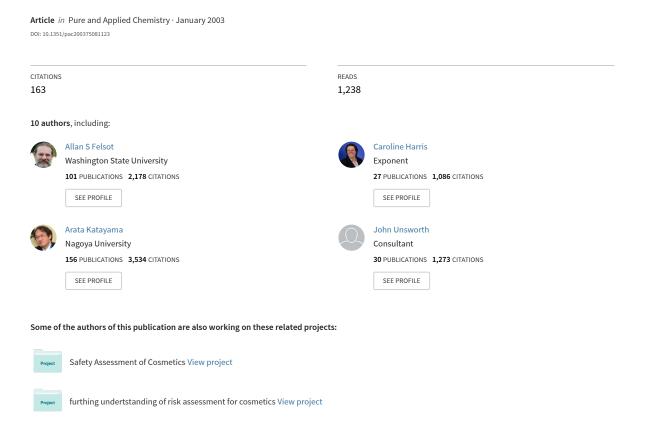
# Regulatory limits for pesticide residues in water (IUPAC Technical Report)



Pure Appl. Chem., Vol. 75, No. 8, pp. 1123–1155, 2003. © 2003 IUPAC

#### INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

### CHEMISTRY AND THE ENVIRONMENT DIVISION COMMISSION ON AGROCHEMICALS AND THE ENVIRONMENT\*

# REGULATORY LIMITS FOR PESTICIDE RESIDUES IN WATER

### (IUPAC Technical Report)

D. J. HAMILTON $^{1,\ddagger}$ , Á. AMBRUS $^2$ , R. M. DIETERLE $^3$ , A. S. FELSOT $^4$ , C. A. HARRIS $^5$ , P. T. HOLLAND $^6$ , A. KATAYAMA $^7$ , N. KURIHARA $^8$ , J. LINDERS $^9$ , J. UNSWORTH $^{10}$ , AND S.-S. WONG $^{11}$ 

Department of Primary Industries, Brisbane, Australia; <sup>2</sup>Joint FAO/IAEA Division, Vienna, Austria;
 <sup>3</sup>Syngenta Crop Protection AG, Basel, Switzerland; <sup>4</sup>Food and Environmental Quality Laboratory, Washington State University, Pullman, WA USA; <sup>5</sup>Exponent International, Harrogate, UK;
 <sup>6</sup>Cawthron Institute, Nelson, New Zealand; <sup>7</sup>Research Center for Advanced Waste and Emission Management, Nagoya University, Nagoya, Japan; <sup>8</sup>Kyoto University, Kyoto, Japan;
 <sup>9</sup>National Institute for Public Health and Environment, Bilthoven, Netherlands;
 <sup>10</sup>Bayer CropScience, Lyon, France; <sup>11</sup>Taiwan Agricultural Chemicals and Toxic Substances Research Institute, Taichung Hsien, Taiwan Republic of China

\*Membership of the Commission during the preparation of this report (1998–2001) was as follows:

Chairman: K. D. Racke (USA); Secretary: D. J. Hamilton (Australia); Titular Members: A. S. Felsot (USA, 1995–2001); D. J. Hamilton (Australia, 1991–2001); A. Klein (Germany, 1989–1999); H. A. Kuiper (Netherlands, 1994–2001); J. Linders (Netherlands, 1996–2001); K. D. Racke (USA, 1993–2001); R. D. Wauchope (USA, 1989–2001); Associate Members: C. A. Bellin (USA, 1998–2001); E. Carazo (Costa Rica, 1999–2001); R. M. Dieterle (Switzerland, 1999–2001); R. H. Gonzalez (Chile, 1999–2001); C. Harris (UK, 1999–2001); A. Katayama (Japan, 1998–2001); H.-G. Nolting (Germany, 1996–1999); B. Petersen (USA, 2001); S. Reynolds (UK, 1995–2001); B. Rubin (Israel, 1997–2001); M. Russell (USA, 1997–1999); M. Skidmore (UK, 1991–1998); K. Tanaka (Japan, 1995–2001); J. Unsworth (France, 1995–2001); S.-S. Wong (Taiwan China, 1995–2001); S. M. Yeh (USA, 1997–2001); B. W. Zeeh (USA, 1991–2000); National Representatives: A. Ambrus (Hungary, 1991–2000); I. Baptista De Alleluia (Brazil, 2001); Y.-H. Kim (Korea, 2000–2001); N. Kurihara (Japan, 1983–1999); G. R. Stephenson (Canada, 1998–2001).

‡Corresponding author

Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC permission on condition that an acknowledgment, with full reference to the source, along with use of the copyright symbol  $\odot$ , the name IUPAC, and the year of publication, are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

## Regulatory limits for pesticide residues in water

### (IUPAC Technical Report)

Abstract: National governments introduced residue limits and guideline levels for pesticide residues in water when policies were implemented to minimize the contamination of ground and surface waters. Initially, the main attention was given to drinking water.

Regulatory limits for pesticide residues in waters should have the following characteristics: definition of the type of water, definition of the residue, a suitable analytical method for the residues, and explanation for the basis for each limit.

Limits may be derived by applying a safety factor to a no-effect-level, or from levels occurring when good practices are followed and also passing a safety assessment, or from the detection limit of an analytical method, or directly by legislative decision.

The basis for limits and guideline values issued by WHO, Australia, the United States, New Zealand, Japan, Canada, European Union, and Taiwan is described, and examples of the limits are provided. Limits have been most commonly developed for drinking water, but values have also been proposed for environmental waters, effluent waters, irrigation waters, and livestock drinking waters. The contamination of ground water is of concern because it may be used as drinking water and act as a source of contamination for surface waters. Most commonly, drinking water standards have been applied to ground water.

The same terminology may have different meanings in different systems. For example, guideline value (GV) in WHO means a value calculated from a toxicology parameter, whereas in Australia, a GV is at or about the analytical limit of determination or a maximum level that might occur if good practices are followed. In New Zealand, the GV is the concentration where aesthetic significance is influenced. The Australian health value (HV) is conceptually the same as the WHO GV. The New Zealand maximum acceptable value (MAV) and the Canadian maximum acceptable concentration (MAC) are also conceptually the same as the WHO GV.

