N-Methyl Carbamate Pesticides in Infant Foods Available in the Canadian Marketplace

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Overview

• Project: Surveillance of Foods for Infants
  – description
  – focus on pesticides

• Study
  – rationale and objective
  – method of analysis

• Survey results
  – comparison with other data
Surveillance of Foods for Infants

• formerly called Child Health Initiative

• designed to assess the exposure of infants and children to toxic chemicals

• two areas of surveillance
  – baby foods and infant formulas
  – human milk

• some of the analytes of interest include pesticides, persistent organic pollutants, trace elements and natural toxins
Pesticides of Concern

• This project will result in the determination of the incidence and levels of:
  – organochlorine insecticides
  – organophosphate insecticides
  – $N$-methyl carbamates
  – triazines
  – anilides
  – substituted ureas
  – benzoic acid herbicides
  – acaracides
  – fungicides
Why Pesticides?

• Infants and children are thought to be more susceptible to the effects of pesticide exposure than adults due to their higher metabolic rates, less mature immune systems and different activity patterns.

• Infants consume more food per body mass relative to adults. Food consumption patterns for children are known to differ from adults and include greater amounts of fresh produce and juice.
Pest Management Regulatory Agency (PMRA)

- PMRA is currently re-evaluating a number of selected organophosphate and carbamate pesticides.

- The N-methyl carbamates that are subject to re-evaluation include:
  - carbaryl
  - carbofuran
  - methomyl
  - oxamyl
  - propoxur
Study Rationale

• Very little exposure determinations via dietary uptake are performed on infant exposure.

• The data output of this project will provide PMRA with Canadian exposure data for pesticides in infant foods.
Study Objective

• To determine the incidences and levels of ten N-methyl carbamate pesticides in infant foods available in the Canadian marketplace.

  – Aldicarb
    • including breakdown products aldicarb sulfoxide and aldicarb sulfone
  – Carbaryl
  – Carbofuran
    • and breakdown product 3-hydroxy carbofuran
  – Methiocarb
  – Methomyl
  – Oxamyl
  – Propoxur
N-Methyl Carbamate Pesticides

- class of insecticides that are used against a variety of target pests on fruit, vegetable and grain crops

- act as cholinesterase inhibitors, disrupting the nervous system

- implicated as endocrine disrupters
Structure of *N*-Methyl Carbamate Pesticides

- the general structure of these compounds is an *N*-methyl substituted carbamic acid with the variation in the ester moiety

\[ \text{O} \quad \text{R-O-C-NH-CH}_3 \]

- the R group can be an alkyl or aryl ester
Structure of $N$-Methyl Carbamate Pesticides - Examples

Aldicarb

Carbaryl
Survey: Sample Collection and Preparation

- Samples of commercially prepared infant foods (157) were purchased from retail stores across Canada during the fiscal years 2001/2 and 2002/3.
- Infant jarred foods containing fruits, vegetables, pastas and or meats, infant cereals and infant juices were sampled.
- Samples were analyzed as received.
## Types of Samples

<table>
<thead>
<tr>
<th>Types of Samples</th>
<th>Domestic</th>
<th></th>
<th>Imported</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Regular</td>
<td>Organic</td>
<td></td>
</tr>
<tr>
<td>Fruits</td>
<td>25</td>
<td>0</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Vegetables</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td>Strained meats</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Combination dinners</td>
<td>22</td>
<td>0</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Juices</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Desserts</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cereals</td>
<td>12</td>
<td>2</td>
<td>14</td>
<td>0</td>
</tr>
</tbody>
</table>
Method of Analysis

**Juice:** Apply directly to Waters Oasis HLB SPE

**Fruit/Vegetable/Meat:** Extract with acetonitrile; dry and apply residue dissolved in water to Waters Oasis HLB SPE

Confirmation
HPLC (No PCRS)
Fluorescence detection

Same HPLC conditions with water replacing the post column reagents.

**Cereals:** Extract in acetone/dichloromethane (DCM) and apply dried residue dissolved in DCM/methanol to aminopropyl (NH2) SPE

HPLC
Post-column derivatization (PCRS)
Fluorescence detection

**Column:** Waters Nova-Pak C18, 3.9 x 150 mm, 4μm, 35°C

**Mobile Phase:** water/methanol/acetonitrile gradient, 1.5 mL/min

**PCRS:** 0.05 M NaOH, OPA, 0.5 mL/min, 75°C

**Fluorescence:** 339 nm ex., 445 nm em.
Chromatograms: Standard and Sample With Derivitization

- Aldicarb Sulfoxide
- Aldicarb Sulfone
- Oxamyl
- Methomyl
- 3-Hydroxy carbophuran
- Aldicarb
- Propoxur
- Carbaryl
- Methiocarb

N-methyl carbamate standard 1.26 μg/mL with derivitization

RT = 16.77 minutes
24,500,000 area counts

Apple dessert containing 18 ng/g carbaryl with derivitization

RT = 16.77 minutes
1,750,000 area counts
Chromatograms: Standard and Sample Without Derivitization

