Determination of parathion, aldicarb, and thiobencarb in tap water and bottled mineral water in Mashhad, Iran

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Abstract
Water is a necessity for life. Currently, because of different contaminations in tap water, most people prefer using bottled mineral waters. Pesticides (e.g., organophosphorous, carbamates, etc.) are among the most dangerous chemicals that may be found in drinking waters, which can cause long- and short-term complications. Because all people consume at least 2 L of water per day, water-quality monitoring is vital. In this study, we determined the concentration of three pesticides (aldicarb, parathion, and thiobencarb) in 13 tap-water samples collected from 13 different urban areas and 10 samples of bottled mineral water in Mashhad, a major city in northeast Iran. Samples were analyzed by gas chromatography coupled with a pulsed flame photometric detector after solid-phase extraction. Results showed that 2 of 13 tap-water samples and 2 of 10 bottled mineral water trademarks were contaminated either by parathion or by thiobencarb or both, with concentrations ranging between 0.6 and 0.8 ppb. According to the defined guideline values, determined concentrations of pesticides are below the permissible World Health Organization level for these toxic agents, and it is considered that drinking these tap waters and bottled mineral waters are safe for human consumption.

Keywords: Aldicarb, bottled mineral water, gas chromatography, parathion, tap water, thiobencarb
consumed primarily because of the unavailability of potable water and for safety reasons. However, bottled water may not be safer or healthier than tap water (Ahmad and Bajahan, 2007). Bottled waters are principally produced from springs, ground, surface, and tap waters. Also, some bottled waters are sourced from tap waters, with no added health benefits, by manufacturers.

Many people now prefer bottled water to tap water for a number of reasons. They may not like the taste, smell, or color of tap water. Others are worried about their health and see bottled water as more natural, pure, and a healthier alternative to tap water (Samek, 2004).

Drinking water is good quality water that may be consumed freely without any adverse effects on health and should be free from harmful levels of impurities, such as bacteria, viruses, toxic minerals, and organic substances (Evandi and Bolle, 2001).

Bottled mineral water is beginning to assume a prominent place in the human diet (Garzon and Eisenberg, 1998). One of the reasons why people prefer bottled water is the public concern that tap water might be contaminated with organic and inorganic chemicals (Mayne and Edwards, 1990). Significant levels of contaminants (e.g., Pb) may come from materials in contact with the drinking water distribution system (Van Dijk-Looijaard and Van Genderen, 2000). Chemicals can also be produced during the water potabilization process: Organic matter in water (especially surface water) can react with disinfectant agents (e.g., chlorine), leading to the formation of disinfec tant by-products (i.e., DBPs—halogenated organic compounds) that, because of their properties, might pose a risk to human health (Carraro et al., 2000; Van Leeuwen, 2000).

Organophosphorous pesticides (OPs) are one kind of effective, broad-spectrum insecticide. It constitutes a very important group owing to their extended use in agricultural practice and in many over exposures such as suicide. Single massive exposure to OPs can lead to breathing failure (Yang et al., 1999). Chronic sublethal exposure to OPs have been related to symptoms of chronic fatigue syndrome, multiple chemical sensitivity, and personality change (Wang and Du, 2010).

Parathion is one of the most important OPs. It interacts with enzyme acetylcholinesterase (AChE) and disrupts nerve function, causing paralysis or even death. Because it is highly toxic, its use was banned in many countries (Buratti et al., 2003). However, it is still used widely by farmers in Iran, exposing people and animals to a great hazard.

Carbamates are another effective form of insecticide, which also act via inhibition of AChE action. The carbamate-AChE bond is much less stable than the one formed after a reaction with an OP agent, and spontaneous decarbamylation (via slow hydrolysis) occurs after a while, resulting in the reactivation of AChE (Lee, 2003).

Aldicarb, 2-methyl-2 (methylthio) propionaldehyde O-(methylcarbamoyl)-oxime, is an oxime carbamate insecticide introduced in 1962 by the Union Carbide Corporation (USA) (Pelekis and Emond, 2009).

Thiobencarb (S-4-chlorobenzyl diethylthiocarbamate) has been extensively used in modern agricultural practices for the control of barnyard grass in paddy rice fields. Application of this herbicide results in its residue in surface water (Xia, 2005).

It is well known that their application may be a contaminant source for the aquatic environment. Environmental contamination of natural waters by pesticide residues is currently of great concern (Kolpin et al., 1998). Pesticide residue reaches the aquatic environment through direct runoff, leaching, careless disposal of empty containers, equipment washings, and so on (Shukla et al., 2006).

The aim of the present study was to ascertain the quality of collected waters by direct measurement of pesticide residues in drinking-water samples.

Methods

Reagents and materials
Standard samples of thiobencarb, parathion, and aldicarb were purchased from Fluka (Buchs, Germany). Standard Sep-Pak C18 silica cartridges (no. 51900; Waters Corporation, Milford, Massachusetts, USA) were used for extraction. Manifold apparatus (Manifold; Waters) was used in the solid-phase extraction (SPE) procedure. Acetone and ethyl acetate were purchased from Merck (Darmstadt, Germany). All chemicals were of analytical grade and were used as received without further purification.

