

Distributions, associations, and partial aggregate exposure of pesticides and polynuclear aromatic hydrocarbons in the Minnesota Children's Pesticide Exposure Study (MNCPEs)

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The Minnesota Children's Pesticide Exposure Study (MNCPEs) provides exposure, environmental, and biologic data relating to multipathway exposures of children for four primary pesticides (chlorpyrifos, malathion, diazinon, and atrazine), 14 secondary pesticides, and 13 polynuclear aromatic hydrocarbons (PAHs). Monitoring was performed on a probability-based sample of 102 children aged 3–12 in Minneapolis/St. Paul and in a nearby rural area (Goodhue and Rice counties). This paper provides estimated distributions of this population's exposures and exposure-related measurements and examines associations among the various measures via rank (Spearman) correlations. In addition, it provides some aggregate and cumulative exposure estimates for pesticides, and compares the relative intakes from inhalation and dietary ingestion. Intakes for the four primary pesticides appeared to come principally from the ingestion rather than the inhalation route; this was clearly true for chlorpyrifos but was less certain for the other three primary pesticides because of their higher degree of nondetects. Solid food rather than beverages was clearly the main contributor to the ingestion intake. Despite the dominance of the ingestion route, the urinary metabolite of chlorpyrifos exhibited a stronger association with the air measurements than with the dietary measures. Personal-air samples exhibited strong rank correlations with indoor air samples for chlorpyrifos, malathion, and diazinon (0.81, 0.51, and 0.62, respectively), while personal-air atrazine levels correlated well with outdoor levels (0.69); personal-air diazinon levels also correlated well with outdoor levels (0.67). For the PAHs, many significant associations were evident among the various air samples and for the air samples with the dust samples, especially for those compounds with consistently high percent measurable values (particularly fluoranthene, phenanthrene, and pyrene). *Journal of Exposure Analysis and Environmental Epidemiology* (2003) 13, 100–111. doi:10.1038/sj.jea.7500261

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Introduction

In the field of environmental health, individuals and subgroups of populations are considered to be at potentially greater health risk when they are more biologically susceptible and exposed to hazardous substances. Among those who are both more susceptible and more exposed (Sexton, 1997) are children, a group that is recognized as a particularly vulnerable subpopulation to many environmental hazards (NRC, 1993). Their behavioral patterns, personal

hygiene, and diets may yield greater exposures to contaminants in the environments where they live and play. Moreover, their rapidly developing organ and immune systems may put them at greater risk from these exposures relative to adults and their relative dose per body weight may be greater than for adults.

The National Research Council (NRC) recommended that estimates of total pesticide exposure should account for all important sources and pathways of pesticide intake (aggregate intake), should reflect the unique characteristics of the diets of infants and children, and should consider exposures to multiple pesticides having a common end point of toxicity (cumulative intake). Subsequently, the Food Quality Protection Act of 1996 (FQPA) was passed by Congress that requires several factors to be considered in making risk assessments as part of the tolerance setting procedure. These factors include the special biological susceptibility of children, cumulative effects of exposures to pesticides having a common mode of toxicological action, and aggregate exposures occurring across different pathways.

1. Abbreviations: BW, body weight; EPA, US Environmental Protection Agency; FQPA, Food Quality Protection Act; MNCPEs, Minnesota Children's Pesticide Exposure Study; NHEXAS, National Human Exposure Assessment Survey; NRC, National Research Council; OP, organo-phosphate; PAH, polynuclear aromatic hydrocarbon; PAI, partial aggregate intake; PCI, partial cumulative intake

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The Minnesota Children's Pesticide Exposure Study (MNCPEs) was designed to collect exposure, environmental, and biologic data relating to multipathway pesticide exposures of children for four primary pesticides: chlorpyrifos, malathion, diazinon, and atrazine. The MNCPEs was a special study developed as part of the National Human Exposure Assessment Survey (NHEXAS) (Sexton et al., 1995; Pellizzari et al., 1995). Monitoring was performed on a probability-based sample of 102 children aged 3–12 in Minneapolis/St. Paul and in a nearby rural area (Goodhue and Rice counties). In addition to the four primary pesticides, similar data were obtained (for a subset of sample types) for 14 secondary pesticides and for 13 polynuclear aromatic hydrocarbons (PAHs).

The goals of the MNCPEs directly support the needs for performing aggregate and cumulative exposure estimates for pesticides, specifically organophosphorus pesticides as directed by FQPA. One of these goals was to estimate distributions of the children's exposures and of exposure-related measurements for pesticides and PAHs. A second goal was to estimate and investigate associations among the various measures. This paper addresses these two goals and, in addition, provides some distributional information on the children's aggregate and cumulative intakes of pesticides.

Methods

The MNCPEs was conducted in three phases: (1) identification of households with age-eligible (3–12 years) children; (2) screening of 308 households using a questionnaire and an inventory of pesticide product storage and usage; and (3) intensive monitoring to estimate multipathway pesticide exposures for 102 selected households/children. The final probability-based sample of 102 involved oversampling of the nonurban homes and of homes indicating higher product usage. The survey design, the target analytes measured, the collection and analytical methods and protocols used for various sample types, quality control and assurance procedures, calculation of population-based sample weights, and data analysis and modeling methods have been previously described (Quackenboss et al., 2000). Adgate et al. (2000) describe some of the issues involved in the conduct of the MNCPEs.