Each of the possible ways of defining the residues has its merits. A residue limit in water expressed as the sum of parent and toxicologically relevant transformation products makes sense where it is derived from the acceptable daily intake (ADI). For monitoring purposes, where it is best to keep the residue definition as simple as possible for the sake of practical enforcement and economy, the parent or a marker residue is preferable. It is also possible for parent and degradation products (hydrolysis and photolysis products and metabolites) to become physically separated as the water moves through soil strata, which suggests that separate limits should be set for parent and important degradation products.

The Commission has made 12 recommendations for regulatory limits for pesticide residues in water. The recommendations will act as a checklist for authorities introducing or revising limits or guidelines for pesticide residues in water.

## RECOMMENDATIONS OF THE IUPAC COMMISSION ON AGROCHEMICALS AND THE ENVIRONMENT

- The terminology for pesticide residue limits in water should be harmonized. As a first step, IUPAC should prepare and issue recommended terminology for the various limits and guidelines for pesticide residues in water. International agencies and national governments would then be encouraged to adopt the terminology when introducing or revising their regulations or recommendations.
- 2. The aim or purpose of establishing a set of pesticide residue limits in water should be clearly enunciated so that they are used only for the intended purpose.
- 3. The nature of the water to which the pesticide residue limits apply should be defined and explained.
- 4. The methods for establishing pesticide residue limits in water should be described and should include the data requirements, assumptions, reasons for choice of factors (assessment, uncertainty, or safety) and the nature of the water to which the limits apply.
- 5. The rationale for each pesticide residue limit should be explained publicly in a transparent way. The explanation should summarize the available data, draw attention to inadequacies or inconsistencies of data and show in a logical way the derivation of the recommended value. The explanation should include, where relevant, the choice of factor (assessment, uncertainty, or safety), availability of analytical methods, and residue definition.
- 6. The compound or compounds to be included in a residue limit for water should be stated. It is preferable to set individual residue limits for parent pesticide and each relevant transformation product.
- 7. Analytical methods for residues in water should be developed with limits of quantification (LOQs) low enough to match concentrations related to relevant biological effects.
- 8. A pesticide residue limit in water that is designed for monitoring or regulatory purposes should be established at a level no lower than the LOQ of a practical analytical method.
- 9. A process designed to reduce the levels of pesticide residues in water should not introduce contaminants that pose new risks.
- 10. Guidelines for drinking water calculated from the acceptable daily intake (ADI) should follow the WHO system [60-kg body weight, consumption 2 l/day, allocate 1 or 10 % tolerable daily intake (TDI) or ADI depending on the pesticide uses and properties].
- Guideline levels should never be taken as a licence to degrade a water supply to the guideline levels.
- 12. Short-term deviations above a regulatory limit for residues in water do not necessarily mean that the water is unsuitable for the intended purpose. The amount and duration of the deviation should be subject to a risk assessment taking into account the basis for the regulatory limit.

#### **CONTENTS**

- 1. INTRODUCTION
- 2. REGULATORY LIMITS
- 3. DEFINITION OF THE TYPE OF WATER
- 4. DESCRIPTION OF THE SITUATION WHERE THE LIMIT OR GUIDELINE APPLIES
- 5. DEFINITION OF THE RESIDUE AND AN EXPLANATION FOR THE CHOSEN RESIDUE DEFINITION
- 6. SUITABLE REGULATORY ANALYTICAL METHOD
- 7. BASIS FOR THE REGULATORY LIMIT
  - 7.1 "Safety" or "margin of safety" limit

WHO

Australia

**United States** 

New Zealand

Japan

Canada

European Union

Taiwan

- 7.2 "Good practices" limit
- 7.3 "Zero residue (LOD or LOQ)" limit
- 7.4 Legislative limit
- 8. INTERPRETATION OF RESIDUE-MONITORING DATA
- 9. DISCUSSION
- 10. CONCLUSION
- 11. ACKNOWLEDGMENT
- 12. REFERENCES
- 13. GLOSSARY OF ACRONYMS

#### 1. INTRODUCTION

Contamination of ground water by pesticide residues was for many years generally regarded as unlikely because the soil profile acts as a purifying filter [1]. Residue contamination of surface waters was regarded as transitory because the focus was on organochlorine pesticides such as DDT, which were of very low water solubility and had a strong tendency to attach to particulate matter and to disappear from clear water. About 20 years ago, information had accumulated that some herbicide compounds, which were generally more water-soluble and more widely used than the organochlorines, were being detected in both surface and ground waters. Policies were developed to reduce contamination of ground and surface waters, and regulatory limits and guideline levels were introduced for residues in drinking water.

Setting regulatory limits for pesticide residues in waters is complex. First, we must decide which type of water is relevant to the proposed limit (e.g., drinking water, reservoir water, lakes and streams, ground water, water for aquaculture, irrigation water, and drinking water for farm animals). Second, should we adopt a risk assessment-based approach or a "no more than reasonable if good practices are followed" approach, or a combination of the two? Different approaches will lead to different maximum limits being set. A limit based on a risk to human health or the environment may allow much higher levels of residue in the water than would ever occur in practice. An arbitrarily chosen maximum limit may be economically wasteful in requiring correction of harmless residues that do not meet the standard while ignoring more hazardous contaminants that are technically not pesticides. An important principle is that the establishment of guideline levels or standards does not imply that the water quality should be degraded to the recommended levels.

Greim [2] noted that drinking-water standards rely on a variety of criteria that are difficult to comprehend even for experts and imply that the standard levels are of different toxicological significance, which is understood neither by the public nor by regulatory agencies. As a result, a drinking-water level exceeding the standard level is of great concern to the public.

This paper will examine the general principles for establishing regulatory limits and then will discuss how these principles have been applied to limits and guideline levels for residues in water.

Concentrations of residues in water are expressed in some documents as mg/l and in others as  $\mu$ g/l. In this paper, we will use  $\mu$ g/l throughout for consistency and ease of understanding.

The common names for pesticides have been approved by the Technical Committee 81 of the International Organization for Standardization (ISO) and published in ISO 1750–1981 and its Addenda and Amendments.

#### 2. REGULATORY LIMITS

Regulatory limits for pesticide residues in water must have a number of characteristics if they are to be useful and to survive legal challenges. The authority of regulatory limits may derive from science (e.g., a relationship between the limit and a toxic hazard) or legislative enactment or both. Comparisons of regulatory limits established by different national authorities should take into account the underlying derivations. Differences may still exist even when the limits are linked to a measurable property such as toxicity or limit of quantification of an analytical method and when they apply to the same type of water (e.g., drinking water at the tap).

