from continuous planting of corn without nitrogen fertilizer restriction to crop rotations with nitrogen fertilizer restriction in Iowa.

	Nitrogen Fertilizer Price				
Crop Rotation	\$0.05	\$0.15	\$0.25	\$0.35	\$0.45
	-- Dollars per pound (kg) reduction in excess nitrogen --				
-On Cropland with a High Leaching Potential					
Continuous Planting of Corn	0.32 (0.70)	0.28 (0.62)	0.23 (0.51)	0.19 (0.42)	0.14 (0.31)
Soybean-Corn Rotation	0.21 (0.46)	0.06 (0.13)	-0.14 (-0.31)	-0.44 (-0.97)	-0.98 (-2.16)
Meadow-Corn Rotation	0.41 (0.90)	0.29 (0.64)	0.12 (0.26)	-0.16 (-0.35)	-0.67 (-1.47)
-On Cropland with a Moderate Leaching Potential					
Continuous Planting of Corn	0.65 (1.43)	0.60 (1.32)	0.45 (0.99)	0.43 (0.95)	0.35 (0.77)
Soybean-Corn Rotation	0.44 (0.97)	0.21 (0.96)	-0.14 (-0.31)	-0.46 (-1.01)	-0.81 (-1.78)
Meadow-Corn Rotation	0.83 (1.83)	0.61 (1.34)	0.27 (0.59)	-0.07 (-0.15)	-0.49 (-1.49)

Note that it is assumed that the price of corn is \$2.10/bu (\$0.95/kg).

Compliance cost

Finally, a farmer is inherently concerned with the effect on net farm income of adopting a different crop rotation. This effect can be computed simply as the difference in net farm income from the continuous planting of corn (assuming that this is the practice initially employed by the farmer) and the planting under a soybean-corn or meadow-corn rotation. The effect is nominally referred to as the compliance cost. The compliance costs for the three different cropping schemes were computed assuming that farmers were planting their crops, first, on land with a high potential for leaching and, second, on land with a moderate potential for leaching. The analysis focuses on crop rotations for corn production because corn uses large amounts of nitrogen fertilizer. Moreover, the continuous planting of corn (i.e., planting corn from one planting season to the next) is targeted for change because it is a common farming practice accounting currently for 26% of the total number of corn acres planted (Gill and Daberkow 1991). The continuous planting of corn uses nitrogen fertilizer inefficiently and is potentially the source of a large amount of nitrate leaching into the ground water. This occurs because of the large quantity of excess nitrogen, n_e, defined as the difference between the amount of nitrogen applied in the form of fertilizer and the amount of nitrogen removed from the field, based on field experiment data from Iowa (Voss and Shrader 1988). The results are presented in Table 3a. They show that when the nitrogen fertilizer price is relatively low, a fertilizer use restriction on cropland that is highly vulnerable to potential leaching will have a slightly smaller compliance cost relative to cropland with a moderate leaching potential. The compliance cost on both types of cropland decreases as the price of nitrogen fertilizer increases. The soybean-corn rotation with a restriction on fertilizer use has the lowest compliance cost. In fact, this compliance cost becomes negative (i.e., the net farm income under the soybean-corn rotation actually exceeds the net farm income from the continuous planting of corn) for a price of nitrogen fertilizer exceeding $0.25/lb ($0.55/kg).

Associated with each of the cropping patterns discussed will be a change in nitrogen fertilizer use. These changes will impact net farm income. The effect on net farm income of a change in nitrogen fertilizer use for each option is given in Table 3b. The reduction in net farm income associated with the change in nitrogen fertilizer use when the cropland is highly vulnerable to potential leaching relative to cropland with a moderate leaching potential is quite significant. For example, at a nitrogen fertilizer price of $0.15/lb ($0.33/kg), the fall in net farm income when excess nitrogen is reduced by 1 lb (or 1 kg) under the soybean-corn rotation in areas with a moderate potential for leaching is nearly twice (four times) as great as that found in areas with a high potential for leaching. Given that analogous results hold over most of the range in the price of nitrogen fertilizer considered, it can be concluded that reducing excess nitrogen in soils with a moderate leaching potential results in a greater decline in net farm income than would be realized if the soil possesses a high potential for leaching when the nitrogen fertilizer price is between $0.15 and $0.35/lb ($0.33 and $0.77/kg).

This result can be explained as follows. Under the no fertilizer use restriction scenario, corn grown on the cropland with a moderate leaching potential commands a higher net return than corn grown on highly leachable cropland because moderately leachable cropland requires the application of less nitrogen fertilizer assuming that the nitrogen available for plant uptake is equal for the two types of cropland. When a zero excess standard is enforced, net incomes from crops grown on both types of cropland, however, will be reduced to the same level because the nitrogen fertilizer application rate will be the same. The reason for the same application rate on both types of cropland is because, in the long run, there will be no residual nitrogen carry-over on moderately leachable cropland, even though it is capable of carrying part of the residual nitrogen over to the next time period. Thus, if a no excess standard is enforced, the income loss (compliance cost) will be relatively higher for moderately leachable cropland.

CONCLUSION

This paper has been concerned with the excess application of nitrogen fertilizer that is a threat to contaminate ground water. The effects of several policy options designed to reduce nitrogen fertilizer use have been investigated. For a farmer currently growing corn from one year to the next, adopting a soybean-corn rotation can reduce the excess nitrogen in the soil and increase net farm income in the process. Adopting a meadow-corn rotation in deference to continuously planting corn, on the other hand, can reduce by a significant amount the excess nitrogen in the soil and available for potential leaching into the ground water but this would involve a relatively sizeable reduction in net farm income. Additionally, in order to achieve a goal of zero excess nitrogen in the soil over time, both rotation schemes must involve a limitation on the nitrogen fertilizer application rate. Practicing the continuous planting of corn while coincidentally limiting the use of nitrogen fertilizer can effectively reduce the excess nitrogen in the soil to zero for a relatively low price for nitrogen fertilizer. Adoption of a soybean-corn rotation, however, while limiting the nitrogen fertilizer application rate will have the lowest compliance cost for a farmer irrespective of the price of nitrogen fertilizer and also irrespective of the vulnerability of cropland to potential leaching.

Finally, a fertilizer use restriction on cropland that is highly vulnerable to potential leaching will have a smaller compliance cost (i.e., a lower cost to the farmer) per pound (kg) reduction in the nitrogen fertilizer application rate relative to cropland with a moderate leaching potential.

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Environment International, Vol. 19, pp. 193-202, 1993
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0160-4120/93 $6.00 +.00

LABORATORY EVALUATION OF VECTOBAC^{R}-12AS AND TEFLUBENZURON AGAINST *CULEX* AND *AEDES* MOSQUITO LARVAE UNDER DIFFERENT PHYSICAL CONDITIONS

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EI 9206-154 M (Received 9 June 1992; accepted 11 August 1992)

Vectobac^{R}-12AS was effective in reducing larval populations of *Culex quinquefasciatus, Aedes albopictus,* and *Aedes aegypti* at the mg/L level. Susceptibility to the *Bacillus thuringensis* (H-14) formulation varied according to different species and strains of mosquito larvae, especially significant among *albopictus* strains. Teflubenzuron was also highly effective in inhibiting normal development of mosquito larvae into adults at the µg/L level. Mortality occurred mainly in the pupal stage. Lower concentrations resulted in abnormal adults partly exuviated from the pupal cases. The larvicidal property of Vectobac^{R}-12AS was affected by temperature and larval density. Low water temperature (5°C) and high population density (200-250 larvae/L medium) favored better survival of the larvae. Similarly, the susceptibility of Bora-bora larvae to teflubenzuron increased with increasing temperatures and complete darkness. However, the pH did not cause significant change on the potency of both Vectobac^{R}-12AS and teflubenzuron. High dosage and prolonged application of Vectobac^{R}-12AS may impose some stress on the survival of certain small crustaceans. Likewise, a high dosage of teflubenzuron imposed a detrimental effect on the water flea, brine shrimp, and freshwater shrimp, but little or no detrimental effect on the freshwater fish investigated.

INTRODUCTION

Mosquitoes have been a perpetual problem of insect pest control. They are not only annoying but also threatening to public health because of their disease-transmitting capacity. They breed fast, some species finish their life cycle in about a week, and most can breed continuously in great numbers throughout the year in a subtropical humid climate such as that of Hong Kong. Over 1600 species of mosquitoes have been described globally, and at least 70 of these species occur in Hong Kong, a number which is greater than that of Britain (Chau 1982).

In Hong Kong, there are 28 species of *Culex. Culex quinquefasciatus* is the most common of all local mosquitoes. Their larvae are found in all kinds of water collections, especially in polluted waters rich in organic matter (Chau 1982). It is the major nuisance mosquito, breeding extremely well at construction sites, and can transmit Japanese encephalitis and filaria. Of the 12 local species of *Aedes, Aedes albopictus* (Asian tiger mosquito) demonstrates wide distribution; the larvae are found in all sorts of small water collections of tree holes, empty cans, and old rubber tires. The species is a vector of dengue fevers in southeast Asia. *Ae. albopictus* was first detected in Houston, Texas in 1985; possibly immigrated to the United States in imported used tires (Francy et al. 1990). By 1988, detection of the species was reported in 17 states. The presence of *Ae. albopictus* was reported in Brazil in 1986 and subsequently had spread to several Brazilian states (Forattini 1986). Due to its susceptibility to a number of arboviruses, the potentiality of *Ae. albopictus* to become an arbovirus vector will be high. Because of the abundance of the above species in the field, the availability of laboratory strains of these species and *Ae. aegypti*, *C. quinquefasciatus*, *Ae. albopictus*, and *Ae. aegypti* were chosen for the present study.