The collection of field samples was performed by one organization. Four laboratories were responsible for the analysis of samples for pesticides while all PAH analysis was performed in one laboratory. Quality control data were provided and included in the database; Pellizzari et al. (2002) addressed the precision and bias of the MNCPEs data and provided summaries of the analytic methods used in this study.

The various types of samples obtained were:

- Direct exposure measurements: a 6-day integrated-average personal-air sample, and 4-day integrated food and beverage samples, obtained as duplicate-diet samples.
- Environmental measurements: indoor and outdoor air samples, and drinking water, surface wipe dust, and soil samples.
- Biological marker measurement: urine samples (analyzed for pesticide metabolites).

Table 1 summarizes the types of samples acquired and indicates the units for the concentration or loading measurements. Note that not all measurements were obtained for the secondary pesticides or sample types collected for the PAH analysis.

Table 2 shows estimated distributions of demographic characteristics for the sample (unweighted) and the target population (weighted). These results were obtained from a baseline questionnaire administered to 173 potential participants; results are shown for all of these respondents and for the final set of monitoring respondents (hereafter called participants). Given the small sample sizes, it is clear that there are no great disparities between the weighted and unweighted frequency distributions. The exception to this was for the urban/rural classification; however, that difference results from the survey design, which involved extensive oversampling of the rural population to obtain an adequate sample size for that subpopulation.

Tables 3 and 4 indicate the target number of observations and the actual number of usable observations, by chemical and medium. Table 3 shows these results for the four primary pesticides, while Table 4 is for the remaining chemicals. Note that nine to 11 media are represented for the primary chemicals (Table 3), while only a smaller subset of media are represented for the nonprimary chemicals (six for the remaining pesticides and five for the PAHs). The target numbers (near the top of each table) reflect the study design:

- For most media, samples were required of all participants; for those media with target sample sizes of 102 households or children, weighted data analyses are theoretically possible.³
- Some nonresponse was allowed for personal-air and urine samples (target sample sizes of 74 and 90, respectively). However, after additionally compensating for nonresponse via weight adjustments for the groups of participants providing these sample types, these groups, like the sample of 102, were regarded as probability samples of the target population; hence, weighted data analyses for these sample types were regarded as theoretically feasible.

³A weighted analysis makes use of sampling weights, which reflect the differential selection probabilities of participants. It allows the resultant estimates (e.g., of means or medians or proportions) to apply to the target population, rather than to just the sample of participants, and also allows for standard errors of the estimates to be generated that properly account for the unequal weighting and other features (e.g., stratification, clustering) of the sampling design.

Table 1. Types of samples for pesticide and PAH measures.

Medium	Type of sample	Time frame (days)	Units	Primary pesticides	Secondary pesticides	PAHs
Personal air conc.	6-Day IA ^a	1-7	ng/m ³	✓	✓	✓
Indoor air conc.	6-Day IA	1-7	ng/m ³	✓	✓	✓
Outdoor air conc.	6-Day IA	1-7	ng/m ³	✓	✓	✓
Food -conc. all solid foods	4-Day IA (Dup. Diet)	3-6	µg/kg	✓ ^b	✓ ^b	✓
Beverage-conc.	4-Day IA (Dup. Diet)	3-6	µg/kg	✓	✓ ^c	
Food + beverage-conc.	4-Day IA (calculated)	3-6	µg/kg	✓	✓ ^c	
Drinking water conc.	Grab sample	4	µg/l	✓	✓	
Surface dust loading	Wipe	4	ng/cm ²	✓		✓
Soil conc.	Surface soil, grab sample	4	µg/kg	✓		
Urine-Day 3	Morning void	3	µg/l	✓ ^d		
Day 5	Morning void	5		✓ ^d		
Day 7	Morning void	7		✓ ^d		

Primary pesticides = chlorpyrifos, malathion, diazinon, atrazine.

^aIA = integrated average

^bFor pesticides, calculated from two sample analyses, one on "high-pesticide foods" and one on "remaining" foods.

^cOnly for seven of the 14 secondary pesticides.

^dFor metabolites of chlorpyrifos, malathion, and atrazine.

Table 2. Percentage distributions of demographic characteristics, based on baseline questionnaire responses.

Characteristic	Categories	All respondents (N ≈ 173)		Monitored participants (N ≈ 102)	
		Unweighted	Weighted	Unweighted	Weighted
Gender	Male	45.7	41.7	47.0	42.1
	Female	54.3	58.3	53.0	57.9
Age	3-5 years	24.9	26.7	27.7	30.1
	6-9 years	45.0	39.0	40.6	37.0
	10-13 years	30.2	34.3	31.7	32.9
Household income	<\$50 K	37.3	36.5	34.3	35.9
	\$50 K-\$75 K	42.0	45.1	48.5	52.0
	≥\$75 K	20.7	18.4	17.2	12.1
Race	White	86.7	85.0	85.3	84.7
	Non-White	13.3	15.0	14.7	15.3
House location	Urban	69.4	93.3	70.6	93.3
	Rural ^a	30.6	6.7	29.4	6.7

^aRural area was oversampled.

Table 3. Number of observations, by chemical and medium — for four primary pesticides.

Chemical	Pers air	Indr air	Outdoor air	Food	Bev	Drink water	Surf dust	Soil	Urine metabolites day 3/day 5/Day 7 ^a
Target n ^b	74C	102H	52H	102C	102C	55H	102H	102H	90C
Chlorpyrifos	60	82	52	96	101	55	99	102	87/87/89
Malathion	61	88	51	96	101	55	99	102	88/89/89
Diazinon	48	75	52	101	101	55	99	102	
Atrazine	42	60	46	100	101	55	99	102	88/89/89

Shaded cells indicate that weighted analysis is not recommended.