Regulatory limits for residues in water should include the following characteristics:

- Definition of the type of water and description of the situation where the limit applies
- Definition of the residue and an explanation for the chosen residue definition (as for residues in food crops)
- Suitable regulatory analytical method
- The basis for the limit should be explained, for example:
  - a "safety" limit or a "margin of safety" limit, where the limit is calculated from a biological property such as a no-observed-effect-level (NOEL);
  - a "good practices" limit, where the limit is derived from field trials that demonstrate the maximum levels that might occur in practice;
  - an "LOQ" limit, where the limit is based on the limit of quantification of an analytical method; or
  - a legislative limit, where the limit is set in legislation.

Guideline levels should have similar characteristics, but do not have legislative authority. The purpose of guideline levels should be stated, for example, as an indicator whether good practices are being followed or if a particular water body is becoming contaminated.

Jiménez et al. [3] explained that the goal of establishing standards is to achieve benefits while minimizing the risk at a specific cost. In practice, risks and benefits are not known, and in the developed countries, very strict values may result from the pressure of ecological groups, thus producing standards based on political reasons rather than on scientific or logical reasoning. It is not appropriate for developing countries to copy such standards or guidelines without analysing the context under which they have been selected. It is essential for each country to establish priorities according to its actual needs and to formulate the criteria according to its economical and technological situation. In Mexico, the priority pesticides for water guidelines are alachlor, atrazine, bentazone and simazine; the selection was based on either their toxicity, soil mobility, or frequency of use, or a combination thereof.

Regulatory limits for pesticide residues should be established and administered in context with risks from other contaminants and practices to achieve an overall benefit. Van Dijk-Looijaard and Van Genderen [4] described the use of ozone on raw water to reduce pesticide residue concentrations below

the drinking-water standard of  $0.1 \mu g/l$  in Europe. In the process, the ozone generates the genotoxic carcinogen bromate. The removal of one or two less-toxic pesticides at the expense of adding bromate is a questionable situation, but is permitted by current regulations.

#### 3. DEFINITION OF THE TYPE OF WATER

Definitions by the European Union (EU) [5] are as follows.

*Surface water* means inland waters except ground, transitional, and coastal waters, except in respect of chemical status for which it shall also include territorial waters.

*Ground water* means all water that is below the surface of the ground in the saturation zone and in direct contact with the ground or subsoil.

*Inland water* means all standing or flowing water on the surface of the land, and all ground water on the landward side of the baseline from which the breadth of territorial waters is measured.

*River* means a body of inland water flowing for the most part on the surface of the land, but which may flow underground for part of its course.

Lake means a body of standing inland surface water.

Transitional waters are bodies of surface water in the vicinity of river mouths, which are partly saline in character as a result of their proximity to coastal waters, but which are substantially influenced by freshwater flows.

Coastal water means surface water on the landward side of a line, every point of which is at a distance of one nautical mile on the seaward side from the nearest point of the baseline from which the breadth of territorial waters is measured, extending where appropriate up to the outer limit of a transitional water.

The European Union also defines water intended for human consumption [6]. It is all water either in its original state or after treatment, intended for drinking, cooking, food preparation, or other domestic purposes, regardless of its origin, and whether it is supplied from a distribution network, from a tanker, or in bottles or containers; and all water used in any food-production undertaking for the manufacture, processing, preservation, or marketing of products or substances intended for human consumption unless the competent national authorities are satisfied that the quality of the water cannot affect the wholesomeness of the foodstuff in its finished form.

In Australia, *drinking water* is defined as water intended primarily for human consumption, but which has other domestic uses. It may be consumed directly as it comes from the tap or indirectly in beverages or foods prepared with water, and among its other uses are bathing and showering [7]. The guidelines are intended to meet the needs of the consumers and apply at the point of use, for example, at the tap. The National Health and Medical Research Council Australian Drinking Water Guidelines, however, do not apply to bottled or packaged water.

In Taiwan, *drinking water* refers to water supplied for drinking by the general public [8]. *Drinking-water sources* include tap water (public water supplied via pipes or other conduits), surface water (the entirety or sections of waters in rivers, lakes, dams, ponds, or other systems), ground water (subsurface water), and other designated waters. Only surface and ground waters that are consistent with drinking-water quality standards are suitable for drinking water.

In New Zealand, *drinking water* is water intended to be used for human consumption, food preparation, utensil washing, oral hygiene, or personal hygiene [9]. *Potable water* is drinking water that does not contain any determinands that exceed the maximum acceptable values (MAVs). *Raw water* is water that has not received any treatment to make it suitable for drinking. *Secure ground water* is water contained beneath the land surface, which is abstracted by a secure well head; it must not be under the direct influence of surface water or demonstrate significant and rapid shifts in characteristics; less than 0.005 % of the water should have been present in the aquifer for less than one year.

The U.S. Environmental Protection Agency (EPA) defines *surface water* as all water that is open to the atmosphere and subject to surface runoff [10]. *Ground water under the direct influence of sur-*

face water means any water beneath the surface of the ground with significant occurrence of insects or other macroorganisms, algae, or large-diameter pathogens such as *Giardia lamblia* or *Cryptosporidium*, or significant and relatively rapid shifts in water characteristics such as turbidity, temperature, conductivity, or pH, which closely correlate to climatological or surface water conditions.

#### 4. DESCRIPTION OF THE SITUATION WHERE THE LIMIT OR GUIDELINE APPLIES

An EU document [6] cited principles for establishing standards of water quality for human consumption and stated that the values are to be complied with at the point where water intended for human consumption is made available to the appropriate user.

In the United States, the maximum contaminant level (MCL) is the maximum permissible level of a contaminant in water that is delivered to any user of a public water system [11].

Larson et al. [12] also stated that the U.S. standards for drinking water (MCL and MCLG, maximum contaminant level goal) apply to finished (treated) drinking water supplied by a community water supply and require that the annual average concentration of the specific contaminant be below the MCL.

Sidhu [13] described the U.S. processes for deriving MCLs and MCLGs and suggested that the primary drinking-water standards may also serve as guidelines in environmental regulations such as domestic sewage treatment requirements, disposal of hazardous wastes, surface water industrial discharge controls, agricultural fertilizer and pesticide practices, and ground water remediation levels.