Like other insects, mosquitoes are acquiring resistance to chemical pesticides through increased individual tolerances and selection of resistant progeny. At present, the control of mosquitoes in Hong Kong is carried out by the Pest Control Unit of the Urban Service Department. Fuel oil is sprayed over the possible breeding grounds of mosquitoes, including rivers, streams, ponds and other stagnant waters. Potential breeding places due to human activities, and numerous building sites in the colony are regularly inspected. The use of oil for control has an undesirable impact on aquatic life and would also cause damage to machinery used at construction sites.

The isolation of *Bacillus thuringiensis*, subspecies *israelensis* (B.t.i., or B.t. serotype H-14), from Culicidae by de Barjac (1978) proved to be encouraging because of the high selectivity of B.t.i. for certain Diptera, particularly mosquitoes. This led to the subsequent rapid development of commercial production of bacterial insecticides in Europe and the USA and dissemination by the World Health Organization (WHO) for worldwide evaluation (Lacey and Lacey 1990).

Bacillus thuringiensis israelensis has been investigated by various workers and shown to be effective against mosquitoes and mosquito larvae of the genera *Aedes*, *Culex* (Hall et al. 1977; Ignoffo et al. 1981) *Anopheles*, *Mansonia* (Foo and Yap 1982), *Anopheles* (Lacey and Inman 1985), and *Psorophora* (Meisch et al. 1990). Many workers noted that response to B.t. H-14 was different for different mosquito species and strains.

Insect growth regulators (IGRs) are compounds that alter the normal growth patterns of insects causing metabolic errors and asynchronous development, which eventually result in death of the insect. IGRs have several advantages as pesticides, such as their specificity, affecting usually only target pests and sparing predators and parasites; their low toxicity to other forms of life including man, livestock, and wildlife; and their effectiveness at low dosages. IGRs have become an important tool for the control of mosquitoes with minimum environmental impact (Schaefer and Wilder 1973; Staal 1975). Different groups of insect growth regulators have been de-veloped to provide alternatives to the conventional organochlorine and organophosphate insecticides. According to their mode of action, IGRs are broadly classified into two categories: those that inhibit specifically chitin synthesis and juvenile hormone mimics that inhibit pupation.

The benzoylphenyl ureas are potent chitin synthesis inhibitors and have been evaluated for their insecticidal activity including their use as mosquito controlling agents (Schaefer et al. 1975, 1978; Amalraj et al. 1988). A more recent benzoylphenyl urea IGR, teflubenzuron or CME 134 has adequately controlled lepidopterous larvae on soybeans (Herbert and Harper 1985); eggs and larvae of the Egyptian cotton leafworm, *Spodoptera littoralis*, found on alfalfa and cotton (Ascher and Nemny 1984); the parasite *Encarsia formosa* and its white fly host, *Trialeurodes vaporariorum* (Oomen and Wagers 1984); important pests in orchards (Becker and Deletraz 1987); and immature culicine mosquitoes (Schaefer et al. 1988).

At the time of this study, a commercial *Bacillus thuringiensis* (H-14) formulation, Vectobac^R-12AS had been registered locally for public health pests control. The present investigation was aimed to study Vectobac^R-12AS and teflubenzuron with regard to: (1) their efficacy as mosquito larvicides against field-collected local strains and lab-reared strains tested in the lab; (2) the influence of pH, temperature, population density, and light intensity on their performance; and (3) the effect of Vectobac^R-12AS and teflubenzuron on nontarget aquatic organisms.

Although *Bacillus thuringiensis* (H-14) and teflubenzuron are dosage effective in suppressing mosquito larvae, yet more abundant use in the field may promote insect resistance just like the conventional insecticides. Mild cross resistance to teflubenzuron has been observed for the diamondback moth, *Plutella xylostella* (Perng and Sun 1987), and the cotton leafworm, *Spodoptera littoralis* (Ishaaya and Klein 1990). Similarly, resistance to *Bacillus thuringiensis* was reported for the diamondback moth (Tabashnik et al. 1990, 1991). An intention for future investigation is to devise an integrated, controlled use of *Bacillus thuringiensis* and teflubenzuron formulations for mosquito control based on findings of the present study.

MATERIALS AND METHODS

Test mosquitoes

Well-established, wild-type, lab-strain (ZS) mosquito eggs of *Culex quinquefasciatus* and *Aedes albopictus* were supplied by the Zhongshan University, China. Mosquito eggs of *Aedes aegypti* (Bora-bora) were obtained as a gift from the Institut Pasteur, France (IP). Wild-type, lab-strain (MA) eggs of *Ae. aegypti* were from the School of Biological Sciences, Universiti Sains Malaysia, Pulau Penang, Malaysia. The field-collected larval populations of *C. quinquefasciatus* were sampled from the polluted Ng Tung River in Sheung Shiu (SS) and the roof top of Hong Kong Baptist College (BC); *Ae. albopictus* was obtained from rain puddles in Fan Ling (FL) and the country park of the Shing Mun Reservoir (SM). Vectobac^R-12AS (1200 ITU/mg), and teflubenzuron (reagent grade) were kindly supplied by the Abbott Laboratories (North Chicago, USA), and Celamerck GmbH & Co. (Ingelheim, Federal Republic of Germany), respectively.

Rearing of mosquito larvae

Soft, reconstituted water (ASTM Standards E729-80, 1987) was used to hatch the laboratory-strain mosquito eggs and for subsequent rearing. The larval food used (flour 70%, soybean flour 20%, pig's liver 5%, and dry yeast 5%) was recommended by the Research Institute of Entomology, Zhongshan University. The larvae were kept at constant temperature (25±2°C) and photoperiod 14:10 (light:dark). The field-collected mosquito larvae were acclimatized under the same rearing conditions for 2-3 d before testing.

Laboratory tests using Vectobac^R-12AS

Twenty early fourth instar mosquito larvae were placed in 200 mL of test medium in a 250-mL beaker (reconstituted water dilution of Vectobac^R-12AS) at 25±2°C, photoperiod 14:10 (light:dark), and checked for 24-h posttreatment mortality (three replicates for each concentration; each trial was replicated three times on three different days). A series of at least five concentrations and a control (reconstituted water) were used in LC$_{50}$ determinations. Tests were discarded if the control mortality was greater than 10%. LC$_{50}$, LC$_{95}$, and the slope were determined for each bioassay using probit analysis (SAS Institute 1985). Duncan's multiple range test (Little and Hills 1978) was employed to assess significant differences between treatment means.

The mortality responses of lab-strain *quinquefasciatus* larvae (ZS-Lab) to Vectobac^R-12AS were tested for varying pH, temperature, and population density.

Table 1. Concentration response of mosquito larvae to Vectobac^R-12AS, 24-h posttreatment. Zs were laboratory strains provided by the Zhonshan University, China. Strain Bora-bora was from the Institut Pasteur, France. SS, BC, FL, and SM were local strains. Sample size, n = 1080 larvae per strain except Bora-bora (n=540). a : Slope ± standard error. b: LC$_{50}$ or LC$_{95}$ (fiducal limit), mg formulation/L. c: Values in a column followed by the same letter are not significantly different from each other (Duncan's multiple range test, p<0.05).

Strain	Slope ± SE^a	LC$_{50}$(95% FL)^{bc}	LC$_{95}$(95% FL)^{bc}
C. quinquefasciatus			
ZS-Lab	2.93±0.23	0.09(0.08-0.10)C	0.31(0.25-0.40)B
SS-Field	3.31±0.49	0.05(0.04-0.16)C	0.15(0.12-0.25)B
BC-Field	1.82±0.52	0.12(0.07-0.21)B	0.96(0.40-44.7)A
Ae. albopictus			
ZS-Lab	3.80±0.57	0.09(0.08-0.11)BC	0.25(0.19-0.40)B
FL-Field	1.40±0.43	0.02(0.01-0.04)D	0.20(0.13-1.02)B
SM-Field	6.78±0.80	0.23(0.22-0.25)A	0.41(0.37-0.48)B
Ae. aegypti (Bora-bora)			
IP-Lab	13.83±2.78	0.21(0.18-0.23)A	0.27(0.24-0.46)B

The LC_{95} concentration of Vectobac^{R}-12AS (0.3 mg/L) found for *quinquefasciatus* ZS-Lab strain larvae (Table 1) was selected to test these environmental conditions. In addition, a two times this LC_{95} concentration of Vectobac^{R}-12AS (0.6 mg/L) was used to test the early hourly response of the mosquito larvae to the density effect. The pH range tested was pH 6-9, temperature range was 5-35°C, and density range was 50-350 larvae/L of test medium.

Laboratory tests using teflubenzuron

A stock solution of 1 g/L was prepared by dissolving teflubenzuron in acetone. The 24-h LC_{50} tests on *Ae. aegypti* (Bora-bora, IP-Lab) and wild-type, lab-strain (MA-Lab) of the same species were performed similar to the 24-h LC_{50} tests using Vectobac^{R}-12AS. The control medium was prepared by diluting 0.1 mL of acetone in 10 L of soft reconstituted water.