^aMetabolites are 3,5,6-trichloro-2-pyridinol; malathion dicarboxylic acid; atrazine mercapturate.

^bRefers to number of children (C) or households (H) targeted for sample collection.

- Only subsets of participants (not randomly selected) provided outdoor air and drinking water samples; hence weighted data analyses were not feasible for those media. This is reflected by the shading of all cells in Tables 3 and 4 for these media.

The other shaded cells in Tables 3 and 4 indicate those cases where weighted data analyses were deemed inappropriate (though theoretically feasible), either because the data losses resulted in representation of less than 85% of the target population or because of excessive variability in the sampling

Table 4. Number of observations, by chemical and medium — for secondary chemicals.

Chemical	Pers air	Indr air	Outdoor air	Food	Bev	Drink water	Surf dust
Target <i>n</i> ^a :	74C	102H	52H	102C	102C	55H	102H
<i>cis</i> -Permethrin	64	89	51	100		55	
4,4'-DDT	68	97	52	55	101	55	
Heptachlor	69	98	52	101	101	55	
4,4'-DDE	62	97	52	97	101	55	
<i>cis</i> -Chlordane	69	98	52	101	101	55	
<i>trans</i> -Permethrin	68	96	51	101		55	
Metolachlor	66	92	51	101		55	
<i>trans</i> -Chlordane	69	98	52	101	101	55	
Dieldrin	63	89	52	100	101	55	
Alachlor	65	84	52	86		55	
Endosulfan I	57	91	51	101		55	
Dichlorvos	54	66	52	101		55	
4,4'-DDD	69	96	52	53	101	55	
Simazine	66	95	52	100		55	
Benzo(a)pyrene	60	92	52	69			102
Benzo(a)anthracene	67	97	52	71			102
Acenaphthylene	16	22	42	67			102
Anthracene	67	95	51	71			102
Chrysene	68	98	52	71			102
Benzo(e)pyrene	67	97	52	58			102
Benzo(ghi)perylene	69	98	52	76			102
Benzo(k)fluoranthene	63	93	51	67			102
Fluoranthene	69	98	51	72			102
Phenanthrene	69	98	52	76			102
Pyrene	69	98	51	73			102
Indeno{1,2,3-cd}pyrene	68	98	52	76			102
Benzo(b)fluoranthene	65	97	52	70			102

Shaded cells indicate that weighted analysis is not recommended.

^aRefers to number of children (C) or households (H) targeted for sample collection.

weights (coefficient of variation >150%) among the responding participants.

Since weighted analyses did not appear appropriate for many media/chemical combinations, it appeared unrealistic to perform some weighted analyses and some unweighted analyses; hence, for consistency throughout this paper, only unweighted analysis results are reported. As noted above (see Table 2), severe biases relative to the target population are not expected by ignoring the sampling weights, except possibly in those cases where large rural/urban differences (e.g., in concentration levels) might exist.

The summary statistics that are reported herein are therefore quite simple:

- the percent measurable (percent of samples above the detection or quantification limit)
- various percentiles (e.g., median or 90th percentile of participants' concentrations, or loadings),
- Spearman (rank) correlations.⁴

⁴Rank correlations are preferred since they are insensitive to extreme values and do not depend on the particular measurement scale (e.g., concentrations or logarithms of concentrations). The correlation between two measures is not reported if either measure has less than 10% measurable values.

In order to assess the relative importance of the routes of exposure, it is necessary to convert the exposure units to comparable intake units; unfortunately, no direct measures of dermal exposure were available. For the inhalation route, intakes were computed by multiplying the personal-air concentrations by an inhalation rate value obtained from the Exposure Factors Handbook (Vol. I, pp. 5–24, 1997) and by dividing by the participant's reported body weight (BW). The inhalation rates used were the following:

For the ingestion route (dietary portion only), the quantity of the duplicate-diet food and beverage samples were first multiplied by their respective concentrations (e.g., kg food × μg pesticide/kg food) and then added to produce an estimate of the amount of chemical ingested. This was then divided by the number of days represented by the sample (usually 4) and then by the participant's reported BW. Intake units for both routes were converted to ng/day/kg BW; intakes not adjusted for BW were also computed.

Results and discussion

Chlorpyrifos

Table 5 provides summary statistics (sample size, percent measurable, median, and 90th percentile) for chlorpyrifos

Table 5. Chlorpyrifos distributions and metabolite correlations.

