Bull. Environm. Contam. Toxicol. 28, 322–328 (1982)

Purgeable Organic Compounds in Mother's Milk

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It is becoming increasingly important to correlate ambient environmental pollutant levels with human body burden. Establishment of this correlation ("exposure assessment") may provide a link between pollution and health effects. This correlation is of interest for both scientific research and regulatory risk assessment.

Measurement of pollutant body burden levels generally requires invasive techniques (exceptions are breath and urine sampling) which are undesirable from the subjects' viewpoint. Some invasive techniques are generally regarded as acceptable (e.g., blood samples), while others are generally considered unacceptable from living donors (adipose tissue, internal organs, etc.). Mother's milk is an attractive medium for several reasons: (1) sample collection is reasonably straightforward; (2) milk contains a high amount of fat, so fat-soluble pollutants are likely to be found in higher concentrations in milk than in blood or urine; (3) large (50-100 mL) volumes are easily collected for analysis, increasing analytical reliability and detection limits; and (4) the population of nursing mothers is large relative to pathology samples such as adipose tissue. In addition, an assessment of pollutant concentrations in mother's milk may be used to predict the pollutant intake by the nursing infant. The major disadvantages of mother's milk as a human-sampling medium relate to the sampling demography: only young-to-middle-aged females are nursing. Thus, in using mother's milk in a probability-based sampling framework, the extrapolation to the general population, would be fraught with difficulties, such as locating donors.

By far, most of the literature on environmental pollutants in mother's milk deals with chlorinated insecticides such as DDT, their metabolites such as DDE, or PCBs (ERICKSON et al. 1980). Only one reference (NIOSH) to the presence of a volatile organic pollutant, 1,2-dichloroethane, was found during an extensive literature search (ERICKSON et al. 1980). The 1,2-dichloroethane was found in the milk of a lactating woman purposively exposed to the compound in air.

The purpose of this study was to identify environmental pollutants in human milk by gas chromatography/ mass spectrometry (GC/MS) and to evaluate the utility of using this body fluid in

0007-4861/82/0028-0322 $01.40

specific pollutant studies for populations in the vicinity of chemical manufacturing plants and/or industrial user facilities.

MATERIALS AND METHODS

Selection of Sampling Sites. Four urban areas (Bridgeville, PA; Bayonne, NJ; Jersey City, NJ; and Baton Rouge, LA) were selected as sampling sites based upon the probability of emissions of various halogenated pollutants. Details on the rationale for site selection are presented elsewhere (ERICKSON et al. 1980).

Sample Collection. At each of the four sites, arrangements were made to work through clinical facilities to recruit a suitable panel of respondents. These facilities included the Bayonne Hospital in Bayonne, NJ; the Medical Center Hospital in Jersey City, NJ; Magee-Women's Hospital in Pittsburgh, PA; and the East Baton Rouge Parish Health Clinic in Baton Rouge, LA. At each site, a professional staff member was responsible for recruiting suitable respondents, administering a questionnaire, and specimen collection. Potential participants (lactating women) were screened to determine whether or not they met certain study criteria, which included: ability and desire to provide a sufficient milk sample of approximately 100 mL, permanent residence within the area of interest for at least the preceding 12 months, and location only inside the area of interest for the seven days preceding sample collection. After potential participants were screened, up to 12 women at each site who met all the criteria for participation were asked to provide a milk sample and complete the questionnaire.

The milk was manually expressed directly into a precleaned 120 mL wide-mouth bottle with a Teflon- lined cap; no breast pumps or other devices were allowed. Immediately after the milk was collected, the bottle was capped and the sample frozen until all samples were collected and ready for shipment. A minimum of 60 mL (half-full bottle) was required for each sample. If insufficient milk was collected, the sample was discarded and an additional subject added to the study. All samples were shipped on dry ice and stored frozen until analysis.

Sample Analysis. The development of the techniques has been presented elsewhere (MICHAEL et al. 1980). Volatile compounds are recovered by warming the milk sample and purging helium through it. The vapors are then trapped on a Tenax cartridge (1.6 x 6 cm) which can be introduced by thermal desorption directly into the glass capillary GC/MS for analysis. The recovery of the purge step was validated using cow's milk samples spiked with ^{14}C-chloroform, ^{14}C-carbon tetrachloride, ^{14}C-chlorobenzene and ^{14}C-bromobenzene. The average recoveries were 88, 88, 63, and 35 percent, respectively. The recoveries correlate roughly with volatility (inversely with boiling point).