Because mortality may occur during the larval, pupal stage, or adult emergence, the cumulative mortality was studied by subjecting Bora-bora larvae to eight concentrations of teflubenzuron (0.2-2.0 µg/L) for 2-h treatment. After treatment, the larvae were transferred to fresh soft reconstituted water, kept under the normal rearing conditions (25°C, 14:10 light:dark), and provided with food. Mortality counts were made daily until adult emergence was complete. For studying morphogenetic abnormalities, posttreatment dead larvae, pupae, larval-pupal intermediates, and partly enclosed adults were collected for observation.

The mortality response of Bora-bora to teflubenzuron under pH range of 6-9 and temperature range of 5-35°C was investigated similar to the coresponding tests using Vectobac^{R}-12AS. The response of these mosquito larvae to teflubenzuron under continuous illumination (Cool White^{R} fluorescent light; light intensity at surface of water was 2145 lux) or complete darkness was also tested.

Tests on nontarget organisms

Consumers usually tend to use higher than recommended dosage of insecticide for insect control; at the same time, there may be accumulation of the insecticide if it was administered frequently. Therefore, nontarget organisms commonly found in the sampling site of the Ng Tung River were subjected to a Vectobac concentration of 10 times the LC_{95} (1.5 mg/L) determined for SS-Field *quinquefasciatus* mosquito larvae from Ng Tung River (Table 1), and mortality of the nontarget organisms was recorded for three weeks. Organisms tested included a cladoceran (water flea), a cyclopoid copepod, and an ostracopod (seed shrimp). Twenty individuals were placed in a covered 100-mL beaker containing 60 mL of test medium, and the setup was triplicated. The fresh test medium was renewed every week. Only ground brewer's yeast was supplied as food. Controls without insecticide treatment were run concurrently.

To investigate the environmental impact of teflubenzuron towards the aquatic ecosystem, some aquatic nontarget organisms including a freshwater shrimp (*Palaemonetes* sp.), water flea (*Sida crystallins*), brine shrimp (*Artemia salina*), and freshwater fish (*Gambusia patruelis*) were chosen for laboratory acute-toxicity tests by determining their 24-h, 48-h, or 96-h teflubenzuron median lethal concentrations. Supply of water fleas were from lab monoculture and fed on *Chlorella*; brine shrimps were reared in artificial sea water and fed on yeast suspension; the freshwater shrimps and fish were bought from a pet shop and acclimatized before experimentation. All test animals were maintained in the laboratory at conditions similar to the mosquito larvae.

Table 2. Concentration response of mosquito larvae to teflubenzuron, 24-h posttreatment. IP = Bora-bora. MA = Wild-type, lab-strain from Universiti Sains Malaysia. Sample size, n=1080 larvae per strain. a,c: as in Table 1. b: LC_{50} or LC_{95} (fiducal limit), µg/L.

Strain	Slope ± SE^{a}	LC_{50}(95% FL)^{bc}	LC_{95}(95% FL)^{bc}
Aedes aegypti			
IP-Lab	2.08±0.48	0.60(0.55-0.65)A	3.70(3.04-4.75)A
MA-Lab	2.71±0.37	0.41(0.38-0.44)A	1.68(1.48-1.94)B

Table 3. Cumulative mortality of Bora-bora larvae to 2-h treatment of various concentrations of teflubenzuron. Sample size, n = 180 larvae per concentration.

Concentration (μg/L)	% Cumulative mortality Larva	Pupa	Adult	Total Mortality (%)
2.0	26	57	3	86
1.4	19	58	0	77
1.0	9	54	4	67
0.8	4	53	4	61
0.6	5	40	9	54
0.5	2	29	12	43
0.4	2	11	21	34
0.2	3	2	11	16
Control	0	1	1	2

Table 4. Temperature response of lab-strain *C. Quinquefasciatus* larvae to Vectobac^{R}-12AS. Sample size, n = 80 larvae for each temperature. Vectobac^{R}-12AS concentration = 0.3 mg/L. a: Values in a vertical column followed by the same letter are not significantly different from each other (Duncan's multiple range test, $p<0.05$).

Temperature (°C)	5-h Mortality (%)^{a}	24-h Mortality (%)^{a}
5	0.0 C	39.1 B
15	12.8 B	83.1 A
25	16.3 B	90.7 A
35	62.0 A	97.0 A

RESULTS

Response of mosquito larvae to Vectobac^{R}-12AS

Table 1 indicates the 24-h LC$_{50}$ and LC$_{95}$ of Vectobac^{R}-12AS for different mosquito larvae. The LC$_{50}$ of Vectobac^{R}-12AS was statistically different between the *Culex* and *Aedes* larvae. Significant difference was also observed for different strains of the same species, with field-strain *albopictus* showing greater dissimilarity from the laboratory-strain (Duncan's multiple range test, $p<0.05$, Table 1). The LC$_{95}$s of Vectobac^{R}-12AS were found to be quite uniform among the three species and various strains; only BC-Field *quinquefasciatus* larvae demonstrated a higher value of LC$_{95}$.

Environmental effects on Vectobac^{R}-12AS efficacy

The increase in temperature from 5-35°C resulted in a marked increase in mortality of *C. quinquefasciatus* (ZS-Lab) larvae, from 0-62%, 5-h posttreatment with Vectobac^{R}-12AS (Table 4). The 24-h mortality increased more gradually with increasing temperatures, and a significant greater change in mortality was observed when the temperature rose from 5–15°C. The 24-h mortality at various pHs (6-9) did not reflect any significant difference.

When the population density in the Vectobac^{R}-12AS test medium increased from 50 to 300 larvae/L, statistically there was no significant difference in the 24-h mortality. A 29% drop in mortality was seen when the density increased to 350 individuals (Table 6a). When the concentration of Vectobac^{R}-12AS was doubled, mortality of 25-35% was recorded in the 4th hour of posttreatment for population densities of 50-150 larvae/L test medium, in contrast to the 0% mortality observed at higher population densities of 200-250 larvae/L of the test medium. A similar trend of response was detected after 7-h of posttreatment, with 70.6-80.0% mortality in tests of 50-150 larvae/L medium vs. 7.1-7.5% mortality recorded for

Table 5. Temperature response of Bora-bora larvae to teflubenzuron. Sample size, n = 80 larvae for each temperature. Teflubenzuron concentration = 3 µg/L. a:Values in a vertical column followed by the same letter are not significantly different from each other (Duncan's multiple range test, $p<0.05$).

Temperature (°C)	24-h Mortality (%)a
5	67.1 B
15	85.4 A
25	87.2 A
35	90.3 A

Table 6a. Density effect of Vectobac®12AS (0.3 mg/L) on lab-strain *C. Quinquefasciatus larvae*. a: Values in a column followed by the same letter are not significantly different from each other (Duncan's multiple range test, $P<0.05$).

Population density per L Vectobac	24-h Mortality (%)[a]
50	93.3 A
100	80.0 A
200	100.0 A
250	94.2 A
300	81.3 A
350	52.4 B

Table 6b. Density effect - Hourly mortality response of lab-strain *C. Quinquefasciatus* larvae to Vectobac®-12AS (0.6 mg/L). a: Values in a column followed by the same letter are not significantly different from each other (Duncan's multiple range test, $P<0.05$).

Population density per L Vectobac	Mortality (%)[a]				
	3 h	4 h	5 h	6 h	7 h
50	0.0	30.0	55.0	60.0	70.6 A
100	0.0	25.0	52.5	67.5	80.0 A
150	0.0	35.0	56.7	66.7	78.3 A
200	0.0	0.0	0.0	1.3	7.5 B
250	0.0	0.0	1.0	3.0	7.1 B

Table 7. Biological activity of teflubenzuron against Bora-bora larvae under continuous light or complete darkness, 2-h posttreatment. sample size, n = 180 larvae per test. a: Slope - standard error. b: LC_{50} (fiducal limit), μg/L. c: Values in a column followed by the same letter are not significantly different from each other (Duncan's multiple range test, $P<0.05$).

Condition	Slope+SE[a]	LC_{50}(95% FL)[bc]
Light	1.21±0.83	5.29(4.61-6.24)A
Dark	1.51±0.66	4.53(4.08-5.10)B

Table 8. Effect of Vectobac®-12AS (1.5 mg/L on nontarget organisms. * Able to reproduce.

Test organisms	Mortality %		
	week 1	week 2	week 3
Branchiopod* (water flea)	0.0	9.9	22.0
Control	0.0	5.2	11.6
Copepod (cyclopoid copepod)	5.0	24.7	72.0
Control	0.0	14.0	51.0
Ostracopod* (seed shrimp)	0.0	0.0	13.0
Control	0.0	3.0	10.0

Table 9. Effect of teflubenzuron (LC_{50}) on nontarget organisms. * Freshwater fish did not show any observable lethal effect after 96-h treatment.

	LC_{50} (μg/L)		
Test organism	24-h	48-h	96-h
Water flea (*Sida crystallins*)		10.35	
Brine shrimp (*Artemia salina*)			50.00
Freshwater shrimp (*Palaemonetes* sp.	40.00		
Freshwater fish (*Gambusia patruelis*)			* $>10^4$

200-250 larvae/L medium (Table 6b). Hence, a significant difference in mortality was found between the noncrowded and crowded populations.

Response of mosquito larvae to teflubenzuron

Only LC_{95} of teflubenzuron for Bora-bora and MA-Lab *Ae. egypti* showed a significant difference from each other (Duncan's multiple range test, $p<0.05$; Table 2). The cumulative mortality of stage-tested Bora-bora (Table 3) revealed that most mortality occurred in the pupal stage. At high concentrations of teflubenzuron, a higher mortality percentage occurred in the larval stage; while, at low concentrations, a higher percentage of mortality occurred in the adult stage.