Medium	Units	Distributional statistics				Spearman corr. with urine metabolite		
		N	% Meas	Median	90th Percentl	Day 7	Days 5 and 7	Days 3, 5 and 7
Personal air conc.	ng/m ³	60	95	1.577	11.7	0.42**	0.38**	0.32*
Indoor air conc.	ng/m ³	82	91	1.742	16.17	0.33**	0.30*	0.21
Outdoor air conc.	ng/m ³	52	10	b	0.071	0.09	0.07	0.17
Solid food conc.	µg/kg	96	57	0.532	1.255	0.19	0.12	0.12
Beverages conc.	µg/kg	101	0	b	b	n	n	n
Food + beverages conc.	µg/kg	96	57	0.202	0.585	0.21	0.15	0.17
Drinking water conc.	µg/l	55	2	b	b	n	n	n
Surface dust load	µg/cm ²	99	62	1.154	1.330	-0.16	-0.14	-0.20
Soil conc.	µg/kg	102	3	b	b	0.11	0.18	0.15
Solid food intake	ng/day	96	57	263	838	0.22*	0.13	0.15
Food + beverage intake	ng/day	96	57	263	838	0.22*	0.13	0.15
Personal air intake	ng/day	60	95	18.3	126	0.42**	0.35**	0.29*
Partial aggregate intake	ng/day	57		304	648	0.29*	0.28*	0.26
Food + beverage intake	ng/day/kg BW	95		10.3	29.5	0.19	0.11	0.12
Personal air intake	ng/day/kg BW	59		0.648	4.952	0.39**	0.37**	0.32*
Partial aggregate intake	ng/day/kg BW	56		11.7	30.7	0.14	0.21	0.15
3,4,6-trichloro-2-pyridinol								
Urine conc. — day 3	µg/l	87	93	7.2	18.1	0.29**		
Urine conc. — day 5	µg/l	87	87	6.7	18.9	0.35**		
Urine conc. — day 7	µg/l	89	97	8.3	21.1			

b = value below detection or quantitation limit.

n = not calculated because of low percent measurable (<10%).

*Statistically significant at the 0.05 level.

**Statistically significant at the 0.01 level.

that summarize the distributions for the various media; results are presented for concentrations and loadings and, where possible, for intakes and partial aggregate intakes (PAIs), an expression of aggregate exposure. The PAIs represent the total across the inhalation and ingestion routes and are referred to as “partial” since intakes associated with both dermal and nondietary ingestion are not included. Similar distributional statistics are shown near the bottom of the table for the urine concentrations of its metabolite (3,4,6-trichloro-2-pyridinol). The right-hand part of the table shows the Spearman correlations between the row measurement and the metabolite concentrations. The correlations are shown for the day-7 urine measure, which was made near the end of the monitoring period, for the day-5 plus day-7 average, and for the day-3 plus day-5 plus day-7 average. As a result of the timing of the food collection and the approximately 1-day half-life of chlorpyrifos in children (Hines and Deddens, 2001), one might expect better correlations for food and beverage measurements with the day-7 or the day-5 plus day-7 metabolite measures.

Chlorpyrifos in solid food was only measurable for 57% of the participants, as compared to 95% measurable for the personal-air exposures; however, a comparison of the intakes in Table 5 reveals that ingestion is clearly the more dominant route of exposure. This is also evident from Table 6, which shows the median intakes separately by route of exposure

and by area (urban/nonurban). The solid foods are the source of the dietary exposure, as the beverage samples all were nondetects (and only one tap-water sample exhibited a measurable concentration). For those 56 participants for whom both an inhalation and an ingestion intake for chlorpyrifos could be determined, the median PAI was 11.7 ng/day/kg BW and the 90th percentile was 30.7 ng/day/kg BW. The vast majority of the intake was from the ingestion route for most individuals: the 10th percentile, median, and 90th percentiles of the distribution of percent ingestion being 59, 92, and 99%, respectively.

The three 3,4,6-trichloro-2-pyridinol concentrations in urine — on days 3, 5, and 7 of the participants' monitoring periods — all appear to have similar distributions, with detectable amounts in about 90% of the samples; however, the correlations of the day-3 *versus* the day-7 measurements (0.29) and the day-5 *versus* the day-7 measurements (0.35) suggest that there is substantial within-person (i.e., day-to-day) variability in the metabolite levels.

Despite the dominance of the food intakes relative to the air intake, the personal- (and indoor) air measurements tended to show the strongest associations with the urine metabolite measures. When the correlations were statistically significant, the day-7 metabolite measure tended to show somewhat better (larger) correlations than the other two.

Table 6. Chlorpyrifos intakes, for urban (U) and non-urban (R) areas.

Quantity	Area	<i>n</i>	% Meas.	Median (ng/day/kgBW)
Inhalation intake	R	18	90	0.4
	U	40	98	0.9
Ingestion intake	R	27	54	12.3
	U	68	59	10.3

Table 7 presents the Spearman correlations for the various media measurements (media with less than 10% detects were excluded). It shows a strong positive and highly significant association between personal-air exposures and indoor-air concentrations (correlation of 0.81). There also appears to be some indication of a negative association between the air measurements and the dust measurements. The dietary measurements did not exhibit any significant associations with the other measures.

Malathion

Table 8 presents the media distributional results for malathion in the various media and for malathion dicarboxylic acid in urine. Personal air and food exposure measurements had similar percent measurable values (54 and 46%, respectively). Except for air and food, the other media exhibited low percent measurable values. The metabolite was detected in urine less than 50% of the time; the low correlations (about 0.20) among the metabolite measures on the three different days suggest that there is substantial day-to-day variation in individuals' levels. It should also be noted that the half-life for malathion in humans is 3 h (Feldmann and Maibach, 1974; Gallo and Lawryk, 1991).

As with chlorpyrifos, intake via ingestion seems to dominate the inhalation route (Tables 8 and 9), but none of the environmental or exposure measures exhibited statistically significant Spearman correlations with the urine metabolite concentrations. Among the 56 participants having data on both routes, the median PAI was 70.7 ng/day/kg BW and the 90th percentile was 211 ng/day/kg BW. The percent of the PAI coming from ingestion was very high; for instance, over 90% of the participants had more than 98% of the PAI associated with ingestion.

