Carbaryl in Drinking-water

Background document for development of
WHO Guidelines for Drinking-water Quality
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Preface

One of the primary goals of WHO and its member states is that “all people, whatever their stage of development and their social and economic conditions, have the right to have access to an adequate supply of safe drinking water.” A major WHO function to achieve such goals is the responsibility “to propose ... regulations, and to make recommendations with respect to international health matters ....”

The first WHO document dealing specifically with public drinking-water quality was published in 1958 as *International Standards for Drinking-water*. It was subsequently revised in 1963 and in 1971 under the same title. In 1984–1985, the first edition of the *WHO Guidelines for Drinking-water Quality* (GDWQ) was published in three volumes: Volume 1, Recommendations; Volume 2, Health criteria and other supporting information; and Volume 3, Surveillance and control of community supplies. Second editions of these volumes were published in 1993, 1996 and 1997, respectively. Addenda to Volumes 1 and 2 of the second edition were published on selected chemicals in 1998 and on microbiological aspects in 2002. The third edition of the GDWQ was published in 2004, the first addendum to the third edition was published in 2005, and the second addendum to the third edition was published in 2008.

The GDWQ are subject to a rolling revision process. Through this process, microbial, chemical and radiological aspects of drinking-water are subject to periodic review, and documentation related to aspects of protection and control of public drinking-water quality is accordingly prepared and updated.

Since the first edition of the GDWQ, WHO has published information on health criteria and other supporting information to the GDWQ, describing the approaches used in deriving guideline values and presenting critical reviews and evaluations of the effects on human health of the substances or contaminants of potential health concern in drinking-water. In the first and second editions, these constituted Volume 2 of the GDWQ. Since publication of the third edition, they comprise a series of free-standing monographs, including this one.

For each chemical contaminant or substance considered, a lead institution prepared a background document evaluating the risks for human health from exposure to the particular chemical in drinking-water. Institutions from Canada, Denmark, Finland, France, Germany, Italy, Japan, Netherlands, Norway, Poland, Sweden, United Kingdom and United States of America (USA) prepared the documents for the third edition and addenda.

Under the oversight of a group of coordinators, each of whom was responsible for a group of chemicals considered in the GDWQ, the draft health criteria documents were submitted to a number of scientific institutions and selected experts for peer review. Comments were taken into consideration by the coordinators and authors. The draft documents were also released to the public domain for comment and submitted for final evaluation by expert meetings.
During the preparation of background documents and at expert meetings, careful consideration was given to information available in previous risk assessments carried out by the International Programme on Chemical Safety, in its Environmental Health Criteria monographs and Concise International Chemical Assessment Documents, the International Agency for Research on Cancer, the Joint FAO/WHO Meeting on Pesticide Residues and the Joint FAO/WHO Expert Committee on Food Additives (which evaluates contaminants such as lead, cadmium, nitrate and nitrite, in addition to food additives).

Further up-to-date information on the GDWQ and the process of their development is available on the WHO Internet site and in the current edition of the GDWQ.
Acknowledgements

The first draft of Carbaryl in Drinking-water, Background document for development of WHO Guidelines for Drinking-water Quality, was prepared by Mr J.K. Fawell, United Kingdom, to whom special thanks are due.

The work of the following working group coordinators was crucial in the development of this document and others contributing to the second addendum to the third edition:

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Professor Y. Magara, Hokkaido University, Japan (Analytical achievability)
Dr A.V. Festo Ngowi, Tropical Pesticides Research Institute, United Republic of Tanzania (Pesticides)
Dr E. Ohanian, Environmental Protection Agency, USA (Disinfectants and disinfection by-products)

The draft text was discussed at the Working Group Meeting for the second addendum to the third edition of the GDWQ, held on 15–19 May 2006. The final version of the document takes into consideration comments from both peer reviewers and the public. The input of those who provided comments and of participants in the meeting is gratefully acknowledged.

The WHO coordinators were Dr J. Bartram and Mr B. Gordon, WHO Headquarters. Ms C. Vickers provided a liaison with the Programme on Chemical Safety, WHO Headquarters. Mr R. Bos, Assessing and Managing Environmental Risks to Health, WHO Headquarters, provided input on pesticides added to drinking-water for public health purposes.

Ms Penny Ward provided invaluable administrative support at the Working Group Meeting and throughout the review and publication process. Ms Marla Sheffer of Ottawa, Canada, was responsible for the scientific editing of the document.