N-methyl carbamate standard 1.25 μg/mL without derivitization

Apple dessert containing 18 ng/g carbaryl without derivitization
## Limits of Detection / Quantification

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>LOD</th>
<th>LOQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Juices</td>
<td>0.3 ng/mL (1, 2)</td>
<td>1.0 ng/mL (1, 2)</td>
</tr>
<tr>
<td>Cereals</td>
<td>1.2 ng/g (1)</td>
<td>4.0 ng/g (1)</td>
</tr>
<tr>
<td></td>
<td>2.8 ng/g (2)</td>
<td>8.0 ng/g (2)</td>
</tr>
<tr>
<td>Fruits/Vegetables</td>
<td>0.6 ng/g (1)</td>
<td>2.0 ng/g (1)</td>
</tr>
<tr>
<td>/Meats</td>
<td>1.4 ng/g (2)</td>
<td>4.0 ng/g (2)</td>
</tr>
</tbody>
</table>

1 Aldicarb sulfone, aldicarb sulfoxide, oxamyl, methomyl, 3-hydroxycarbofuran, aldicarb, propoxur, carbofuran, carbaryl

2 Methiocarb
Mean Spike Recoveries
(25 ng/g or ng/mL)

Juice (n=2)  Cereal (n=14)  Fruits/Vegetables/Meats (n=21)
## Survey Results

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Analyte</th>
<th>Incidence Domestic</th>
<th>Incidence Imported</th>
<th>Range (ng/g)</th>
<th>Mean Positives (ng/g)</th>
<th>Mean All * (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fruits</td>
<td>carbaryl</td>
<td>8 / 25</td>
<td>0 / 20</td>
<td>1.0 – 11</td>
<td>5.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Vegetables</td>
<td>ND</td>
<td>0 / 14</td>
<td>0 / 19</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Strained Meats</td>
<td>methomyl</td>
<td>1 / 4</td>
<td>0 / 0</td>
<td>--</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Combination dinners</td>
<td>carbaryl</td>
<td>1 / 22</td>
<td>0 / 5</td>
<td>--</td>
<td>0.6</td>
<td>0.03</td>
</tr>
<tr>
<td>Juice</td>
<td>ND</td>
<td>0 / 6</td>
<td>0 / 0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Desserts</td>
<td>carbaryl</td>
<td>3 / 14</td>
<td>0 / 0</td>
<td>1.5 – 18</td>
<td>7.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Cereal</td>
<td>ND</td>
<td>0 / 14</td>
<td>0 / 14</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>All sample types</td>
<td>carbaryl</td>
<td>12 / 99</td>
<td>0 / 58</td>
<td>0.6 – 18</td>
<td>5.4</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>methomyl</td>
<td>1 / 99</td>
<td>0 / 58</td>
<td>0.8</td>
<td>0.005</td>
<td></td>
</tr>
</tbody>
</table>

* Where all result < LOD = 0 ng/g
**Commodities That Were Found to Contain Detectable Levels of Residue**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Commodity</th>
<th>Maximum detected ng/g</th>
<th>Maximum Residue Limit (MRL) ng/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbaryl</td>
<td>peaches and peach dessert, prunes</td>
<td>5.3</td>
<td>10,000</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>apple sauce, dessert and apple-strawberry blend</td>
<td>18</td>
<td>5,000</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>strawberry dessert</td>
<td>2</td>
<td>7,000</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>mixed fruit</td>
<td>11</td>
<td>100 – 10,000</td>
</tr>
<tr>
<td></td>
<td>(apples, pears, apricot, orange juice, pineapple)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbaryl</td>
<td>turkey, rice with vegetables</td>
<td>0.6</td>
<td>100 – 5,000</td>
</tr>
<tr>
<td></td>
<td>(carrots, potatoes, corn, peas, parsnip, squash, onions)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methomyl</td>
<td>chicken with broth</td>
<td>0.8</td>
<td>100</td>
</tr>
</tbody>
</table>
Comparison to Other Studies
Carbaryl

• Health Canada - Child Health Initiative (2000)
  – apple and grape juices
  – range: 2.1 – 93 ng/mL

• US Food & Drug Administration - Total Diet Study (1991 – 2001)
  – various infant foods
  – range: 1 – 49 ng/g

• Health Canada - Child Health Initiative (2003)
  – various infant foods
  – range: 0.6 – 18 ng/g
Conclusions

• Carbaryl was the most frequently (7.6%) detected \textit{N}-methyl carbamate in infant food samples studied, at concentrations ranging from 0.6 ng/g to 18 ng/g with a mean level of 5.4 ng/g.

• Carbaryl was generally detected in fruit samples.

• Methomyl, was detected in a single chicken sample at a level of 0.8 ng/g.

• In all cases, \textit{N}-methyl carbamate residues were well below the maximum residue limit (MRL) established in the Canadian Food and Drug Regulations for Canadian foods.
Next Steps

• These data will be shared with the PMRA for inclusion in dietary exposure estimates for young children.

• The data will be published in a scientific journal.

• Additional exposure studies are planned
  – Human milk survey for similar analytes of interest
Questions?