The Spearman correlations among media (with 10% or more detects) are presented in Table 10. Indoor air malathion concentrations correlated with personal air (0.51, $P < 0.01$) and with solid food (0.25, $P < 0.05$) concentrations; otherwise the intermedia correlations were not statistically significant.

Diazinon

Distributional summaries by media are presented for diazinon in Table 11. Only the air samples had a sufficient

Table 7. Chlorpyrifos: Spearman correlations^a.

	Indoor air conc.	Outdoor air conc.	Solid food conc.	Food + Beverage conc.	Surface dust loading
Personal air conc.	0.81**	0.23	0.06	0.06	-0.18
Indoor air conc.		-0.01	0.11	0.11	-0.29**
Outdoor air conc.			-0.18	-0.16	-0.18
Solid food conc.				0.94**	-0.08
Food + beverage conc.					-0.12

^aCorrelations are not shown for media having < 10% measurable.

*Statistically significant at the 0.05 level.

**Statistically significant at the 0.01 level.

percent measurable to be useful in data analysis (about 2/3 of the personal and indoor samples were measurable). The personal-air concentration measurements exhibited highly significant associations with both the indoor and outdoor air concentrations (Table 12). As a result of the low percent detected for the ingestion route measures, it was difficult to determine which route was the primary contributor to intake.

Atrazine

Table 13 summarizes the distributional results. As indicated by the low percent measurable values (about 20% measurable for the air samples; less than 10% for the food, drinking water, and surface dust samples; and 0% for the beverage and soil samples), the occurrence of atrazine was low. Owing to the low percent measurable values for both air and food samples, the relative importance of the ingestion and inhalation was not discernible. In contrast to chlorpyrifos and malathion, the urinary metabolite (atrazine mercapturate) was only rarely detected, which was consistent with the low occurrence of exposure. At least partly for this reason, none of the environmental or exposure measurements exhibited strong correlations with the metabolite levels. The correlations of PAIs *versus* the urine metabolite concentrations were significant; this is probably indicative of the fact that 19 of the 40 PAIs were actually reported as zero and that the metabolite concentrations were somewhat lower for those individuals than for those with positive PAI values.

The strongest intermedia associations for atrazine, which are summarized in Table 14, were for outdoor air: a 0.69 Spearman correlation with personal-air measurements ($P < 0.01$). This, along with the lack of an indoor *versus* personal-air association and an indoor *versus* outdoor association, suggests a stronger outdoor influence for this chemical than for the prior three.

Secondary Pesticides

Data for the secondary pesticides are summarized over the relevant media in Table 15, which presents the percentage measurable and the median concentration or loading. Since cases with less than 50% detected are indicated by the shaded

Table 8. Malathion distributions and metabolite correlations.

Medium	Units	Distributional statistics				Spearman corr. with urine metabolite		
		N	% Meas	Median	90th Percentl	Day 7	Days 5 and 7	Days 3, 5 and 7
Personal air conc.	ng/m ³	61	54	0.628	2.108	0.18	0.17	0.13
Indoor air conc.	ng/m ³	88	67	1.179	3.380	0.09	0.20	0.17
Outdoor air conc.	ng/m ³	51	12	b	0.089	0.22	0.22	0.13
Solid food conc.	µg/kg	96	46	b	10.22	-0.03	0.20	0.09
Beverages conc.	µg/kg	101	0	b	b	n	n	n
Food + beverages conc.	µg/kg	96	46	b	3.925	-0.09	0.18	0.09
Drinking water conc.	µg/l	55	0	b	b	n	n	n
Surface dust load	ng/cm ²	99	0	b	b	n	n	n
Soil conc.	µg/kg	102	0	b	b	n	n	n
Solid food intake	ng/day	96	46	b	5888	-0.06	0.14	0.06
Food + beverage intake	ng/day	96	46	b	5888	-0.06	0.14	0.06
Personal air intake	ng/day	61	54	7.2	26.1	0.21	0.16	0.12
Partial aggregate intake	ng/day	57		1954	6237	-0.04	0.18	0.19
Food + beverage intake	ng/day/kg BW	95		b	210	-0.11	0.08	0.01
Personal air intake	ng/day/kg BW	60		0.239	0.871	0.19	0.13	0.13
Partial aggregate intake	ng/day/kg BW	56		70.9	211	-0.14	0.07	0.12
Malathion dicarboxylic acid								
Urine conc. — day 3	µg/l	88	43	1	2.6	0.19		
Urine conc. — day 5	µg/l	89	29	1	1.8	0.23*		
Urine conc. — day 7	µg/l	89	36	1	4.3			

b = value below detection or quantitation limit.

n = not calculated because of low percent measurable (<10%).

*Statistically significant at the 0.05 level.

**Statistically significant at the 0.01 level.

Table 9. Malathion intakes, for urban (U) and non-urban (R) areas.

Quantity	Area	n	% Meas.	Median (ng/day/kgBW)
Inhalation intake	R	18	20	0
	U	41	71	0.4
Ingestion intake	R	27	36	66
	U	68	50	79

cells, the medians appearing in such cells fall below detection or quantitation limits and therefore may be imprecise. For the secondary pesticides, the percent measurable values for the personal-air samples varied from 5% for simazine to 86% for *cis*-Permethrin, with eight of the 14 pesticides having more than a 50% measurable values. In general, the pesticide indoor-air samples had percent measurable and median concentration (or loading) values comparable to those of the personal-air samples. Only two of the pesticides had more than 50% measurable values in the food samples and none had over 4% measurable in the drinking water or beverage samples.