Many individuals from various countries contributed to the development of the GDWQ. The efforts of all who contributed to the preparation of this document and in particular those who provided peer or public domain review comment are greatly appreciated.
**Acronyms and abbreviations used in the text**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADI</td>
<td>acceptable daily intake</td>
</tr>
<tr>
<td>CAS</td>
<td>Chemical Abstracts Service</td>
</tr>
<tr>
<td>ECD</td>
<td>electron capture detector</td>
</tr>
<tr>
<td>FAO</td>
<td>Food and Agriculture Organization of the United Nations</td>
</tr>
<tr>
<td>GAC</td>
<td>granular activated carbon</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>HPLC</td>
<td>high-performance liquid chromatography</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>LOAEL</td>
<td>lowest-observed-adverse-effect level</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared</td>
</tr>
<tr>
<td>NOAEL</td>
<td>no-observed-adverse-effect level</td>
</tr>
<tr>
<td>NPD</td>
<td>nitrogen–phosphorus detector</td>
</tr>
<tr>
<td>PAC</td>
<td>powdered activated carbon</td>
</tr>
<tr>
<td>USA</td>
<td>United States of America</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VIS</td>
<td>visible</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
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1. GENERAL DESCRIPTION

1.1 Identity

CAS No.: 63-25-2
Molecular formula: C_{12}H_{11}NO_{2}

The IUPAC name for carbaryl is 1-naphthyl methylcarbamate.

1.2 Physicochemical properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>142 °C</td>
</tr>
<tr>
<td>Density</td>
<td>1.23</td>
</tr>
<tr>
<td>Water solubility</td>
<td>40 mg/l at 30 °C</td>
</tr>
<tr>
<td>Log octanol–water partition coefficient</td>
<td>1.59–2.3</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>$1.56 \times 10^{-7} - 4.13 \times 10^{-8}$ kPa at 24–25 °C</td>
</tr>
</tbody>
</table>

1.3 Major uses

Carbaryl is a broad-spectrum carbamate insecticide that is used to control insect pests in crops, trees and ornamental plants. It also has some uses in public health and veterinary practice.

1.4 Environmental fate

Carbaryl is not usually persistent in the environment and is hydrolysed in water, the rate depending on temperature and pH; at low concentrations, it may be hydrolysed within hours under favourable conditions. It does not significantly bioconcentrate in fish. It adsorbs to soils with a high organic content, but adsorption is much lower in sandy soils. At usual rates of application, it rapidly dissipates, with a half-life of 1 month or less. It is degraded by photodecomposition, hydrolysis and microbial activity; the rate of degradation is more rapid under hot climatic conditions (IPCS, 1992).

2. HUMAN EXPOSURE

Carbaryl has not been reported in drinking-water; however, it could occur following overspraying or spillage into surface water. Exposure through drinking-water is, therefore, considered to be low unless in exceptional circumstances. The major route of carbaryl intake for the general population is food, but residues are considered to be relatively low. These range from trace amounts to about 0.05 mg/kg of food. It has been reported that the intake in the USA was 0.15 mg/day per person but has declined to 0.003 mg/day per person (IPCS, 1992).

3. TOXICOLOGICAL SUMMARY

Carbaryl acts through inhibition of brain cholinesterase, and this is also its primary mode of toxicity. The effect is rapidly reversible and relates to the peak plasma
concentration. FAO/WHO (2002a) developed an acute reference dose of 0.2 mg/kg of body weight based on a 5-week study in dogs in which the NOAEL was equal to 3.8 mg/kg of body weight per day and the application of a safety factor of 25.

However, carbaryl is considered to be a non-genotoxic carcinogen in mice, in which it causes vascular tumours in males. On this basis, FAO/WHO (2002a) established an ADI of 0–0.008 mg/kg of body weight. This was based on a LOAEL of 100 mg/kg of diet, which was equal to 15 mg/kg of body weight per day. A safety factor of 2000 was applied, which consisted of 10 to reflect interspecies variation, 10 to reflect intraspecies variation and an additional 20 to reflect the occurrence of the rare and malignant tumour for which a no-effect level could not be identified.

A subsequent evaluation of possible developmental neurotoxicity (FAO/WHO, 2002b) concluded that the LOAEL for toxicity to offspring was 10 mg/kg of body weight per day on the basis of a bilateral decrease in the size of the forebrain (line A) in F1 adult males (7.7–9.8%), a bilateral decrease in the length of the cerebellum (line F) in female pups (15–22%) and a bilateral increase in the length of the cerebellum (line F) in F1 female adults (7.4–15%). The NOAEL was 1 mg/kg of body weight per day.