Morphogenetic abnormalities

As a consequence of disruption of chitin synthesis by teflubenzuron, the following morphological abnormalities were generally observed: darkening of the larval skin, extended pupa (no longer C-shaped), partly exuviated adult with part of the abdomen still in the pupal case, legs of the emerged adult still attached to the pupal case, pupa-adult intermediate, and the splitting of the abdominal cuticle of partly exuviated adult.

Environmental effects on teflubenzuron

Similar to the response to temperature of Vectobac-treated *quinquefasciatus* larvae, a significant increase in 24-h mortality was observed in teflubenzuron-treated Bora-bora larvae when the water temperature increased from 5-15°C. Thereafter, the increase in mortality was insignificant with increasing temperatures (Table 5). Again, like tests with Vectobac, between the pH range of 6-9, the mortality due to 4 μg/L teflubenzuron was not significantly different from each other. Under continuous light, the biological activity of teflubenzuron against Bora-bora larvae was found to be different from complete darkness (Table 7).

Effect of Vectobac^{R}-12AS on nontarget organisms

The effect of Vectobac^{R}-12AS on nontarget crustaceans is summarized in Table 8. The test organisms had zero or low (5%) mortality in the first week after the Vectobac treatment. The mortality was still quite low in the 2nd and 3rd week (0-22%; except the copepod which had 72% mortality). When compared with the mortality of the controls, there was no sharp difference between the experimental and control organisms. The water flea and seed shrimp were able to reproduce and juveniles were detected among the adults, although the number of juveniles was small and was not recorded. The higher mortality of the test organisms observed in Week 3 might be largely due to the inadequate food supplied (yeast), and hence the experiment was terminated after Week 3.

Effect of teflubenzuron on nontarget organisms

Results from a probit analysis indicated that the freshwater shrimp and water flea were relatively more susceptible towards teflubenzuron than the brine shrimp and freshwater fish (lower LC_{50}s, Table 9), even though their mortality counts were made 24 or 48 h rather than 96 h after teflubenzuron exposure. However, the lowest LC_{50} was that of Bora-bora (0.6 μg/L, Table 2) and the value was lower at least two orders of magnitude.

DISCUSSION

Response of mosquito larvae to Vectrobac^{R}-12AS and teflubenzuron

Vectobac^{R}-12AS contains the spores and delta-endotoxin crystals of *Bacillus thuringiensis* (H-14) as active ingredients. In the present investigation, the effectiveness of Vectobac^{R}-12AS on *C. quinquefasciatus, Ae. albopictus*, and *Ae. aegypti* larvae was positive. The experimental mosquito larvae demonstrated both species and strain difference towards this *Bacillus* formulation. The sensitivity of some of these mosquito larvae (LC_{50} of *quinquefasciatus* strains, ZS-Lab, and FL-Field *albopictus*) towards Vectobac^{R}-12AS was even greater than *Ae. aegypti* (Table 1), although the latter species has been documented to be highly sensitive towards B.t. H-14 (WHO 1979). A mean value of 0.36 mg Vectobac/L was found from the seven LC_{95}s for the different mosquito strains used in the present study. This value is close to the recommended dosage of 0.28 mg Vectobac/L (converted from the recommended rate of 2 oz/10 gallon spray to an acre or 141.9 g/100 L spray to a hectare; the surface area of the 250-mL beaker used for testing = 3.92×10^{-7} hectare; the volume of the test medium = 200 mL). Because a significant difference in susceptibility towards *Bacillus* formulations was usually present among different species and strains of mosquitoes, a preliminary test on the pest's susceptibility would be valuable prior to effective field applications.

The regression slope represents the rate of declination of efficacy of the insecticide. For Vectobac^{R}-12AS, the slope was large for Bora-bora and SM *albopictus*, small or flat for BC *quinquefasciatus* and FL *albopictus*, but intermediate for ZS, SS *quin-*

quefasciatus, and ZS *albopictus* strains (Table 1). This may mean that the efficacy of Vectobac^R-12AS drops most rapidly for Bora-bora, followed by SM *albopictus*, and then the remaining strains. Smaller regression slopes also indicate that the formulation concerned is effective over a wide dosage range (Yap et al. 1990).

Because only two strains of *Ae. aegypti* were tested against teflubenzuron, strain difference was not very evident. The LC_{50} of the Bora-bora strain did not demonstrate any significant difference from the wild-type, but showed a 2.2-fold increase in the LC_{95} (Table 2). A 5-10 fold increase in the LC_{95}s would indicate cross resistance, but data obtained in the present study did not support this situation.

The amount of teflubenzuron required to control mosquito larvae is significantly small, at the µg/L level, when compared to the amount of Vectobac^R-12AS needed for the same purpose. Due to its mode of action (interfering chitin formation), teflubenzuron does not exhibit fast knockdown, while morphogenetic abnormalities of pupal and adult stages, and delayed mortality were observed after teflubenzuron application.

Environmental effects

Environmental conditions have demonstrated their influence on the performance of Vectobac^R-12AS. Lower water temperatures may result in lower metabolic rate of the mosquito larvae and in accordance lower feeding rate and mortality. This accounts for the 24-h low mortality (39.1%) when the temperature was 5°C and the much higher mortality (83.1-97.0%) when the temperature reached 15°C and higher (Table 4). Similar temperature effects were found for teflubenzuron, with a significant increase in mortality when the temperature increased from 5 to 15°C, but showed a milder increase in mortality thereafter (Table 5). It would be useful to monitor the water temperature and make appropriate adjustment of dosage, when B.t. H-14 formulations and teflubenzuron are applied in the field.

Both Vectobac^R-12AS tested against *C. quinquefasciatus* larvae and teflubenzuron against Bora-bora larvae were found to be rather pH independent. It is reported that *C. quinquefasciatus* larvae generally show broad pH tolerances and are found in habitats with pH varying from 6.6-9.5 (Laird 1988). The field-collected *C. quinquefasciatus* larvae were found in habitats with pH 8.5 and 8.9, whereas the lab strain used in the test was reared in reconstituted water at pH 7.5. Alkaline pH would activate the endotoxin crystals. However, the present test did not indicate a significant increase in 24-h mortality of the tested mosquito larvae at alkaline pH of 8 and 9.

When the larval density was 1 larva per 3.3 mL of Vectobac^R-12AS test medium (300 larvae/L; Table 6a), a slight drop in 24-h mortality was observed. However, a more distinct decrease in larval mortality was seen when the larval density increased further to 1 larva per 2.9 mL (350 larvae/L) of test medium. If higher concentration of Vectobac^R-12AS was intended for faster larval reduction, the density effect would be more obvious, and a distinct drop in mortality was recorded when the larval density was 1 larva per 5 mL (200 larvae/L) of test medium (Table 6b). Hence, the population density of the mosquito larvae should be taken into account when B.t. formulations are used.

When tested under artificial Cool White^R light of 2415 lux, the LC_{50} (for Bora-bora towards teflubenzuron) showed a significant 1.17-fold increase when compared with LC_{50} obtained under complete darkness (Table 7). The higher susceptibility to teflubenzuron is probably due to the increase in feeding activity under complete darkness.

Nontarget organisms

The preliminary test of the toxic effect of Vectobac^R-12AS on the three nontarget crustaceans may indicate that high dosage and prolonged administration of Vectobac^R-12AS can impose some stress on the survival of certain small crustaceans important at the bases of food chains. Although the mortality found in the present test is to be considered with some reservation due to the limitations (unbalanced diet used and high mortality in some controls) of the test mentioned above, the safety of H-14 formulations to nontarget organisms should be more widely investigated.

The three nontarget crustaceans showed varying degree of susceptiblity to teflubenzuron indicating species variation. The reason for choosing them for testing was because water fleas and shrimps were reported to be sensitive to chemical treatment (Schaefer et al. 1988) and results obtained were comparable. Susceptibility may be due to their filtering mode of feeding which results in the accumulation of high levels of toxic substances even when the environment has low level of toxicants. The most tolerant organism in the test was the freshwater fish, and teflubezuron did not cause any toxic effect at a level of 10 mg/L. The LC_{50} (0.6 µg/L) and LC_{95} (3.7 µg/L) of teflubenzuron against *Ae. aegypti* (Bora-bora) were much lower than that of the relatively sensitive crustaceans. Hence, under a well-controlled usage of teflubenzuron, the detrimental effects towards the nontarget organisms can be minimized.

Both Vectobac^R-12AS and teflubenzuron are selective insecticides of low mammalian toxicity and harmless to many beneficial arthropods, thus, causing much less detrimental effects to the environment. Their efficacy in controlling mosquito larvae is found to be comparable to conventional insecticides. Because their effectiveness can be affected by temperature, life stage, feeding activity, and population density of the pests, proper timing of application, and adequate dosage are of importance.

Acknowledgment — The research was supported by a Hong Kong Baptist College research grant. The authors wish to thank the Abbott Laboratories for the *Bacillus* H-14 formulation, the Celamerck GmbH & Co. for the supply of teflubenzuron, the Institut Pasteur for the *Ae. aegypti* eggs, the Universiti Sains Malaysia for the wild-type *aegypti* eggs, the invaluable advice of Mr. Kar-wai Chau, and Mr. T.C. Chan for his technical assistance.