Application of drinking-water limits as guidelines for other waters seems inappropriate and perhaps reflects a tendency to use a limit just because it exists, irrespective of its basis and design for a specific purpose. The U.S. drinking-water standards are designed to apply to finished (treated) drinking-water supplies.

Barbash and Resek [14] explained that the contamination of ground water by pesticides is of concern because the ground water may be used for drinking and it may be a source of pesticide contamination of surface waters which support aquatic ecosystems. The surface waters may also be used as drinking-water supplies. Most commonly, drinking-water limits have been applied to ground water.

## 5. DEFINITION OF THE RESIDUE AND AN EXPLANATION FOR THE CHOSEN RESIDUE DEFINITION

In discussing the WHO guidelines, Younes and Galal-Gorchev [15] pointed out that while considerable information is available on the toxicity of mammalian metabolites of pesticides, information on the nature and toxicity of environmental degradation products of pesticides is not so well known. Consequently, environmental degradation products have not been taken into account in the WHO guidelines for drinking-water quality.

In the OECD countries and the EU Member States, several documents have been developed and discussed concerning guidance and criteria of dossiers and studies required to support the registration of plant protection products [16]. In these documents, a definition of the residue is required, taking into account the specific properties of the substance. These relate to inherent properties such as physicochemical characteristics, but also to compartment-related properties such as metabolism, excretion, and degradation in environmental compartments.

Therefore, a distinction is made for which compartment the residue is relevant:

- residues relevant to maximum residue limits (MRLs) for food;
- residues relevant to consumer safety, subdivided in nature and levels of residues and dietary exposure of consumers;
- residues relevant to worker safety; or
- residues relevant to the environment subdivided into the compartments water, soil, and air.

Depending on the rate of transformation in the compartments under consideration, the main part of the residue may consist of the active substance, the main metabolite, a mix of several metabolites (including or excluding the active substance), or even bound residues. The residue definition for water does not normally include bound residues. When the transformation of the active substance occurs with rapid rates (e.g., up to 20 days half-life), the formation of main metabolites may be the most important factors determining the residue. At very high rates of transformation or degradation, with half-lives from a couple of hours to a few days (e.g., by hydrolysis), the main reaction product may even be considered as the active part. Depending on the transformation rates of the individual metabolites, it is necessary to judge which metabolite or complex of metabolites should be considered the relevant residue. If the transformation of the active substance occurs with moderate rate, say up to 60 days half-life, generally the active substance is the relevant residue. Also, at even slower transformation rates (e.g., above 60 days half-life), the active substance should be considered as the relevant residue.

For evaluation purposes, it is generally not possible or even advisable to include the metabolite with the parent compound. Separate evaluation is recommended to get a clear and detailed picture of the assessment of risk. Sometimes, when information is available only with respect to bioassays, all biological activity is combined in the possible effects on the microbial population used. It may be appropriate in those cases to require additional information from the registrant relating to individual components.

In the European Union, a guidance document is under development on relevant metabolites, taking into account the degradation and metabolism studies of the parent compounds [17]. If, in the rate and route of <sup>14</sup>C-labeled pesticide degradation studies in soil or water, a transformation product has been identified in amounts exceeding 10 % of the applied dose, that product should be considered as a major degradation product. Other degradation products are considered of minor importance and are excluded from an additional risk assessment.

Each major product is considered to be potentially relevant, and an additional risk assessment using some key parameters should determine its relevancy. The aim of the procedure of an additional risk assessment is to define a substance as relevant or nonrelevant. If a substance is determined "relevant" for the compartment at risk, all the information required for the active substance should be delivered to the authorities. The studies on degradation in soil are also used for estimating the risk for ground water contamination and the potential for surface water exposure to major degradation products through processes such as drainage.

The additional risk assessment takes into account specific information on the metabolite concerning its pesticidal activity, toxicology and ecotoxicology.

With respect to pesticidal activity, a potential relevant metabolite should be tested in a biological screen at the maximum application rate. Showing an effect below 5 % (of the parent activity) should be considered as having no consequential pesticidal activity. The additional toxicity testing for the potential relevant metabolite may include a 90-day subchronic study with rats, resulting in a no-observed-adverse-effect-level (NOAEL), a package of genotoxicity studies, including Ames test, gene mutation test with mammalian cells and a chromosome aberration test. Expert judgment may be required in determining a metabolite to be nonrelevant based on these results. If the margin of safety is above 1000, the substance should be considered nonrelevant. Finally, for the additional ecotoxicity testing, a distinction is made between the aquatic and the terrestrial ecosystem. If surface water is shown to be the compartment at risk, ecotoxicity tests with the standard organisms, fish, daphnids, and algae are required. To interpret the results, the toxicity—exposure ratio should be calculated and compared to the appropriate trigger values, generally 100 for acute and 10 for chronic exposure.

A European Crop Protection Association proposal [18] deals with metabolites of pesticides in soils or aquatic systems and the question of whether they need to be included in standards for water. The document proposes to refer to metabolites that exceed defined trigger levels as major metabolites warranting further investigation.

Major metabolites would be examined for their ecological relevance, i.e., by comparison of ecotoxicity and predicted exposure for organisms in soil, water, and sediment. Potential presence in ground water would be assessed on the basis of drinking-water standards of toxicological acceptability. If the metabolite meets the tests of exposure below acceptable ecotoxicological and toxicological levels and has no pesticidal activity, then it would be considered nonrelevant requiring no further investigation.

Larson et al. [12] provided information on the relative toxicity of pesticides and their transformation products to aquatic organisms: algae, fish, and invertebrate organisms. Differences in toxicity between parent and transformation product in some cases are organism-dependent, for example, p,p'-TDE is more toxic to some species of fish and less toxic to others than the parent p,p'-DDT. The toxicity of metabolites closely related to the parent may be anticipated to an extent, for example, endosulfan sulfate is more toxic to fish than endosulfan, fenitrooxon is more toxic to invertebrate insects than parent fenitrothion. The toxicity of other transformation products is not so readily anticipated: metabolites 3-methyl-4-aminophenol and 1-naphthol are reported to be more toxic to fish than the parent compounds fenitrothion and carbaryl, respectively. Clearly, those transformation products of similar or enhanced ecotoxicity should be either included in the residue definition of the parent for aquatic environmental quality criteria or have a separate guideline level.