Cumulative Intakes for Organo-Phosphate Pesticides

Since the common mechanism of biological action for organo-phosphate (OP) pesticides, cumulative intakes, an

Table 10. Malathion: Spearman correlations^a.

	Indoor air conc.	Outdoor air conc.	Solid food conc.	Food + beverage conc.
Personal air conc.	0.51**	0.31	0.12	0.17
Indoor air conc.		0.06	0.25*	0.19
Outdoor air conc.			0.15	0.13
Solid food conc.				0.93**

^aCorrelations are not shown for media having <10% measurable.

*Statistically significant at the 0.05 level.

**Statistically significant at the 0.01 level.

expression of cumulative exposure, are of interest. Since direct exposure measurements for two routes of exposure for four OP pesticides in the MNCPEs were available, some insight into the distribution of such cumulative OP intakes was possible. In particular, data for chlorpyrifos, malathion, and diazinon were available for personal air, solid food, and beverage samples, and data for dichlorvos were available for personal air and solid food samples. Only a partial cumulative intake (PCI) was calculated, since the dermal route and other OP pesticides (e.g., parathion) were not included, since beverage data were not available for dichlorvos, and since nondietary ingestion was not measured.

Table 11. Diazinon distributions.

Medium	Units	N	% Meas	Median	90th Percentl
Personal air conc.	ng/m ³	48	65	0.275	2.215
Indoor air conc.	ng/m ³	75	68	0.290	3.227
Outdoor air conc.	ng/m ³	52	13	b	b
Solid food conc.	μg/kg	101	3	b	b
Beverages conc.	μg/kg	101	0	b	b
Food + beverages conc.	μg/kg	101	3	b	b
Drinking water conc.	μg/l	55	0	b	b
Surface dust load	ng/cm ²	99	7	b	b
Soil conc.	μg/kg	102	4	b	b
Solid food intake	ng/day	101	3	b	b
Food + beverage intake	ng/day	101	3	b	b
Personal air intake	ng/day	48	65	2.9	28.8
Food + beverage intake	ng/day/kg BW	100		b	b
Personal air intake	ng/day/kg BW	48		0.094	0.776

b = value below detection or quantitation limit.

Table 12. Diazinon: Spearman correlations^a.

	Indoor air conc.	Outdoor air conc.
Personal air conc.	0.62**	0.67**
Indoor air conc.		0.28

^aCorrelations are not shown for media having <10% measurable.

*Statistically significant at the 0.05 level.

**Statistically significant at the 0.01 level.

These PCI distributions are summarized, overall and by route, in Table 16, by presenting the 10th, 50th, and 90th percentiles. Table 16 also summarizes in a similar manner the distribution of the percentage of the total inhalation-plus-ingestion intake attributable to the ingestion route. The upper portion of the table is based on three OP pesticides and those 35 participants having complete data on all three chemicals for both routes. The lower portion is based on four OP pesticides and those 24 participants having complete data on all four chemicals for both routes. The results indicate that the PCI distributions have a large range of values that are highly skewed to the right (i.e., toward higher values). Despite this large variability across participants, it is clear that the vast majority of the intake appears to come from food and beverages, as opposed to inhalation, for virtually all participants.

Polynuclear Aromatic Hydrocarbons

For the 13 PAHs listed in Table 17, all but one had over a 50% measurable rate for personal air. In general, somewhat lower percent measurable values and median values were observed for the indoor and outdoor air samples than for the personal air samples. Food PAH percent measurables ranged from 17 to 99%, while surface dust PAH percent measurables ranged from 3 to 47% across the 13 PAHs.

Fluoranthene, phenanthrene, and pyrene were detected in virtually all of the air and food samples.

Table 18 presents the intermedia Spearman correlations for the PAHs for the five media for which such measures were available — personal air, indoor air, outdoor air, food, and surface dust. As might be expected, the strongest associations tended to occur for those chemicals having the higher percent measurables and tended to occur among the air samples (personal, indoor, and outdoor). For fluoranthene, phenanthrene, and pyrene, statistically significant ($P < 0.01$) correlations of surface dust loadings with personal-air and indoor-air concentrations were also noted. With one exception, and as expected, the food samples exhibited no statistically significant ($P < 0.05$) associations with any of the other media for any of the chemicals; the exception was phenanthrene, with a food-versus-personal-air correlation of 0.31, which was statistically significant at the 0.05 level.

Summary and conclusions

The MNCPEs involved the collection of environmental, exposure, and biologic data relating to multipathway pesticide and PAH exposures of a probability-based sample of 102 children aged 3–12 in Minneapolis/St. Paul and in two nearby rural counties. In addition to the four primary pesticides — chlorpyrifos, malathion, diazinon, and atrazine — data were obtained (for a subset of sample types) for 14 secondary pesticides and for 13 PAHs. Selected percentiles were calculated in order to characterize the various media-specific distributions and intermedia associations were examined through rank (Spearman) correlations. To the extent possible, statistics characterizing aggregate and cumulative exposure (based on intake units) of OP pesticides were also generated. Since no direct dermal exposure

Table 13. Atrazine distributions and metabolite correlations.