Sampling
In June 2010, according to a water distribution map of the city, 13 tap-water samples of tap water from 13 different urban areas in Mashhad, Iran, and 10 samples of different bottled mineral water trademarks were collected in 1-L glass bottles, previously rinsed with the same water sample, and hermetically closed. After collection, samples were stored at 4°C and analyzed in 1 week.

SPE procedure
According to the adopted method of Bruzzoniti (Bruzzoniti et al., 2006), the SPE cartridge was first conditioned with four aliquots of 3 mL of ethyl acetate to remove air and leaching, then with three aliquots of 3 mL of ultrapure water to equilibrate the phase with the solvent of the matrix. Next, a 1,000-mL water sample was loaded by a vacuum pump. The cartridge was then washed with three aliquots of 3 mL of ultrapure water. Water was then removed, maintaining a vacuum for 40 minutes. Analytes were eluted from SPE sorbents by acetone. Collected aliquots were then dried, using gaseous N2. The residual was reconstituted with 1 mL of acetone. To prevent any possible damage to GC by foreign bodies,
the reconstituted solution was centrifuged at 400 rpm for 5 minutes. The solution was then transferred by a syringe of 2 µL to GC and was analyzed by gas chromatography/pulsed flame photometric detector (GC-PFPD). A blank of 1,000 mL of deionized water was processed in parallel on SPE columns.

**GC-PFPD**

Once the final elution had been dried down and redissolved, it was then transferred to GC-PFPD. GC-PFPD analysis was carried out on a Varian CP-3800 GC directly coupled to a Varian PFPD detector (Varian, Inc., Lexington, Massachusetts, USA). The GC column was a DB-5 capillary column (0.25-µm film thickness, 0.32 mm ID×30 m in length), obtained from J&W Scientific (Folsom, California, USA).

The injector was used in splitless mode, and the injector temperature was set to 250°C. Nitrogen was used as the carrier gas at a flow rate of 1 mL/min. The column was held at 60°C for 2 minutes after injection, then programmed to 180°C (5 minutes) at a rate of 20°C/min, and, finally, to 220°C (2 minutes) at a rate of 4°C/min. PFPD detector temperature was set at 225°C.

**Results**

**Calibration**

Calibration curves were obtained by analyzing five different mixtures of pesticides with different concentrations (Table 1). Each standard mixture was prepared, according to the procedure described before, and injected to GC. Response versus the amount of pesticides injected, ranging from 0.62 to 15 ppb, showed a good linearity. The limit of quantitation (LOQ) of the analytical method, defined as a signal-to-noise ratio of 3, was 0.62 ppb for thiobencarb, parathion, and aldicarb. The minimum detectable amounts (LOD) was estimated as 0.62 ppb for aldicarb and 0.1 ppb for parathion and thiobencarb (Table 2).

After each chromatographic run, blank (i.e., ethyl acetate) was processed to check the baseline and the instrumental response. The powerful separation capabilities of GC, coupled to the high selectivity and sensitivity properties of the PFPD detection technique, overcomes the problems resulting from partial coelutions in the chromatographic step.

**Evaluation of extraction procedure**

Two other standard mixtures of pesticides, with the concentrations of 1.25 and 5 ppb, were prepared according to the previously described procedure and injected to GC. According to chromatograms, area under the curve was calculated and it was shown that extraction-recovery rates ranged from 90 to 97% (Table 3).

The SPE-GC-PFPD procedure for pesticide extraction and detection was also run on consecutive days and in the same day to determine the intra- and interday variance, respectively, to show method and instrument ruggedness. To achieve this, two standard mixtures of pesticides, with the concentrations of 2.5 and 5 ppb, were prepared and injected to GC. Results are shown in Tables 4 and 5.

**Determination of different pesticides in samples**

Thirteen different urban area tap-water samples and 10 different trademarks of mineral waters were collected. They were extracted and injected to GC. Based on GC chromatograms (Figures 1, 2, and 3), pesticide concentrations in samples were calculated. Results showed that 4 of 23 samples were contaminated by pesticides, with concentrations ranging between 0.6 and 0.8 ppb for parathion and thiobencarb. Whereas 2 samples of bottled mineral water trademarks were contaminated by both parathion and thiobencarb, 2 samples of tap waters were contaminated by thiobencarb only (Table 6).

**Discussion and conclusion**

Water is the basic element of living beings: they could not have appeared and could not survive without it. In the reference man, 60% of body weight (i.e., approximately 45 L) is represented by total body water (Petraccia et al., 2006).

The use of organophosphorus or carbamate pesticides has brought significant economic benefits to agriculture. At the same time, increased use of these pesticides has also caused contamination of surface and ground waters, especially in agricultural regions. It is well known that their application may be a contaminant source for the aquatic environment. There is an increasing interest to monitor the concentrations of pesticides in surface and ground waters. The powerful separation capabilities of GC, coupled to the high selectivity and sensitivity properties of the PFPD detection technique, overcomes the problems resulting from partial coelutions in the chromatographic step.