Fact sheets issued by Canada for specific pesticides explicitly state the residue to which the *maximum acceptable concentration* (MAC) applies [19]. For example, the MAC for aldicarb applies to the total for aldicarb and its metabolites, aldicarb sulfoxide and aldicarb sulfone. The reason is that the two metabolites are also acetylcholinesterase inhibitors with the sulfoxide approximately equipotent with the parent compound and the sulfone somewhat less potent. In a second example, the atrazine MAC applies to atrazine and its metabolites. Atrazine is frequently found along with the metabolite deethylatrazine and is sometimes accompanied by other *N*-dealkylated metabolites. Deethylatrazine, although not as acutely toxic as atrazine, was equally effective in producing hormone imbalances in the test animals.

#### 6. SUITABLE REGULATORY ANALYTICAL METHOD

A WHO Consultation [20] stated that guideline values should not normally be set lower than analytical LOQs achievable in qualified laboratories under routine operating conditions.

Analytical methods must be available to measure residues at specified regulatory limits or guideline values, so the regulatory limit for a residue should be no lower than the LOQ of a practical analytical method. A suitable approach for determining the method LOQ is to find the lowest concentration where recoveries are repeatable and quantitative. For example, the following procedure describes a commonly accepted range for recoveries.

The method LOQ is the lowest concentration tested for which an acceptable mean recovery is obtained. The acceptable range is usually between 70 and 110 %, and the relative standard deviation should be a maximum 20 %. The signal corresponding to the LOQ should lie within the calibration curve.

The mean recovery can be determined by analysis of at least five fortified samples at the LOQ and two unfortified (control) samples of the relevant matrix. If necessary, recoveries should be corrected for control values. However, the control values should not exceed 30 % of the LOQ, and the uncorrected recovery results should also be reported. For the validation of an analytical method, the European Union requests the analysis of an additional five fortified samples at  $10 \times \text{LOQ}$  [21]. In analytical series, procedural fortified samples at the LOQ should be included, verifying the performance of the analytical method applied and its correct use.

An EU document [6] cited principles for establishing standards of water quality for human consumption and stated that the methods used to analyze the quality of the water intended for human consumption should be such as to ensure that the results obtained are reliable and comparable.

The EPA specifies detection limits to be achieved for analysis of contaminants in drinking water [22]. The detection limits, included in Table 4, are generally in the range of  $0.01-1~\mu g/l$ . The EPA also specifies the accuracy to be achieved in the analysis of performance evaluation samples provided by EPA. Laboratories must achieve quantitative results for most contaminants within  $\pm 40$  to  $\pm 50~\%$  or within 2 standard deviations.

#### 7. BASIS FOR THE REGULATORY LIMIT

Regulatory limits or guideline levels may be derived in various ways:

- a "safety" or "margin of safety" limit;
- a "good practices" limit;
- an "LOQ" limit; and
- a legislative limit.

Each of these will be discussed in turn.

First, there is a limit based on toxicity or ecotoxicity testing which produce values calculated from experimentally determined no-effect levels or acceptable effect levels. An additional margin of safety may be added by including a safety factor in the calculation. Guideline levels for drinking water have often been derived in this way; the calculation assumes that a person of standard weight consumes 2 l/day water and that the residue consumed accounts for an agreed part of the ADI, usually 1 or 10 %. The ADI includes a safety factor, usually 100, so there is a margin of safety in such guideline levels or regulatory limits. Countries may disagree on such limits even when the same methodology is used because national ADIs may be different and the percent of ADI allocated to drinking water is arbitrary.

Limits derived from ecotoxicity testing have even more possibilities for variation, with choice of species, duration of exposure, and decisions on acceptable degree of mortalities or other effects.

A limit derived from "good practices in the use of a pesticide" will depend on the use pattern needed for controlling the pest (e.g., mosquitoes or weeds) and assumptions about the volume of water receiving the dose. Such a limit is likely to be related to local conditions.

Guideline values or limits based on the LOQ of an analytical method will not be consistent from one authority to another if the analytical methods are different or if they are established at different times. There is a tendency for LOQs to move to lower concentrations as analytical techniques and technology develop.

Legislative limits have the authority of the law and may be based on scientific assessments together with policy of what is in the best interests of the general population, consumers and trade.

The variety of acronyms can be confusing. Some are used widely, while others relate to specific national regulations or guidelines. Acronyms used in this paper are listed in a glossary after the references.

#### 7.1 "Safety" or "margin of safety" limit

#### **WHO**

A WHO Consultation [23] developed guideline levels for nine herbicides in drinking water (Table 1). The guideline values were based on evaluation of each compound's toxicity data. The calculation assumed that an average adult of 70 kg consumes 2 l/day water and that 10 % of the ADI is allocated to drinking water.

Herbicide Guideline level, µg/l Comment Alachlor Alachlor in drinking water at 0.3 µg/l may produce an excess lifetime cancer risk no greater than 1 in 100000. Alachlor should not be used in areas where it may contaminate drinking water via ground water and surface water. 25 Bentazone should not be used in areas where it may contaminate Bentazone drinking water via ground water and surface water. MCPA 0.5 Metolachlor 5 Pendimethalin 17 During the treatment of water with granulated activated charcoal, pendimethalin in the presence of nitrite might produce N-nitroso compounds, which could be carcinogenic. Propanil 175 The guideline value may not be protective if some propanil metabolites, in particular 3,3',4,4'-tetrachloroazobenzene, are present in drinking water. Pyridate 60 Simazine 17 During the treatment of water with granulated activated charcoal, simazine in the presence of nitrite might produce N-nitroso compounds, which could be carcinogenic. Trifluralin 170 Pure trifluralin (>99 %) is relatively free of toxic effects. However,

**Table 1** Guideline levels for herbicides in drinking water [23].

The WHO document drew attention to further points of policy beyond the guideline levels:

the technical product can be contaminated with N-nitroso-

dipropylamine, which is a known carcinogen.

- The possible presence in the commercial product of impurities of toxicological significance was considered, but not taken into the guideline levels.
- Emphasis should be placed on preventive measures and examination of practices to minimize water contamination.
- At registration, more attention should be paid to potential for water contamination.
- The concept of good agricultural practice should be extended to minimizing contamination of ground water.
- Guidelines should be developed for predicting and verifying the environmental fate and distribution of herbicides with regard to contamination of drinking water through ground and surface waters.