Medium	Units	Distributional statistics				Spearman corr. with urine metabolite		
		N	% Meas	Median	90th percentl	Day 7	Days 5 and 7 average	Days 3, 5, and 7 average
Personal air conc.	ng/m ³	42	17	b	26.97	0.15	0.12	0.12
Indoor air conc.	ng/m ³	60	22	b	20.2	0.24	0.22	0.21
Outdoor air conc.	ng/m ³	46	15	b	0.374	-0.12	-0.12	-0.14
Solid food conc.	μg/kg	100	8	b	b	n	n	n
Beverages conc.	μg/kg	101	0	b	b	n	n	n
Food + beverages conc.	μg/kg	100	8	b	b	n	n	n
Drinking water conc.	μg/l	55	4	b	b	n	n	n
Surface dust load	ng/cm ²	99	3	b	b	n	n	n
Soil conc.	μg/kg	102	0	b	b	0.10	0.11	0.09
Solid food intake	ng/day	100	8	b	b	n	n	n
Food + beverage intake	ng/day	100	8	b	b	n	n	n
Personal air intake	ng/day	42	17	b	281	0.15	0.12	0.12
Partial aggregate intake	ng/day	40 ^a		6.1	398	0.43**	0.40**	0.43**
Food + beverage intake	ng/day/kg BW	100		b	b	n	n	n
Personal air intake	ng/day/kg BW	42		b	12.3	0.15	0.12	0.12
Partial aggregate intake	ng/day/kg BW	40 ^a		0.35	14.4	0.44**	0.42**	0.45**
Atrazine mercapturate								
Urine conc. — day 3	μg/l	88	2	b	b	n		
Urine conc. — day 5	μg/l	89	2	b	b	n		
Urine conc. — day 7	μg/l	89	2	b	b			

a = includes 19 cases with zero reported intake.

b = value below detection or quantitation limit.

n = not calculated because of low percent measurable.

*Statistically significant at the 0.05 level.

**Statistically significant at the 0.01 level.

Table 14. Atrazine: Spearman correlations^a.

	Indoor air conc.	Outdoor air conc.
Personal air conc.	0.04	0.69**
Indoor air conc.		-0.14

^aCorrelations are not shown for media having < 10% measurable.

*Statistically significant at the 0.05 level.

**Statistically significant at the 0.01 level.

measurements were obtained, route-specific comparisons of intakes were limited to ingestion and inhalation. While the former intakes could be determined from the data collected in the study, the latter intakes had to employ nominal gender- and age-specific inhalation rates from the EFH.

Intakes for all of the four primary chemicals appeared to come principally from the ingestion rather than the inhalation route; this was clearly true for chlorpyrifos but was less certain for the other three because of their higher degree of non-detects. Solid food rather than beverages was clearly the main contributor to the ingestion intake. Partial cumulative intakes for the OP pesticides, covering the inhalation and ingestion routes to the extent possible, were calculated for each participant having a sufficient amount of data. The

percent of each individual's PCI coming from ingestion was also determined. Distributions summarizing the PCIs and these percentages revealed the clear dominance of the ingestion route over the inhalation route for this group of OP pesticides; for instance, among the 35 participants with adequate data, about half were estimated to have 98% of the PCI coming from food and only about 10% of the participants were estimated to have less than 93% coming from food (70% if dichlorvos is included with the other three OP pesticides).

Despite the dominance of the ingestion route, the urinary metabolite of chlorpyrifos exhibited a stronger (and statistically significant) association with the air measurements than with the dietary measures. This may be because of the half-life of chlorpyrifos in the body (Hines and Deddens, 2001) and the timing and interval of exposure measurements made relative to the kinetics of elimination. For malathion and atrazine, somewhat lower percent measurable values were generally obtained and no significant associations of environmental or personal measures with their urinary metabolites were detected as statistically significant. Personal-air samples exhibited strong rank correlations with indoor air samples for chlorpyrifos, malathion, and diazinon (0.81, 0.51, and 0.62, respectively), while personal-air atrazine levels correlated well with outdoor levels (0.69);

Table 15. Summary statistics for secondary pesticides, by chemical and medium.

Chemical	Percent measurable						Median concentration or loading					
	Pers air	Indr air	Outdr air	Food	Bev	Drk water	Pers air	Indr air	Outdr air	Food	Bev	Drk water
							ng/m ³			µg/kg		µg/l
<i>Cis</i> -Permethrin	86	69	43	18		2	0.2	0.1	0	<0.1		0
4,4'-DDT	77	79	17	36	0	2	0.2	0.2	0	0.4	0	0
Heptachlor ^a	69	87	58	93	0	2	1.1	1.2	0.7	1.3	0	0
4,4'-DDE	66	73	15	31	0	2	0.1	0.2	0	0.3	0	0
<i>cis</i> -Chlordane	64	75	50	35	0	4	0.2	0.3	0.2	0.2	0	0
<i>trans</i> -Permethrin	63	42	14	8		2	0.1	<0.1	0	<0.1		0
Metolachlor	55	65	24	1		0	0.1	0.1	0	0		0
<i>trans</i> -Chlordane	55	74	54	56	0	4	0.5	0.6	0.4	0.5	0	0
Dieldrin	46	58	21	10	0	0	0.1	0.3	0	0	0	0
Alachlor	40	27	8	20		2	0	0	0	0		0
Endosulfan I	30	45	12	1		2	0	0	0	0		0
Dichlorvos	17	11	14	1		0	0	0	0	0		0
4,4'-DDD	17	31	2	9	0	2	0	0	0	0.1	0	0
Simazine	9	12	2	12		0	0	0	0	<0.1		0

Shaded cells indicate less than 50% measurable.