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Environment International, Vol. 19, pp. 203-210, 1993
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0160-4120/93 $6.00 +.00

PREDICTION OF GAS CHROMATOGRAPHIC RETENTION INDEXES OF ENVIRONMENTAL POLYCHLORINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS BY USE OF COMPUTER-CALCULATED MOLECULAR PROPERTIES

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EI 9207-171 M (Received 17 July 1992; accepted 10 November 1992)

The gas chromatographic retention indexes (GCRIs) of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) were predicted by a multiple linear regression method coupled with a set of descriptors composed of the number of chlorine atoms (N_{Cl}), ionization potentials (I_p), electron affinities (E_A) and dipole moments squared (μ^2). The I_P, E_A and, μ of 41 PCDD isomers and 115 PCDF isomers, to which the measured GCRI data are available, were calculated by the MNDO-PM3 semiempirical molecular orbital method.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins(PCDDs) and dibenzofurans(PCDFs) are well-known as toxic environmental chemicals having characteristic physical and chemical properties as summarized in several recent reviews (Kimbrough 1980; Choudhry et al. 1983). High-resolution gas chromatography (GC) is the fundamental technique used for analysis of PCDDs and PCDFs in environmental samples. The GC retention indices (GCRIs) are extensively used to identify which isomers of PCDDs and PCDFs are contained in the sample being analyzed. Predicted data of the GCRIs will facilitate the analysis, especially when standard samples are not readily available.

Prediction of the GCRIs of PCDDs and PCDFs was done by many workers by means of regression procedures coupled with various combination modes of structural and/or physical descriptors such as substitution patterns, molecular connectivity indexes, van der Waal's volumes and surface areas, charge distributions, polarizabilities, ionization potentials, dipole moments, and so on (Hale et al. 1985; Dunn et al. 1986; Donnelly et al. 1987; Koester and Hites 1988; Robbat and Kalegeropoulos 1990; Ong and Hites 1991). Consequently, it has been shown that molecular descriptors adequately chosen and combined are useful to predict the GCRIs of PCDDs and PCDFs.

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The present work investigates the possibilities of predicting the GCRIs of PCDDs and PCDFs by a linear regression analysis based on a new combination of descriptors. These descriptors include the electron affinity parameters of PCDDs and PCDFs which have not been employed in previous regression analyses, but which would influence liquid-phase interactions of those chemicals having chlorine atoms of high electronegativity. Molecular physical properties used as descriptors in this work are calculated by the modified neglect of diatomic overlap, parametric method 3 (MNDO-PM3), which is the up-to-date version of the MNDO semiempirical molecular orbital method.

PREDICTION METHOD

The GCRIs of sample molecules measured in a given liquid phase system are affected in general by dispersion force depending on the polarizabilities and ionization potentials of sample molecules, by induction and orientation forces depending on the dipole moments squared of sample molecules, and also by charge-transfer force depending on the electron affinities or ionization potentials of sample molecules. We attempt to predict the GCRIs of PCDDs and PCDFs by a multiple linear regression procedure based on the following descriptors: (1) the number of chlorine atom (N_{Cl}); (2) ionization potential (I_P); (3) electron affinity (E_A); and (4) dipole moment squared (μ^2). N_{Cl} is generally accepted as a fundamental descriptor representing the van der Waal's effects on the GCRIs of polychlorinated aromatic chemicals such as PCDDs and PCDFs. I_P and E_A can be referred to as the negatives of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, respectively.

For 41 PCDD isomers and 115 PCDF isomers for which measured data of the GCRIs are available, molecular physical properties were calculated by the MNDO-PM3 method (Stewart 1989) contained in the MOPAC (Ver. 6.0) program package. This is a general purpose semiempirical molecular orbital program from the Quantum Chemistry Program Exchange (QCPE) at Indiana University. Initial geometries of PCDDs and PCDFs were assumed as planar. Bond lengths were started as follows: 1.41Å for the C-C bonds of PCDD benzene rings; 1.39Å for the C-C bonds of PCDF benzene rings; 1.48Å for the central C-C bond of the PCDF furan ring; 1.09Å for the C-H bonds; and 1.75Å for the C-Cl bonds. Bond angles were started as follows: 118° for the C-O-C bonds of PCDDs; 104° for the C-O-C bond of PCDFs; 105° for the C-C-C bonds of the PCDF furan ring; and 120° for the other C-C-C bonds, the Cl-C-C, and H-C-C bonds. The optimization computation was performed by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method provided as the MOPAC option subprogram. The MNDO-PM3 calculation was carried out on a FACOM M-760/8 computer supported by the FACOM OS IV/54 operating system. The calculated data of I_P, E_A, and μ are given in Tables 1 and 2. The numbering systems of PCDDs and PCDFs used in this work are shown in Fig. 1.

The multiple linear regression analysis was carried out subject to the GCRI data reported for 41 PCDD isomers (Donnelly et al. 1987) and for 115 PCDF isomers (Hale et al. 1985). The regression analysis was performed on a PC-9801 NEC personal computer by use of the MREG statistical program package (Tanaka et al. 1984).

RESULTS AND DISCUSSION

Prior to the regression analysis, it was confirmed that there was no serious intercorrelation among the four descriptors used. The multiple linear regression equation obtained for 41 PCDD isomers is expressed as follows:

$$\mathrm{GCRI} = 2573.280 + 200.714\,(N_{Cl}) - 124.759\,(I_P) + 103.195\,(E_A) + 20.198\,(\mu^2)$$

$n=41$, $r=0.994$, $s=5.085$.

The multiple linear regression equation obtained for 115 PCDF isomers is expressed as follows:

$$\mathrm{GCRI} = 3191.630 + 284.898\,(N_{Cl}) - 139.363\,(I_P) - 749.022\,(E_A) + 8.034\,(\mu^2)$$

$n=15$, $r=0.995$, $s=2.599$.

The high predictive abilities of these regression equations can be known from the values of the multiple correlation coefficient (r) and the standard deviation (s) of multiple regression.

Figure 2 shows a plot of the measured GCRIs versus the predicted GCRIs obtained for 41 PCDD isomers; and Fig. 3 shows the same plot obtained for 115 PCDF isomers. These plots indicate that there is a good agreement between the measured and predicted GCRI values, and also a tendency of data clustering in the plots corresponding to the different homologue groups, di-through octachloro groups for PCDDs and mono-through octachloro groups for PCDFs. Figure 4 shows a plot of the residuals between the measured

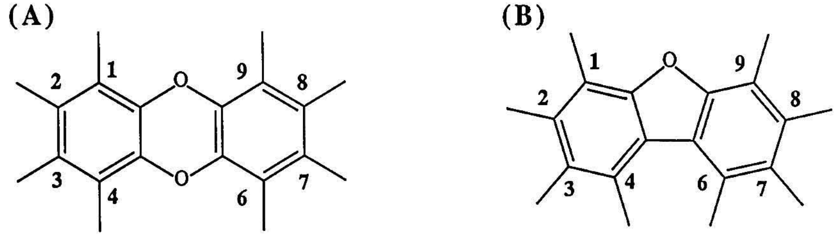

Fig. 1. (A) The numbering systems of dibenzo-*p*-dioxins used in this work. (B) The numbering systems of dibenzofurans used in this work.

Table 1. Molecular descriptors of PCDDs calculated by the MNDO-PM3 Method.

Isomer No.	Substitution Pattern	Number of Chlorines	Electron Affinity (eV)	Ionization Potential (eV)	Dipole Moment (Debye)
1	2,3 -	2	0.544	8.696	1.535
2	2,7 -	2	0.528	8.732	0.039
3	2,8 -	2	0.533	8.729	0.867
4	1,2,4 -	3	0.606	8.445	1.118
5	1,2,3,4 -	4	0.727	8.831	1.559
6	1,2,3,6 -	4	0.721	8.851	1.290
7	1,2,3,7 -	4	0.757	8.806	0.648
8	1,2,3,8 -	4	0.756	8.810	1.112
9	1,2,3,9 -	4	0.717	8.843	1.732
10	1,2,4,6 -	4	0.686	8.925	0.931
11	1,2,4,7 -	4	0.717	8.881	0.244
12	1,2,4,8 -	4	0.725	8.870	0.695
13	1,2,4,9 -	4	0.681	8.938	1.244
14	1,2,6,7 -	4	0.690	8.871	0.042
15	1,2,6,8 -	4	0.717	8.874	0.632
16	1,2,6,9 -	4	0.657	8.937	1.011
17	1,2,7,8 -	4	0.743	8.808	1.097
18	1,2,7,9 -	4	0.708	8.881	1.133
19	1,2,8,9 -	4	0.689	8.863	1.788
20	1,3,6,8 -	4	0.729	8.904	0.013
21	1,3,6,9 -	4	0.681	8.942	0.662
22	1,3,7,8 -	4	0.763	8.820	0.533
23	1,3,7,9 -	4	0.733	8.872	0.491
24	1,4,6,9 -	4	0.619	9.032	0.016
25	1,4,7,8 -	4	0.716	8.858	1.067
26	2,3,7,8 -	4	0.793	8.765	0.061
27	1,2,3,4,7 -	5	0.839	8.867	0.750
28	1,2,3,6,7 -	5	0.826	8.871	0.663
29	1,2,3,7,8 -	5	0.865	8.824	0.421
30	1,2,3,8,9 -	5	0.820	8.871	1.409
31	1,2,4,6,8 -	5	0.812	8.939	0.084
32	1,2,4,7,9 -	5	0.804	8.966	0.414
33	1,2,3,4,6,7 -	6	0.898	8.928	0.988
34	1,2,3,4,6,8 -	6	0.913	8.940	0.522
35	1,2,3,4,7,8 -	6	0.939	8.875	0.067
36	1,2,3,6,7,8 -	6	0.931	8.878	0.836
37	1,2,4,6,7,9 -	6	0.868	9.020	0.018
38	1,2,4,6,8,9 -	6	0.883	8.987	0.453
39	1,2,3,4,6,7,8 -	7	0.999	8.932	0.373
40	1,2,3,4,6,7,9 -	7	0.971	8.991	0.488
41	1,2,3,4,6,7,8,9 -	8	1.057	8.979	0.019

Table 2. Molecular descriptors of PCDFs calculated by the MNDO-PM3 Method.