A WHO Consultation [20] reiterated and expanded on the concepts of the earlier consultation on WHO guideline values for contaminants, including pesticides, for drinking-water quality:

- A guideline value represents the level of a constituent ensuring an aesthetically pleasing water without significant health risk to the consumer.
- The defined drinking-water quality is such that it is suitable for human consumption and all usual domestic purposes.
- Deviation above a guideline value is a signal to investigate the cause prior to remedial action.
- The guideline values, although representing a water quality suitable for lifelong consumption, do not imply that the quality of drinking water should be degraded to the recommended levels.
- Short-term deviations above the guideline values do not necessarily mean that the water is unsuitable for consumption. The amount and duration of the deviation not affecting public health depend on the specific substance.

• National standards based on the guidelines may differ appreciably from the guideline values because of local geographical, socioeconomic, dietary, and industrial conditions.

The Consultation agreed for pesticides that the guideline value would be based on 1 % of the ADI where exposure from food residues approaches the ADI, but in other cases, a higher allocation than 1 % may be used.

Water consumption of 2 l/day was assumed for the calculations.

The Consultation also noted that taste and odor can be the limiting factors for acceptance of drinking water.

Younes and Galal-Gorchev [15] explained the current WHO approach for estimating health-based guidelines (or guideline values, GVs) for pesticide residues in drinking water. Guideline values are shown in Table 2.

**Table 2** Health-based guideline values derived by WHO for pesticide residues in drinking water [15]. GVs are calculated from 1 % of the tolerable daily intake for those pesticides with a potentially high exposure from food and from 10 % TDI for others. The GV for potentially carcinogenic pesticides is based on modeling and is associated with an estimated upper-bound excess lifetime risk of  $10^{-5}$ .

Pesticide	%	GV	Pesticide	%	GV	Pesticide	%	GV
	TDI	μg/l		TDI	μg/l		TDI	μg/l
Alachlor	a	20	1,3-Dichloropropene	a	20	Metolachlor	10	10
Aldicarb	10	10	Dichlorprop	10	100	Molinate	10	6
Aldrin/dieldrin	1	0.03	Diquat	10	10	Pendimethalin	10	20
Atrazine	10	2	EDB	a	0.4 - 15	Pentachlorophenol	a	9
Bentazone	10	300	Fenoprop	10	9	Permethrin	1	20
Carbofuran	10	7	Glyphosate	10	$\mathrm{U}^\mathrm{b}$	Propanil	10	20
Chlordane	1	0.2	Heptachlor + epoxide	1	0.03	Pyridate	10	100
Chlortoluron	10	30	Hexachlorobenzene	a	1	Simazine	10	2
Cyanazine	10	0.6	Isoproturon	10	9	2,4,5-T	10	9
2,4-D	10	30	Lindane	1	2	Terbuthylazine	10	7
2,4-DB	10	90	MCPA	10	2	Trifluralin	10	20
DDT	1	2	Mecoprop	10	10			
1,2-Dibromo-3- chloropropane	a	1	Methoxychlor	10	20			

 $<sup>^{</sup>a}$ GV associated with estimated upper-bound excess lifetime risk of  $10^{-5}$  (one additional cancer case per 100000 population ingesting drinking water which contains the pesticide at the GV for 70 years).

For a pesticide exhibiting threshold toxicity effects, the TDI or ADI was used in conjunction with a daily consumption of 2 l water by a 60-kg adult. For pesticides that are highly persistent, have a high bioaccumulation potential, and are often found in food, only 1 % of the TDI was allocated to drinking water. Examples are DDT, heptachlor, and lindane. In other cases, a default value of 10 % TDI was allocated to drinking water.

For those pesticides considered to be carcinogenic, an extrapolation model was used to derive GVs corresponding to an upper-bound estimate of an excess lifetime cancer risk of 1 per 100 000 of the population exposed.

#### Australia

In Australia, the guidelines for pesticides in drinking water are divided into two categories, GVs and health values (HVs) [7].

<sup>&</sup>lt;sup>b</sup>U: unnecessary to recommend a health-based GV because the calculated value is much higher than concentrations normally found in drinking water.

Guideline values are used by regulatory authorities for surveillance and enforcement purposes. For pesticides that are not approved in water or water catchment areas, the GV is set at or about the analytical limit of determination. Where a pesticide is approved for use in water or water catchment areas, the GV is set at a level consistent with good management practice and which would not result in any significant risk to health of the consumer over a lifetime of consumption. Exceeding the GV indicates that undesirable contamination of drinking water has occurred; it does not necessarily indicate a hazard to public health.

Health values are intended for use by health authorities in managing the health risks associated with inadvertent exposure resulting from a spill or misuse of a pesticide. HVs are calculated from the ADI (usually 10 %) for a 70-kg adult consuming 2 l/day water. For compounds where no toxic threshold can be demonstrated, the risk associated with exposure at very low concentrations may be extrapolated using a risk assessment model from the dose–response relationship at higher doses.

The National Health and Medical Research Council [7] summarized the differences between the Australian and WHO guidelines. Australia uses an adult body weight of 70 kg, whereas WHO uses 60 kg. For genotoxic carcinogenic compounds, WHO uses a risk assessment calculation with the guideline set at the concentration that would give rise to 1 additional cancer per 100 000 people. Australian guidelines for these types of compound take into consideration:

- the limit of determination of an analytical method;
- the concentration, using the WHO method, that would give rise to one additional cancer per million people if water with the compound at that concentration were consumed over a lifetime; and
- a value based on a threshold effect calculation, with an additional safety factor for potential carcinogenicity.

Fact sheets are available for some pesticides, explaining the basis for the GVs (organochlorine pesticides, atrazine and 2,4-D). Guideline and health values for 120 pesticides are provided in the document and are summarized in Table 3. The document stresses that the guidelines should never be seen as a licence to degrade the quality of a drinking-water supply to the guideline level.

Table 3 Drinking-water guidelines for pesticides in Australia [7]. GV is guideline value; HV is health value.