**Table 1.** Five different mixtures of pesticides with different concentrations.

<table>
<thead>
<tr>
<th></th>
<th>Parathion (ppb)</th>
<th>Aldicarb (ppb)</th>
<th>Thiobencarb (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture 1</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Mixture 2</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Mixture 3</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Mixture 4</td>
<td>1.25</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>Mixture 5</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
</tr>
</tbody>
</table>

**Table 2.** Limit of quantitation (LOQ) and limit of detection (LOD) of the analytical method.

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Calibration equation</th>
<th>Correlation coefficient</th>
<th>LOQ (ppb)</th>
<th>LOD (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiobencarb</td>
<td>y = 214154x – 51474</td>
<td>0.9953</td>
<td>0.62</td>
<td>0.1</td>
</tr>
<tr>
<td>Parathion</td>
<td>y = 255027x – 83077</td>
<td>0.9956</td>
<td>0.62</td>
<td>0.1</td>
</tr>
<tr>
<td>Aldicarb</td>
<td>y = 41998x – 5850</td>
<td>0.9960</td>
<td>0.62</td>
<td>0.62</td>
</tr>
</tbody>
</table>
ground waters. The determination of pesticides in water samples is generally carried out by GC methods (Barcelo, 1997; Chinese, 1991; U.S. EPA Method 507, 1995; Van der Hoff and Van Zoonen, 1999).

Among all the analytical steps for the determination of trace pesticides in environmental samples with GC method, sample pretreatment is known as the most difficult to be performed, and the easiest to cause error, because of the lack of an automatic method. The amount of target analytes is usually very small, compared to that of the complicated matrix. Thus, extraction is specially needed to reduce matrix interference and enhance the concentration of target analytes for GC analysis. Extraction selectivity and efficiency, as well as speed, are the key points that mostly concern researchers in this area.

It was reported that SPE before GC represents a convenient method for quickly obtaining clean extracts with optimum recoveries. Meanwhile, SPE was better than liquid-liquid extraction (LLE), as it uses at least 10 times less volume of toxic solvents (Franke and Rokus, 1998; McDowall, 1989; Dufresne et al., 2001).

The PFPD is both sensitive and selective and appears to be the best choice for analysis, especially in routine analysis because of its low cost and reduced consumption of gases (Van der Hoff and Van Zoonen, 1999; Hennion and Barcelo, 1998).

PFPD can reduce sample load on the column and eliminate the interference of natural sulfur compounds, which are the bottleneck of trace-level OP analysis with FPD, in many matrices (available at: http://www.tau.ac.il/chemistry/amirav/pfpd.shtml, accessed on June 18, 2009; Le Harle and Bellier, 2005).

Compared to the nitrogen phosphorus detector (NPD), the PFPD has a similar sensitivity, but without peak tailing and long-term stability problems. Therefore,
Table 6. Four samples were contaminated by pesticides as follows.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tap water1</th>
<th>Tap water2</th>
<th>Bottled mineral water 1</th>
<th>Bottled mineral water 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (ppb)</td>
<td>Parathion</td>
<td>ND</td>
<td>ND</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>Thiobencarb</td>
<td>0.64</td>
<td>0.6</td>
<td>0.86</td>
</tr>
</tbody>
</table>

ND, not detected at limits of quantitation.
the combined use of SPE instead of LLE and GC-PFPD instead of other detectors has the high possibility to increase the sensitivity to OP analysis as well as the lifetime to column.

The European Union (EU) Directive on the quality of drinking water has set the maximum admissible concentrations of each pesticide at 0.1 μg/L and the total concentration of all pesticides at 0.5 μg/L (Council Directive, 1998). World Health Organization (WHO) threshold values for concentrations of pesticides in drinking water, based on toxicological considerations, are less strict than the maximum concentrations allowed by the EU (Sabin et al., 2009).

\[
GV = \frac{\text{ADI} \times \text{Bw} \times \text{p}}{C}
\]

\[
\text{GV for parathion} = \frac{0.005 \text{mg} \times 60 \times 0.01}{2} = 1.5 \text{ppb}
\]

\[
\text{GV for thiobencarb} = \frac{0.007 \text{mg} \times 60 \times 0.01}{2} = 2.1 \text{ppb}
\]

Fortunately, consumption of all drinking waters in Mashhad is safe from the aspect of contamination by parathion, thiobencarb, and aldicarb. Based on defined GV's, even in contaminated samples, the concentration of pesticides was less than WHO-recommended thresholds; but, it has to be mentioned that because exposure to pesticides also occurs through other media (e.g., food), the attribution of the exposure through drinking water to overall risk needs to be known (Younes et al., 1998). On the other hand, many pesticides are persistent and may, therefore, bioaccumulate in the environment (Hayes and Laws, 1991). In addition to acute effects, there is evidence that links long-term exposure to some pesticides with chronic diseases, including cancers (Younes and Gala-gorchev, 2000). Therefore, although there is no health problem related to drinking water in Mashhad, it is strongly recommended that regular water-quality control be performed. To maintain this condition and also for having healthier drinking water, it is much better to perform strict supervision on the use of these chemical agents.

**Acknowledgment**

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**Declaration of interest**

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**References**