Isomer No.	Substitution Pattern	Number of Chlorines	Electron Affinity (eV)	Ionization Potential (eV)	Dipole Moment (Debye)
1	1 -	1	0.632	9.022	0.061
2	2 -	1	0.621	9.035	0.835
3	3 -	1	0.664	8.956	1.420
4	4 -	1	0.627	9.057	1.686
5	1,2 -	2	0.749	9.069	0.756
6	1,3 -	2	0.815	8.993	0.906
7	1,4 -	2	0.789	8.977	0.913
8	1,7 -	2	0.808	8.973	0.997
9	1,8 -	2	0.769	9.010	0.981
10	1,9 -	2	0.744	9.046	0.680
11	2,3 -	2	0.787	8.969	1.570
12	2,4 -	2	0.766	9.080	1.530
13	2,6 -	2	0.767	9.029	1.059
14	2,7 -	2	0.801	9.028	0.455
15	2,8 -	2	0.759	9.087	0.375
16	3,4 -	2	0.795	8.989	2.047
17	3,6 -	2	0.804	9.036	1.877
18	3,7 -	2	0.838	8.918	1.253
19	4,6 -	2	0.767	9.088	2.350
20	1,2,3 -	3	0.906	9.038	1.312
21	1,2,4 -	3	0.897	9.005	1.104
22	1,2,6 -	3	0.883	9.074	0.489
23	1,2,7 -	3	0.917	9.064	0.281
24	1,2,8 -	3	0.877	9.047	0.916
25	1,3,4 -	3	0.944	8.965	1.407
26	1,3,6 -	3	0.943	9.094	1.132
27	1,3,7 -	3	0.974	8.952	0.517
28	1,3,8 -	3	0.939	9.033	0.285
29	1,3,9 -	3	0.914	9.011	0.962
30	1,4,6 -	3	0.915	9.050	1.554
31	1,4,7 -	3	0.949	8.991	1.144
32	1,4,8 -	3	0.916	8.982	0.459
33	1,4,9 -	3	0.886	9.018	0.417
34	2,3,4 -	3	0.910	9.054	1.999
35	2,3,6 -	3	0.918	9.015	1.609
36	2,3,7 -	3	0.951	8.954	0.888
37	2,3,8 -	3	0.916	9.073	0.674
38	2,3,9 -	3	0.920	8.968	1.508
39	2,4,6 -	3	0.897	9.070	1.849
40	2,4,7 -	3	0.932	9.143	1.203
41	2,4,8 -	3	0.895	9.078	0.533
42	2,4,9 -	3	0.902	9.086	1.210
43	3,4,6 -	3	0.922	9.084	2.251
44	3,4,7 -	3	0.955	8.964	2.482
45	3,4,8 -	3	0.923	9.025	1.107
46	3,4,9 -	3	0.927	9.032	1.486
47	1,2,3,4 -	4	1.029	9.025	1.582
48	1,2,3,6 -	4	1.029	9.089	1.101
49	1,2,3,7 -	4	1.059	8.997	0.416
50	1,2,3,8 -	4	1.026	9.094	0.784
51	1,2,3,9 -	4	0.997	9.036	1.490
52	1,2,4,6 -	4	1.018	9.046	1.276
53	1,2,4,7 -	4	1.050	9.057	0.626
54	1,2,4,8 -	4	1.018	9.011	0.277
55	1,2,4,9 -	4	0.988	9.031	1.053
56	1,2,6,7 -	4	1.028	9.087	0.695
57	1,2,6,8 -	4	1.005	9.080	0.516
58	1,2,6,9 -	4	0.988	9.016	0.376

Table 2. Continued.

Isomer No.	Substitution Pattern	Number of Chlorines	Electron Affinity (eV)	Ionization Potential (eV)	Dipole Moment (Debye)
59	1,2,7,8 -	4	1.022	9.043	1.006
60	1,2,7,9 -	4	1.013	9.087	0.791
61	1,2,8,9 -	4	0.955	9.050	1.388
62	1,3,4,6 -	4	1.061	9.055	1.732
63	1,3,4,7 -	4	1.092	8.958	1.110
64	1,3,4,8 -	4	1.064	8.994	0.428
65	1,3,4,9 -	4	1.033	9.000	1.092
66	1,3,6,7 -	4	1.080	9.008	1.151
67	1,3,6,8 -	4	1.062	9.138	0.577
68	1,3,6,9 -	4	1.043	9.031	0.559
69	1,3,7,8 -	4	1.077	8.972	0.614
70	1,3,7,9 -	4	1.067	8.989	0.157
71	1,4,6,7 -	4	1.054	9.060	1.755
72	1,4,6,8 -	4	1.033	9.042	1.210
73	1,4,6,9 -	4	1.014	9.067	0.815
74	1,4,7,8 -	4	1.054	8.979	1.150
75	2,3,4,6 -	4	1.028	9.090	2.162
76	2,3,4,7 -	4	1.060	9.024	1.482
77	2,3,4,8 -	4	1.030	9.110	0.986
78	2,3,4,9 -	4	1.033	9.051	1.669
79	2,3,6,7 -	4	1.059	8.986	1.322
80	2,3,6,8 -	4	1.040	9.106	0.693
81	2,3,7,8 -	4	1.055	9.011	0.161
82	2,4,6,7 -	4	1.041	9.108	1.737
83	2,4,6,8 -	4	1.019	9.089	1.086
84	3,4,6,7 -	4	1.061	9.015	2.400
85	1,2,3,4,6 -	5	1.143	9.096	1.622
86	1,2,3,4,7 -	5	1.171	9.018	0.940
87	1,2,3,4,8 -	5	1.144	9.037	0.680
88	1,2,3,6,7 -	5	1.161	9.035	0.777
89	1,2,3,6,9 -	5	1.108	9.039	0.743
90	1,2,3,7,8 -	5	1.156	9.028	0.370
91	1,2,3,8,9 -	5	1.093	9.104	1.240
92	1,2,4,6,7 -	5	1.150	9.109	1.186
93	1,2,4,6,9 -	5	1.109	9.038	0.743
94	1,2,4,7,9 -	5	1.135	9.091	0.176
95	1,2,4,8,9 -	5	1.083	9.023	0.715
96	1,3,4,6,7 -	5	1.188	9.019	1.655
97	1,3,4,7,8 -	5	1.187	8.972	0.681
98	1,3,4,7,9 -	5	1.174	8.998	0.486
99	2,3,4,6,7 -	5	1.161	9.052	1.897
100	2,3,4,6,8 -	5	1.143	9.142	1.275
101	2,3,4,6,9 -	5	1.178	9.045	0.994
102	2,3,4,7,8 -	5	1.159	9.057	0.770
103	2,3,4,7,9 -	5	1.154	9.044	1.609
104	2,3,4,8,9 -	5	1.129	9.119	0.967
105	1,2,3,4,6,7 -	6	1.264	9.073	1.340
106	1,2,3,4,6,8 -	6	1.249	9.093	0.745
107	1,2,3,4,7,8 -	6	1.263	9.024	0.243
108	1,2,3,4,7,9 -	6	1.248	9.054	0.619
109	1,2,4,6,8,9 -	6	1.199	9.032	0.071
110	2,3,4,6,7,8 -	6	1.254	9.116	1.284
111	1,2,3,4,6,7,8 -	7	1.350	9.087	0.801
112	1,2,3,4,6,7,9 -	7	1.340	9.065	0.756
113	1,2,3,4,6,8,9 -	7	1.308	9.080	0.468
114	1,2,3,4,7,8,9 -	7	1.318	9.066	0.268
115	1,2,3,4,6,7,8,9 -	8	1.408	9.115	0.337

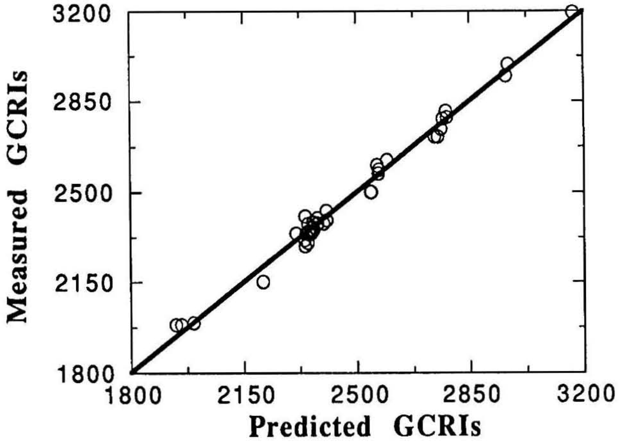

Fig. 2. Plot of the measured GCRIs versus the predicted GCRIs obtained for 41 PCDD isomers.