Samples were analyzed by thermal desorption/glass capillary gas chromatography/electron impact mass spectrometry using an

LKB 2091. The thermal desorption apparatus is described elsewhere (MICHAEL et al. 1980). The Tenax cartridges were desorbed at 270°C under a flow of 15 mL/min helium. An 80 m SE-30 WCOT capillary column was used with 1.7 mL/min helium as the carrier gas. The column was at 30°C for 2 min, then programmed to 240° at 4°/min. The source temperature was 210°C. The mass spectrometer was scanned from 5-490 daltons with a cycle time of 1.7 sec. The accelerating voltage was 3500 V, the ionizing energy 70 eV, and the trap current 50 μA.

Compounds were identified in selected samples by comparison of the mass spectra to standard reference compilations (STENHAGEN et al. 1974, ANON 1970). If the peaks present in the unknown spectrum clearly matched the peaks of the standard compound in the tables and the intensities were about the same, then a positive identification was usually made. If peak intensities of unknowns varied from those of the standards, and there were isomers of the compounds that were not listed in the Eight Peak Index, then the compound was listed as an "isomer".

When the background peaks interfered with spectra of an unknown to an extent that made identification uncertain, the compound identification was labeled as tentative ("tent."). If no standard spectra similar to those of the unknowns appeared in the mass spectral references, but fragments characteristic of a certain class of compounds were identified, tentative identifications were made on the basis of the characteristic fragments and apparent molecular weights. These identifications were also labeled "tent".

RESULTS

All 42 of the purged samples were analyzed by thermal desorption/GC/MS. The mass spectra from eight selected samples were interpreted manually. The total ion current chromatograms were inspected and the samples with the greatest number of peaks or those containing very intense unique peaks (not observed in other samples) were selected. For those eight samples selected, all of the mass spectra were printed and interpreted manually by experienced spectroscopists.

Table 1 summarizes the compounds found in the eight samples and their frequency of occurrence. It is interesting to note that some compounds (e.g. 1,1,1-trichloroethane and hydrocarbons) are common air pollutants, others (e.g., dibromochloromethane) are common water pollutants, others (dimethyldisulfide, furans, aldehydes) may be metabolites, others (chlorofluorocarbons, siloxanes) are known background interferents, and others (iodopentane) are of unknown source. The extent of background contamination of these samples was not fully characterized.

DISCUSSION

The results show that sampling and analysis for organic

TABLE 1

Summary of Qualitative Identifications of Volatile Compounds In Mother's Milk[a]

Compound	No. of Times Found[b]
Halogenated Compounds	
chlorodifluoromethane	1
chlorotrifluoromethane	4
dichlorodifluoromethane	2
chloromethane	2
chloroethane	2
trichlorofluoromethane	7
dichloroethylene	1
Freon 113	8
methylene chloride	8
chloroform	7
1,1,1-trichloroethane	8
carbon tetrachloride	5
trichloroethylene	8
chloropentane	2
dibromochloromethane	1
tetrachloroethylene	7
dichloropropene	1
chlorobenzene	5
chlorohexane	4
iodopentane	1
3-methyl-1-iodobutane	2
chloroethylbenzene	1
dibromodichloromethane	1
dichlorobenzene	8
chlorodecane	1
trichlorobenzene	1
Aldehydes	
acetaldehyde	4
methyl propanal	2
n-butanal	6
methylbutanal	2
crotonaldehyde	1
n-pentanal	7
n-hexanal	8
furaldehyde	2
n-heptanal	7
benzaldehyde	8
n-octanal	3
phenyl acetaldehyde	1
n-nonanal	6
methyl furaldehyde	1
n-decanal	2
n-undecanal	2
n-dodecanal	1
Ketones	
acetone	8
methyl ethyl ketone	5
methyl propyl ketone	2
methyl vinyl ketone	1
ethyl vinyl ketone	4
2-pentanone	4
methyl pentanone	2
methyl hydrofuranone	1
2-methyl-3-hexanone	1
4-heptanone	1
3-heptanone	4
2-heptanone	6
methyl heptanone	2
furyl methyl ketone	1
octanone	2
acetophenone	8
2-nonanone	4
2-decanone	1
alkylated lactone	1
phthalide	1
Other Oxygenated Isomers	
C_4H_6O	1
C_4H_8O	2
$C_5H_{10}O$	5
C_6H_8O	1
$C_6H_{10}O$	2
$C_4H_6O_2$	1
$C_6H_{12}O$	2
$C_7H_{12}O$	4
$C_7H_{10}O$	2
$C_7H_{14}O$	2
$C_6H_6O_2$	1
$C_8H_{14}O_2$	1
$C_8H_{16}O$	2

(continued)

TABLE 1 (cont'd.)