4. PRACTICAL ASPECTS

4.1 Analytical methods and analytical achievability

The concentration of carbaryl in drinking-water may be determined by liquid chromatography with a UV detector, after preconcentration with C8- or C18-bounded silicas (minimum detectable concentration 10 ng/l in 100 ml) (Marvin & Brindle, 1990); the limit of quantification was 0.5 µg/l in 500 ml (Japan Water Works Association, 2001). However, the retention time is short; hence, interference problems arise with co-extracted semi-polar compounds on the pre-column during the enrichment step. When the water–acetonitrile gradient is gentle, the band becomes broad.

After hydrolysis in alkali to naphtholate and diazotization with trimethylaniline in a sodium dodecyl sulfate micellar solution, the concentration of the diazotized carbaryl may also be determined by a spectrophotometer with a UV/VIS/NIR detector (limit of detection 0.2 mg/l) (Alvarez-Rodriguez et al., 1997) or by HPLC with a UV/VIS detector, post-column (limit of detection 0.2 mg/l) (Portela et al., 2003). The concentration of the fluorescent carbaryl may also be determined by HPLC with fluorescent detector, post-column (limit of detection 2.0 µg/l; USEPA, 1998); the limit of quantification was 0.1 µg/l (Japan Water Works Association, 2001).

The concentration of carbaryl as the pentafluoropropionyl derivative may be determined by GC with an ECD (limit of detection 20 ng/l) or with a dual NPD (limit of detection 100 ng/l) (Oh-Shin et al., 1997). Using solid-phase extraction, carbaryl in water may be determined by GC with an ECD or a dual NPD (limit of detection 74.9 ng/l) (Lyytikainen et al., 2003) or with mass spectrometry (limit of detection 100 ng/l) or may be determined by HPLC coupled to atmospheric pressure electrospray ionization–mass spectrometry (limit of detection 100 ng/l) (Nogueira et al., 2003).
4.2 Treatment and control methods and technical achievability

Available data indicate that GAC adsorption, ozonation and coagulation treatment will remove carbaryl from water. The percentage removal efficiency ranges from 43% to 99% (Kumbhat, 1994). A carbaryl concentration below 50 µg/l should be achievable by drinking-water treatment.

Conventional water treatment using aluminium coagulation (aluminium dosage 8 mg/l plus the addition of 1 mg/l of an anionic polymer), a 30-min settling period and filtration removed 56% of the carbaryl present (Kumbhat, 1994).

Pilot studies indicate that GAC adsorption is 99% effective for carbaryl removal (Kumbhat, 1994). An adsorption isotherm for carbaryl on Darco carbon gave loadings of 0.06 and 0.34 mg/g, with equilibrium carbaryl concentrations of 0.1 and 100 µg/l, respectively (El Dib, 1975). Experiments using Waco PAC showed that a dose of approximately 5 mg/l was required to reduce the carbaryl concentration from 500 to 50 µg/l (Hu et al., 1997).

No reaction was found to occur with chlorine: 2 µg/l carbaryl, 10 mg/l chlorine, pH 7, 20 ºC, 24 h (Mason et al., 1990). Carbaryl reacts rapidly with ozone in laboratory tests (Mason et al., 1990). Ozonation of a 21 mg/l solution at an ozone dose of 25 mg/l gave complete removal (Shevchenko et al., 1982).

The ability of different nanofiltration membranes to remove carbaryl from 0.5–1.5 mg/l solutions was examined in laboratory tests (Kiso et al., 2001). The best removal (92%) was obtained with a polyvinyl alcohol/polyamide membrane with a nominal sodium chloride rejection of 92%. Adsorption of the pesticide onto the membrane was found to be an important contributor to overall removal. A removal of 87% from an initial concentration of 0.1 mg/l was obtained using an HNF-1 polyamide/polysulfone hollow fibre nanofiltration membrane (Jung et al., 2005). A polyamide reverse osmosis membrane (XLE) gave 79% removal from a 100 µg/l solution, but no removal was obtained with a cellulose acetate SC-3100 membrane (Kimura et al., 2004).

5. CONCLUSION

The ADI determined by FAO/WHO (2002a) is 0–0.008 mg/kg of body weight. Carbaryl exposure from food is considered to be low, and a health-based value, assuming a 60-kg adult drinking 2 litres of water per day and allowing 20% of the ADI from drinking-water, would be 50 µg/l (rounded value). However, carbaryl does not appear to be found in drinking-water at significant concentrations, and so it is not considered necessary to propose a formal guideline value.

6. REFERENCES


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USEPA (1998) Method 531.1 — Measurement of N-methyl carbamoyloximes and N-methylcarbamates in drinking water by direct aqueous injection HPLC with post-column derivatization. Cincinnati, OH,
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United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, 15 April.