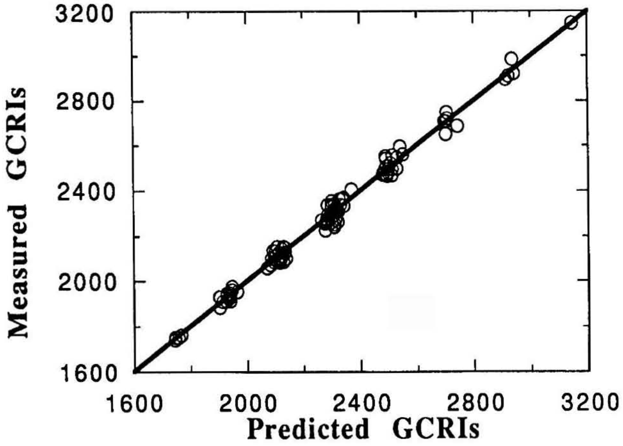

Fig. 3. Plot of the measured GCRIs versus the predicted GCRIs obtained for 115 PCDF isomers.

and predicted GCRIs versus PCDD isomers. Figure 5 shows the same plot for PCDF isomers. These plots indicate that the errors in the predicted data tend to be almost uniform over the range of isomers investigated, which is a desirable result in regression analysis. In the present work, the GCRI data of PCDDs and PCDFs are predicted by a multiple linear regression procedure coupled with a new combination set of descriptors including the electron affinities which would strongly influence liquid phase interactions of PCDDs and PCDFs having chlorine atoms of high electronegativity.

We may expect that regression procedures based on the same set of descriptors as used in this work are useful for prediction of the GCRI data of other classes of polychlorinated environmental chemicals. In this case, of course, different regression coefficients will be needed to predict the GCRIs measured with different column-program combinations. Accordingly, to make full use of the regression method, it is desirable for researchers to have the GCRI data of several different isomers measured on the column of interest so that regression can be used to obtain the best available prediction result.

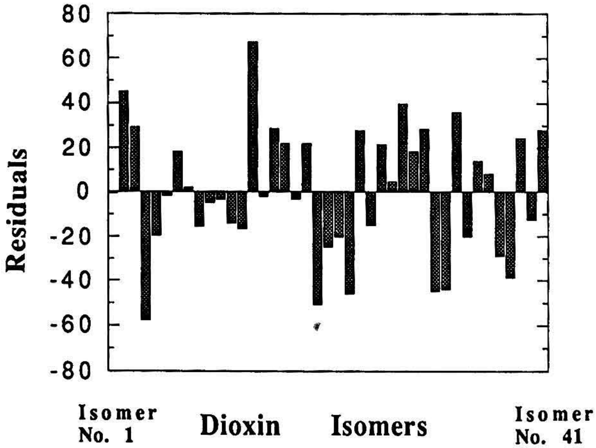

Fig. 4. Plot of the residuals versus the PCDD isomers.

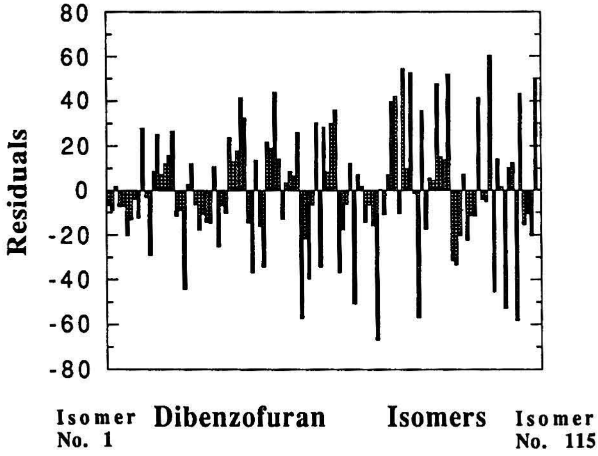

Fig. 5. Plot of the residuals versus the PCDF isomers.

Acknowledgment — The authors are grateful to Dr. Y. Inoue of the Green Cross Central Laboratory for his skillful cooperation in the program installment. Thanks are also due to Dr. H. Mori of the Shimazu Instrumental Analysis Center for his useful comments on the retention data.

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Environment International, Vol. 19, pp. 211-212, 1993
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LETTER TO THE EDITOR

IMPLICATIONS FOR DISEASE MISCLASSIFICATION IN EPIDEMIOLOGICAL STUDIES OF LUNG CANCER RISK FOR NONSMOKERS EXPOSED TO ENVIRONMENTAL TOBACCO SMOKE

Dear Editor:

The U. S. Environmental Protection Agency (EPA) appears to have diminished or dismissed the potentially significant role of disease misclassification in its review of lung cancer risk in nonsmokers reportedly exposed to environmental tobacco smoke (ETS). After reviewing 31 epidemiological studies of lung cancer risk in nonsmokers married to smokers v. those married to nonsmokers (USEPA 1992), EPA concluded that the statistics support the conclusion of a significant risk for nonsmokers exposed to ETS. Adjustments were made for potential misclassification of smoker status, but EPA made no attempt to adjust for potential disease misclassification, which is more likely to result in overestimation than underestimation of relative risk.

Disease misclassification arises when "lung cancer cases" are not primary lung carcinomas but are secondary cancers that have metastasized to the lung from primary tumors originating in other body tissues. Definitive diagnosis of primary lung cancer requires histological or cytological examination of lung tissue.

Diagnoses based on other than histological or cytological examination are equivocal, at best. American Cancer Society researchers noted (Garfinkel et al. 1985) one U.S. study in which 13% of hospital cases were found to be improperly identified as primary lung cancers.

The EPA Review Draft acknowledges the possibility of disease misclassification in epidemiological studies, commenting that it creates "bias toward the null" without further explanation or acknowledgement that such bias is not consistent in the direction of bias nor in magnitude from study to study.

Relative risk in epidemiological studies is determined from the data arrayed as follows:

Lung Cancer Present	ETS Exposed	
	Yes	No
Yes	a	b
No	c	d

with the odds ratio for case-control studies calculated from the formula, OR = ad/bc, and the relative risk for cohort or prospective studies from the formula, RR = (a/a+c)/(b/b+d). (For editorial simplicity, the term relative risk is often used for both kinds of studies and determinations.)

The potential effect of disease misclassification can be illustrated in the study of Hirayama (1984) in Japan, which was among the earliest of the epidemiological assessments said to find lung cancer risk in nonsmokers married to smokers. Hirayama (1984), along with the early Greek study (Trichopoulos et al. 1981) were the only studies in the data bases of the National Research Council (NRC 1986) and the Surgeon General's (USSG 1986) reports to claim statistically significant increased risk for nonsmokers married to smokers.

The Hirayama study was based on 91 540 death certificates, of which 200 reportedly were for nonsmokers who had died of lung cancer. Twenty-one (10.5%)of the certificates reported cause of death determined by autopsy, but the type of lung cancer was not specified, and there is no basis for believing that many were histologically or cytologically confirmed as primary lung carcinomas. For the remaining 179 (89.5%) cases, no basis for the classification of death was reported, indicating that at least 89% and up to 100% of the lung cancer cases in Hirayama's study are of questionable disease classification. The Surgeon General's Report (USSG 1986) noted the potential for disease misclassification with the comment that "Hirayama was unable to assess the accuracy of the diagnoses listed on the death certificate[s]."

Assessing the Hirayama data from the following array

Lung Cancer Present	ETS Exposed	
	Yes	No
Yes	163	37
No	69 482	21 858

EPA (USEPA 1992) reported a crude relative risk of 1.38 (90% C.I. 1.03-1.87). There is potential disease misclassification, however, for all 200 lung cancer cases, with more than four and one-half times as many cases among those exposed to ETS than among those not exposed.

If as few as four of the 163 lung cancer cases exposed to ETS were disease misclassified—i.e., were not primary lung carcinomas—the relative risk would be a statistically nonsignificant 1.34 (C.I. 0.99-1.71).

Of the 31 epidemiological studies in the data base of the EPA Review Draft, all lung cancer cases of 12 studies were reported to have been histologically or cytologically confirmed. In 14 studies, from 2% to 100% of the lung cancer cases had not been definitively confirmed, while in 5 studies, the method and extent of verification were not reported.

Among the 27 case-control studies, ten had 10% or more of lung cancer cases not definitively confirmed as primary carcinomas, including 45 (83%) of 54 cases in the Liu study, 40 (43%) of 94 cases in Akiba, 14 (35%) of 40 cases in Trichopoulos, 108 (26%) of 417 cases in Wu-Williams, and 46 (19%) of 246 cases in Gao, for a total of 253 (30%) of 851 "lung cancer cases" not confirmed as primary. For all case-control studies where the extent of diagnosis confirmation was established, EPA data show 302 lung cancer cases were not definitively confirmed.

Of the cohort or prospective studies, none of the 200 lung cancer cases in the Hirayama study were known to have been confirmed as primary, and the Review Draft notes the absence of information on the other three cohort studies. It also notes that in 10 studies "secondary lung cancers" had not been excluded.

The EPA Review Draft shows 64% of the cases were classified as exposed to ETS, so that there may be nearly twice the likelihood of disease misclassification among "cases" classified as exposed to ETS as among those not exposed. However, any assumptions about the distribution of disease misclassifications in specific studies or in the overall data base would be entirely speculative and insupportable.

The failure to give appropriate consideration in the EPA Review Draft to the significant potential for disease misclassification reduces confidence in risk estimates derived from the data and raises serious questions about public health policies based on such studies.

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This review was conducted at the request of The Tobacco Institute; the statements expressed herein are solely those of the author.

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Environment International, Vol. 19, pp. 213-215, 1993
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BOOKS

Advances in Ecological Research. Vol. 21. M. Begon, A.H. Fitter, A. Macfadyen, eds. Academic Press, London, U.K.; 1991.403 pp. (ISBN 0-12-013921-9) £42.50/$89.00 hardcover.