^aFood concentrations questionable.**Table 16.** Summary of partial cumulative intake distributions for OP pesticides^a.

Chemicals included	Medium	10th Percentile	Median	90th percentile
Chlorpyrifos, Malathion, Diazinon (<i>n</i> = 35)	Personal air	0.3	1.5	4.2
	Food + beverage	21	76	234
	Total	23	81	242
	% Food + beverage	93%	98%	99% +
Chlorpyrifos, Malathion, Diazinon, Dichlorvos ^b (<i>n</i> = 24)	Personal air	0.6	1.8	28
	Food + beverage ^b	31	79	271
	Total	40	95	312
	% Food + beverage	70%	98%	99%

^aResults are for those participants with complete intake data on all the indicated chemicals for both personal air and food/beverage routes.

Intake units are ng/day/kg BW.

^bBeverage data for dichlorvos were not available.**Table 17.** Summary statistics for PAHs, by chemical and medium.

Chemical	Percent measurable					Median concentration or loading				
	Pers air	Indr air	Outdr air	Food	Surf dust	Pers air	Indr air	Outdr air	Food	Surf dust
						ng/m ³			µg/kg	ng/cm ²
Benzo(a)pyrene	58	43	48	22	19	0.07	0.01	0.01	0	0
Benzo(a)anthracene	75	35	42	90	21	0.07	0.02	0.02	0.12	0
Acenaphthylene	81	68	95	90	3	5.5	1.5	0.9	0.2	0
Anthracene	100	96	61	70	23	1.0	0.7	0.2	0.1	0
Chrysene	93	84	63	92	27	0.12	0.05	0.04	0.09	0
Benzo(e)pyrene	70	38	48	41	6	0.07	0.03	0.03	0	0
Benzo(ghi)perylene	94	72	63	18	15	0.12	0.06	0.04	0	0
Benzo(k)fluoranthene	59	29	29	19	23	0.05	0	0	0	0
Fluoranthene	100	100	100	99	24	3.0	2.2	1.3	0.4	0.1
Phenanthrene	100	100	98	97	47	35	29	6.9	1.7	0.2
Pyrene	100	100	100	99	19	2.1	1.9	0.7	0.4	0.1
Indeno{1,2,3-cd}pyrene	44	8	13	17	17	0.09	0.04	0.03	0	0
Benzo(b)fluoranthene	94	81	71	49	8	0.16	0.07	0.06	0.04	0

Shaded cells indicate less than 50% measurable.

^aFood concentrations questionable.

Table 18. Spearman correlations for PAHs.

	Pers air Indr air	Pers air Outdr air	Pers air Food	Pers air Surf dust	Indr air Outdr air	Indr air Food	Indr air Surf dust	Outdr air Food	Outdr air Surf dust	Food Surf dust
Benzo(a)pyrene	0.20	0.50**	-0.10	0.08	0.18	0.12	-0.08	-0.03	-0.32*	-0.01
Benzo(a)anthracene	0.15	0.39*	0.00	0.04	0.20	0.03	-0.21*	-0.10	-0.09	-0.01
Anthracene	0.49**	0.36*	0.09	-0.14	0.39**	0.02	-0.05	0.25	0.09	0.19
Chrysene	0.51**	0.30	0.25	0.09	0.36*	0.13	0.07	0.02	-0.01	0.19
Benzo(e)pyrene	0.45**	0.50**	-0.04	n	0.55**	0.10	n	0.03	n	n
Benzo(ghi)perylene	0.42**	0.43**	-0.16	0.21	0.48**	-0.11	-0.14	-0.04	-0.16	-0.10
Benzo(k)fluoranthene	0.17	0.05	-0.09	0.11	0.17	-0.11	-0.11	-0.25	0.35*	-0.20
Fluoranthene	0.74**	0.60**	0.18	0.48**	0.69**	0.07	0.53**	0.00	0.34*	0.05
Phenanthrene	0.72**	0.54**	0.31*	0.52**	0.47**	0.14	0.42**	0.04	0.15	0.09
Pyrene	0.54**	0.41*	0.04	0.32**	0.48**	-0.06	0.27**	-0.07	0.12	0.12
Indeno[1,2,3-cd]pyrene	n	0.36*	-0.19	0.24*	n	n	n	-0.11	0.00	-0.03
Benzo(b)fluoranthene	0.48**	0.33	0.02	n	0.40**	-0.11	n	0.02	n	n

*Statistically significant at the 0.05 level.

**Statistically significant at the 0.01 level.

Note: Acenaphthalene omitted because of small sample sizes for air samples.

n = not calculated because of low percent measurable (<10%).

Table 19

Age (years)	3-5	6-8	9-11	9-11	12-14	12-14
Gender			M	F	M	F
Rate (m ³ /day)	8.3	10	14	13	15	12

personal-air diazinon levels also correlated well with outdoor levels (0.67).

While the half-lives for malathion and chlorpyrifos are approximately 3 and 27 h, respectively, the half-life for diazinon in humans is 12 h (Wester et al., 1993). Given these differences, the optimization of exposure monitoring and biomonitoring increments for all three pesticides is difficult. Thus achieving a high degree of correlation for all three is not expected.

For PAHs, many significant associations were evident among the various air samples and for the air samples with the dust samples, especially for those compounds with consistently high percent measurable values (particularly fluoranthene, phenanthrene, and pyrene). As expected, no significant associations of food levels with dust or air samples were found.

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