Compound	No. of Times Found[b]
Other Oxygenated Isomers (continued)	
$C_7H_8O_2$	2
$C_7H_{10}O_2$	1
$C_9H_{18}O$	3
$C_8H_6O_2$	1
$C_{10}H_{12}O_2$	1
$C_{10}H_{14}O$	1
$C_{10}H_{16}O$	2
$C_{10}H_{18}O$	3
$C_{10}H_{20}O$	2
$C_{10}H_{22}O$	1
$C_9H_8O_2$	1
$C_{11}H_{20}O$	1
$C_{10}H_{10}O_2$	1
Alcohols	
methanol	1
isopropanol	8
2-methyl-2-propanol	1
n-propanol	1
1-butanol	3
1-pentanol	4
α-furfuryl alcohol	2
2-ethyl-1-hexanol phenol	1
2,2,4-trimethylpenta-1,3-diol	1
α-terpineol	1
Acids	
acetic acid	2
decanoic acid	1
Sulfur Compounds	
sulfur dioxide	1
carbon disulfide	8
dimethyl disulfide	6
carbonyl sulfide	1
Nitrogen Compounds	
nitromethane	1
$C_5H_6N_2$	1
$C_5H_8N_2$	1
$C_4H_4N_2O$	1
methyl acetamide	1
benzonitrile	3
methyl cinnoline	1
Esters	
vinyl propionate	3
ethyl acetate	1
ethyl-n-caproate	1
isoamyl formate	1
methyl decanoate	1
ethyl decanoate	1
Ethers	
dimethyl ether	1
dihydropyran	2
Epoxide	
1,8-cineole	1
Furans	
furan	1
tetrahydrofuran	1
methyl furan	2
methyl tetrahydrofuran	1
ethylfuran	2
dimethylfuran	1
2-vinylfuran	1
furaldehyde	2
2-n-butylfuran	1
2-pentylfuran	7
methylfuraldehyde	1
furyl methyl ketone	1
α-furfuryl alcohol	2
benzofuran	3
Alkanes	
C_3H_8	1
C_4H_{10}	6

(continued)

TABLE 1 (cont'd.)

Compound	No. of Times Found[b]	Compound	No. of Times Found[b]
Alkanes (continued)		Cyclic	
C_5H_{12}	8	cyclopentane	6
C_6H_{14}	8	methyl cyclopentane	6
C_7H_{16}	7	cyclohexane	5
C_8H_{18}	7	ethyl methyl cyclohexane	1
C_9H_{20}	8	$C_{10}H_{14}$ isomers	1
$C_{10}H_{22}$	7	$C_{10}H_{16}$ isomers (other)	4
$C_{11}H_{24}$	7	limonene	8
$C_{12}H_{26}$	7	methyl decalin	1
$C_{13}H_{28}$	3	α-pinene	1
$C_{14}H_{30}$	3	camphene	1
$C_{15}H_{32}$	2	camphor	1
Alkenes		Aromatic	
C_3H_6	2	benzene	8
C_4H_8	5	toluene	8
C_5H_{10}	3	ethylbenzene	8
C_6H_{12}	8	xylene	8
C_7H_{14}	8	phenyl acetylene	1
C_8H_{16}	8	styrene	8
C_9H_{18}	7	benzaldehyde	8
$C_{10}H_{20}$	6	C_3-alkylbenzene isomers	8
$C_{11}H_{22}$	6	C_4-alkylbenzene isomers	6
$C_{12}H_{24}$	1	methyl styrene	2
$C_{13}H_{26}$	1	dimethyl styrene	5
isoprene	1	C_5-alkylbenzene isomers	2
		naphthalene	6
Alkynes		C_6-alkylbenzene isomers	1
C_5H_8	2		
C_6H_{10}	1		
C_7H_{12}	3		
C_8H_{14}	3		
C_9H_{16}	4		
$C_{10}H_{18}$	2		
$C_{12}H_{22}$	1		

[a] Arranged by class in approximate elution order.

[b] Twelve Total Samples: 6-Bayonne, NJ, 2-Jersey City, NJ; 2-Bridgeville, PA; and 2-Baton Rouge, LA.

compounds in mother's milk is feasible. The sample collection technique presented no significant problems. Analysis of the samples was generally satisfactory.

The use of purge and trap with capillary gas chromatography/mass spectrometry/computer analysis for volatile organics was successful, although the intrusion of contaminants during analysis presented problems with some compounds. The wide range of volatile compounds found includes common air and water pollutants and possible metabolites. Thus, it may be possible to use mother's milk as an indicator of body burden if a correlation between exposure and mother's milk concentration is established.

ACKNOWLEDGEMENTS

S. P. Parks, D. L. Newton, L. C. Michael, N. P. Castillo, K. W. Thomas, P. A. Gentry, F. A. McKinney, S. P. Burke, B. L. Bickford, E. Bartholomew, j. Rivkind, T. Strunk, I. Holtzman, L. Trachtman, M. Parker and C. Martine are thanked for their assistance. Finally, we are grateful to the 42 women who kindly donated samples.

This work was supported by U.S.E.P.A. Contract No. 68-01-3849.

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