Pesticide	GV	HV	Pesticide	GV	HV	Pesticide	GV	HV
	μg/l	μg/l		μg/l	μg/l		μg/l	μg/l
Acephate		10	EDB	1	1	Parathion		10
Aldicarb	1	1	Endosulfan	0.05	30	Parathion-methyl	0.3	100
Aldrin and dieldrin	0.01	0.3	Endothal	10	100	Pebulate	0.5	30
Ametryn	5	50	EPTC	1	30	Pendimethalin		300
Amitrole	1	10	Ethion	-	3	Pentachlorophenol	0.01	10
Asulam	•	50	Ethoprophos	1	1	Permethrin	1	100
Atrazine	0.5	20	Etridiazole	0.1	100	Picloram	_	300
Azinphos-methyl	2	3	Fenamiphos		0.3	Piperonyl Butoxide		100
Benomyl	_	100	Fenarimol	1	30	Pirimicarb		5
Bentazone		30	Fenchlorphos		30	Pirimiphos-ethyl		0.5
Bioresmethrin		100	Fenitrothion		10	Pirimiphos-methyl		50
Bromacil	10	300	Fenoprop		10	Profenofos		0.3
Bromophos-ethyl		10	Fensulfothion	10	10	Promecarb		0.03
Bromoxynil		30	Fenvalerate		50	Propachlor	1	50
Carbaryl	5	30	Flamprop-methyl		3	Propanil	0.1	500
Carbendazim		100	Fluometuron		50	Propargite		50
Carbophenothion		0.5	Formothion		50	Propazine	0.5	50
Carbofuran	5	10	Fosamine		30	Propiconazole	0.1	100
Carboxin	2	300	Glyphosate	10	1000	Propyzamide	2	300
Chlordane	0.01	1	Heptachlor,	0.05	0.3	Pyrazophos		30
			include epoxide			, 1		
Chlorfenvinphos		10	Hexaflurate		30	Quintozene		30
Chlorothalonil	0.1	30	Hexazinone	2	300	Simazine	0.5	20
Chloroxuron		10	Lindane	0.05	20	Sulprofos		10
Chlorsulfuron		100	Malathion		50	2,4,5-T	0.05	100
Clopyralid	1000	1000	Methidathion		30	Temephos	300	300
2,4-D	0.1	30	Methiocarb	5	5	Terbacil	10	30
DDT and derivs	0.06	20	Methomyl	5	30	Terbufos	0.5	0.5
Diazinon	1	3	Methoxychlor	0.2	300	Terbutryn	1	300
Dicamba		100	Metolachlor	2	300	Tetrachlorvinphos	2	100
Dichlobenil		10	Metribuzin	1	50	Thiobencarb		30
Dichlorvos	1	1	Metsulfuron-methyl	5	30	Thiometon		3
Diclofop-methyl		5	Mevinphos	5	5	Thiophanate		5
Dicofol		3	Molinate	0.5	5	Thiram		3
Difenzoquat		100	Monocrotophos		1	Triadimefon	100	2
Dimethoate		50	Napropamide	1	1000	Trichlorfon		5
Diphenamid	2	300	Nitralin		500	Triclopyr		10
Diquat	0.5	5	Norflurazon	2	50	Trifluralin	0.1	50
Disulfoton	1	3	Oryzalin		300	Vernolate	0.5	30
Diuron		30	Oxamyl	5	100			
DPA (2,2-DPA)		500	Paraquat	1	30			

#### United States

Nowell and Resek [11] provided a detailed review of U.S. standards for pesticide residues in water.

In the United States, *standards* refer to threshold values that are legally enforceable by agencies of the U.S. government, for example, EPA MCLs for drinking water. MCLs, although established with a human health-based component, also take into account effects on taste and odor, treatment feasibility, cost of treatment, and analytical detection.

Guidelines refer to threshold values that have no regulatory status, but are provided as advice. Agencies may use "criteria", "advisories", "guidance", or "recommendations" as synonyms for guidelines. Federal guidelines generally are designed to protect human health, aquatic organisms or wildlife, but they do not reflect economic feasibility or analytical detection limit. States may use the Federal guidelines as State standards.

Selections of EPA drinking-water standards and advisories for pesticides are listed in Table 4.

For a contaminant that may adversely affect human health and have the potential to contaminate public water systems, the Safe Drinking Water Act requires the EPA to publish a nonenforceable *MCLG*. The MCLG is a nonenforceable health goal that is set at a level at which no known or anticipated adverse effect on the health of persons occur and that allows an adequate margin of safety [24]. The MCLG is set at zero for a known or probable human carcinogen.

At the same time, the EPA is required to issue an MCL or a required treatment technique. The MCL is the maximum permissible level of a contaminant in water that is delivered to any user of a public water system and is set as close to the MCLG as possible. The MCL is an enforceable standard.

**Table 4** EPA drinking-water standards and advisories, listing the MCLs, MCLGs and health advisories. DWEL = drinking-water equivalent level. Data are summarized from EPA [24]. Required detection limits are summarized from EPA [22].

	Star	ndards		advisory, g child		Health advi	sory	Required detection
Pesticide, metabolite	MCL, μg/l	MCLG, μg/l	1-day, μg/l	10-days, μg/l	DWEL, μg/l	Lifetime, µg/l	10 <sup>-4</sup> cancer risk, μg/l	limit, μg/l
Acifluorfen (sodium)			2000	2000	400		100	
Alachlor	2	0	100	100	400		40	0.2
Aldicarb	7	7	10	10	40	7		0.5
Aldicarb sulfone	7	7	10	10	40	7		0.5
Aldicarb sulfoxide	7	7	10	10	40	7		0.8
Aldrin			0.3	0.3	1		0.2	
Ametryn			9000	9000	300	60		
Atrazine	3	3			1000	200		0.1
Bentazone			300	300	1000	200		
Bromacil			5000	5000	5000	90		
Camphechlor (toxaphene)	3	0	4	4	10		3	1
Carbaryl			1000	1000	4000	700		
Carbofuran	40	40	50	50	200	40		0.9
Carboxin			1000	1000	4000	700		
Chloramben			3000	3000	500	100		
Chlordane	2	0	60	60	20		1	0.2
Chlorothalonil			200	200	500		150	
Chlorpyrifos			30	30	100	20		
Cyanazine			100	100	70	1		
2,4-D	70	70	1000	300	400	70		0.1
Dacthal			80000	80000	400	70		
Dalapon (sodium salt)	200	200	3000	3000	900	200		1
Diazinon			20	20	3	0.6		
1,2-Dibromo-3- chloropropane	0.2	0	200	50			3	0.02

(continues on next page)

 Table 4 (Continued).