This is Volume 21 of a series of books dealing with ecological research. This volume contains five reviews. One reviewer describes the origin and spread of the salt marsh grass *Spartina anglica*. The result of a hybridization at the close of the last century, this genetically uniform species has been extremely successful in its particular niche and has a fascinating biology. A second reviewer stresses the importance of the interaction between the gene and the environment in life history theory in contrast to emphasis on the resource constraints of the optimization approach. In another paper, Chanway and his colleagues examine the evidence for the importance of interactions between plants and microorganisms in the rhizosphere in determining the outcome of plant competition and the establishment of community structure. Finally, mycorrhizal associates of plants and the diversity of tropical soils are reviewed. This book is recommended as a library reference.

Ceramic Transactions. Nuclear Waste Management IV. George G. Wicks, Dennis F. Bickford, and L. Roy Bunnell, eds. The American Ceramic Society, Inc., Westerville, OH; 1991. 799 pp. (ISBN 0-944904-45-9) hardcover.

This volume contains the text of papers presented at the 1991 Conference of the American Ceramic Society. Although the title implies the inclusion of chemical waste, the symposium was overwhelmingly dedicated to nuclear waste. A chapter of the volume is dedicated to microwave applications in waste management. Like its predecessors, this volume contains papers of high scientific quality and those of less significance, making it necessary for the reader to critically evaluate the papers.

The Chemical Industry—Friend to the Environment. J.A.G. Drake, ed. Royal Society of Chemistry, Cambridge, U.K.; 1992. 192 pp. (ISBN 0-85186-477-5) £37.50 hardcover.

"The Chemical Industry—Friend to the Environment?" was a symposium organised by the Royal Society of Chemistry of the U.K. This volume contains papers presented at that symposium. The public has mixed views about the Chemical Industry. People appreciate the material comforts the industry provides, such as textiles, ceramics, steel, specialty chemicals, drugs, and prosthetics. However, many people feel that their comfort is spoiled by the chemical poisoning of the environment through slag heaps, beaches, and countryside littered with nonbiodegradable unsightly plastic containers, poor air quality through NO_x, CO_2 and chlorofluorocarbon emissions and nuclear waste. The occasional spillage of hazardous chemicals through road, rail, and sea accidents increases the distrust of the industry. The majority of these topics are addressed in this volume. Although there is an agreement that chemical waste will always be produced, determining the fine line between what are acceptable and what are potentially dangerous thresholds is a continuing challenge to both the industry and the public. Recycling has gone beyond the fashionable stage and is now a serious option for plastics. Plastics must be recycled, used as a fuel, or be biodegradable. The idea that the polluter must pay is receiving general acceptance, but not so readily accepted is the notion that the costs of cleanup may have to be reflected in the price of consumer goods. Emergency preparedness for the chemical industry, much like the system used in nuclear power plants is now being seriously considered by large chemical establishments. This book is recommended as a personal copy.

Neurotoxicity. Identifying and Controlling Poisons in the Nervous System. U.S. Congress, Office of Technology Assessment. Van Nostrand Reinhold, New York; 1992. 361 pp. (ISBN 0-442-01047-8) £36.50 hardcover.

This report is a comprehensive review of the adverse effects of exposure to certain chemicals. There has been recent evidence linking exposure to certain chemicals with Parkinson's, Alzheimer's, and Lou Gehrig's disease, as well as disorders in fetuses, children, the elderly, and workers in industry and agriculture. It's clear that neurotoxic substances found on the job and in the home, including paint, pesticides, medicines, and lead, not to mention illegal drugs, pose serious threats to public health. This report defines neurotoxicity, explores how neurotoxins affect the nervous system, and identifies who is at risk. The book reviews current research, testing, monitoring, and regulatory programs conducted by U.S. agencies. Options for action are explored in terms of broad policy issues, including effectiveness of the regulatory framework, availability of trained research and health care professionals, communication of information to workers and the public, and adequacy of international programs. Classes of neurotoxic substances examined include industrial chemicals and solvents; pesticides such as organophosphorus and carbamate insecticides; therapeutic drugs; substance drugs such as cocaine, heroin, and PCP; foods; food additives; cosmetic ingredients; and naturally occurring substances such as lead and mercury. A crucial section on assessing and managing risk points out that although concerns about carcinogenicity have dominated discussions of risk from toxins, adverse effects on the nervous system may pose an equal or greater danger. Economic considerations associated with testing and regulatory programs are also evaluated.; so is an examination of international regulatory programs. An examination of international regulatory and research activities outlines neurotoxicology breakthroughs in the U.S., Canada, England, Italy, Australia, Japan, and elsewhere. Finally, significant case studies are recounted that deal with exposure to lead, pesticides in agriculture, and organic solvents in the workplace. This book is highly recommended as a reference in libraries and as a personal copy.

Nuclear Engineering. Theory and Technology of Commercial Nuclear Power. 2nd Ed. Ronald Allen Knief. Hemisphere Publishing Corporation, Bristol, PA; 1992. 770 pp. (ISBN 1-56032-089-3) $59.50 softcover.

This textbook resulted from the author's teaching at the University of New Mexico. Of particular interest are sections related to environmental protection. These are radiation effects (pp. 72-96), low level radioactive waste (pp. 567-571), and high level waste (pp. 573-594). In these, the author relies upon expressions such as Maximum Permissible Concentrations (MPC) and other outdated concepts. Despite its shortcomings on environmentally related issues, this textbook is recommended as a desk copy.

Pesticide Application Methods. 2nd ed. G.A. Matthews. Longman Scientific & Technical, Essex, England; 1992. 405 pp. (ISBN 0-582-40905-5) soft-cover.

The application of pesticides is a vital factor in reducing crop loss and is a component of integrated pest management. However, the misuse and improper use of pesticides are environmental issues of primary concern. This book, now in its second revised and enlarged edition, provides information on the different types of application techniques and how they should be used to ensure efficient and effective pesticide control. Detailed information is provided on the role of chemical control in crop protection, discussing targets, formulations and droplets, spray quality and the choice of nozzles, improvements in the design of new equipment, safety precautions, and maintenance issues. This book is highly recommended as a reference book for libraries and as a desk copy for pesticide users.

Plastic Wastes. Management, Control, Recycling, and Disposal. U.S.E.P.A., T. Randall Curlee and Sujit Das. Noyes Data Corporation, Park Ridge, NJ; 1991. 478 pp. (ISBN 0-8155-1265-1) $65 hard-cover.

This book is a reprint of a report prepared by Oak Ridge National Laboratory for the U.S. Environmental Protection Agency. The original report is available from the U.S. National Technical Information Service in Springfield, VA. This comprehensive review assembles in one volume the strategies for managing plastic waste and is recommended as a desk copy and as a reference for libraries.

Scientific Basis for Nuclear Waste Management XV. Claude G. Sombret, ed. Materials Research Society, Pittsburgh, PA; 1992. 751 pp. (ISBN 1-55899-151-4) hardcover.

This volume contains the proceedings of the Fifth International Symposium on the Scientific Basis for Nuclear Waste Management held in November 1991 in Strasbourg, France. The papers received a technical review prior to acceptance. Like its previous volumes, this book contains a wealth of information on glass and ceramics as materials for nuclear waste. Of particular interest is a chapter on natural analogues containing papers on the behavior of uranium ore, OKLO reactor (a natural phenomenon from a chain reaction that occurred several million years ago), and a study of naturally occurring materials in Japan, Mexico, and Brazil.

Beyond Superfailure. America's Toxics Policy for the 1990s. Daniel Mazmanian and David Morell. Westview Press, Boulder, CO; 1992. 278 pp. (ISBN 0-8133-1466-6) softcover.

The Diversity of Life. Edward O. Wilson. Harvard University Press, Cambridge, MA; 1992. 424 pp. (ISBN 0-674-21298-3) $29.95 hardcover.

Dynamics and Control in Nuclear Power Stations. A Symposium in Print organized by the British Nuclear Energy Society. M.H. Butterfield, ed. Thomas Telford, London, U.K.; 1991. 203 pp. (ISBN 0-7277-1661-1) £60.00 softcover.

Ethics of Environment and Development. Global Challenge and International Response. J. Ronald Engel and Joan Gibb Engel, eds. Belhaven Press, London, U.K.; 1992. 264 pp. (ISBN 1-85293-2511) £14.99 softcover. Originally published in 1990 and republished in softcover in 1992.

Vital Signs 1992. The Trends that are Shaping our Future. Lester R. Brown, Christopher Flavin, and Hal Kane. Worldwatch Institute, Washington, D.C.; 1992. 131 pp. (ISBN 0-393-30974-6) $10.95 softcover.

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Article: Repace, J.L.; Lowrey, A.H. A.quantative estimate of nonsmokers' lung cancer from passive smoking. Environ. Int. 11:3-22; 1985.

Report: NIH (National Institutes of Health). Report of the National Institutes of Health ad hoc working group to develop radioepidemiological tables. NIH 85-2748. Washington, D.C : U.S. Department of Health and Human Services; 1985.

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Volume 19 Number 2 1993

INDEXED IN Current Contents, BIOSIS Database, Eng. Ind. Monthly and Author Ind., Environ. Per. Bibl., CABS, Energy Res. Abstr., Energy Data Base, Excerpta Medica, Geo. Abstr., Sci. Cit. Ind., and Biology and Environmental Sciences

ISSN 0160-4120

(326)

0160-4120(1993)19:2;1-#