	Star	ndards		advisory, g child		Health advi	sory	Required detection
Pesticide, metabolite	MCL, μg/l	MCLG, μg/l	1-day, μg/l	10-days, μg/l	DWEL, μg/l	Lifetime, µg/l	10 <sup>-4</sup> cancer risk, μg/l	limit, μg/
Dicamba			300	300	1000	200		
1,3-Dichloropropene			30	30	1000		40	
Dieldrin			0.5	0.5	2		0.2	
Dimethrin			10000	10000	10000	2000		
Dinoseb	7	7	300	300	40	7		0.2
Diphenamid			300	300	1000	200		
Diquat	20	20			70			0.4
Disulfoton			10	10	1	0.3		
Diuron			1000	1000	70	10		
EDB	0.05	0	8	8			0.05	0.01
Endothal	100	100	800	800	700	100		9
Endrin	2	2	20	5	10	2		0.01
ETU (ethylene thiourea)	2	_	300	300	3	2	20	0.01
Fenamiphos			9	9	9	2		
Fenoprop (2,4,5-TP)	50	50	200	200	300	50		0.2
Fluometuron	50	30	2000	2000	500	90		0.2
Fonofos			20	20	70	10		
Glyphosate	700	700	20 000	20 000	4000	700		6
Heptachlor	0.4	0	10	10	20	700	0.8	0.04
Heptachlor epoxide	0.4	0	10	10	0.4		0.8	0.04
Hexachlorobenzene	1	0	50	50	30		2	0.02
Hexazinone	1	U	3000	2000	2000	400	2	0.1
Lindane	0.2	0.2				0.2		0.02
Malathion	0.2	0.2	1000 200	1000 200	10 800	100		0.02
			10 000	10000	20 000	4000		
Maleic hydrazide MCPA				10000		4000		
			100 300	300	20 900	200		
Methomyl	40	40	500 50	500 50	200	40		0.1
Methoxychlor	40	40						0.1
Metolachlor			2000	2000	500	100		
Metribuzin	200	200	5000	5000	900	200		2
Oxamyl	200	200	200	200	900	200		2
Paraquat			100	100	200	30		
Parathion-methyl	1	0	300	300	9	2	20	0.04
Pentachlorophenol	1	0	1000	300	1000	500	30	0.04
Picloram	500	500	20000	20 000	2000	500		0.1
Prometon			200	200	500	100		
Pronamide			800	800	3000	50		
Propachlor			500	500	500	900		
Propazine			1000	1000	700	10		
Propham			5000	5000	600	100		
Propoxur (Baygon)		_	40	40	100	3		
Simazine	4	4	500	500	200	4		0.07
2,4,5-T			800	800	400	70		
Tebuthiuron			3000	3000	2000	500		
Terbufos			5	5	5	0.9		
Trifluralin			80	80	300	5	500	

U.S. MCLs are derived from no-adverse-health-effect-levels for test animals and suitable safety factors, usually 100 or 1000 for suspected or probable carcinogens [12]. Considerations of treatment feasibility, cost of treatment, and analytical detection limits are also included in MCL derivation.

A drinking-water health advisory, issued by the EPA, is an estimate of a concentration that would result in no known or anticipated health effects, or for carcinogens, a specified cancer risk, and is calculated from the NOAEL or lowest-observed-adverse-effect-level (LOAEL) in toxicity tests. The calculation includes an uncertainty factor (10 to 10 000 assessed with scientific judgment), selected for each pesticide depending on the quality and quantity of data available.

One-day, ten-day, and longer-term health advisories for children are calculated from suitable toxicity tests for noncarcinogens for a 10-kg body weight and consumption of 1 l/day. Longer-term health advisories are also calculated for adults—70-kg body weight and 2 l/day water consumption.

The drinking-water equivalent level (DWEL) is calculated from the ADI on the assumption that a person of 70-kg body weight drinks 2 l/day water. The lifetime health advisory is 20 % of the DWEL on the assumption that 80 % of the consumer's exposure to the pesticide is from other sources (e.g., residues in food) with 20 % from drinking water. For noncarcinogens, values for the lifetime health advisory and the MCLG are the same when both are finalized. For pesticides classified as possible human carcinogens, an additional ×10 safety factor is included in the lifetime health advisory.

For human carcinogens or probable human carcinogens, a different approach is taken. A *risk-spe-cific dose* is the concentration associated with a specified cancer risk on the assumptions of a 70-kg body weight, consumption of water 2 l/day over a lifetime (70 years), and a cancer potency estimate for the compound derived from carcinogenicity dose–response data using a linearized multistage model, which is a conservative model. The risk-specific dose at a risk level of  $10^{-6}$  represents the concentration of a carcinogen in drinking water associated with an excess cancer risk of one in a million for a 70-kg person drinking 2 l/day water for a lifetime, 70 years [11].

RSD = 
$$\frac{(70 \text{ kg body weight}) \times (\text{risk level})}{(2 \text{ l/day}) \times (q_1^*)}$$

Risk level: usually specified as 1 in a million, i.e.,  $10^{-6}$ .  $q_1^*$ : cancer potency factor for the pesticide.

A later document [24] defines the  $10^{-4}$  cancer risk, which is the concentration of a chemical in drinking water corresponding to an estimated lifetime cancer risk of 1 in 10 000.

For *ambient surface water*, human health criteria take into account pesticide residues in the water itself and residues in the tissues of edible fish taken from the water [11]. Ambient concentrations in surface water are calculated from residue levels in fish using the bioconcentration factor, which is the ratio between the concentration of the chemical in an organism's tissues to the concentration in the surrounding water. The method assumes all residue in the organism originates from the water, but the residue may originate from the diet or bottom sediment as well as the water itself. The calculation assumes daily consumption of 2 L water and 6.5 g of fish (freshwater and estuarine) or shellfish by an adult of 70-kg body weight. Guideline criteria calculations for noncarcinogens and carcinogens then follow methods parallel to those previously described for drinking water.

For some pesticides, the bioconcentration factors are derived from tests that did not distinguish between dissolved and particulate-associated chemical (likely to be less bioavailable), and it is not specified if the ambient water-quality criteria apply to filtered or whole water, so ambient surface water criteria based on bioconcentration factors should be treated cautiously, particularly for pesticides with high octanol–water partition coefficients.

EPA ambient water-quality criteria for the protection of aquatic organisms are intended to prevent unacceptable effects on important (commercial, recreational, and other) aquatic species, fish, benthic invertebrates, and zooplankton in rivers, streams, lakes, reservoirs, estuaries, and oceans.

The *freshwater criterion maximum concentration* is the highest concentration of a pollutant that freshwater aquatic organisms can be exposed to for a short period (1 h) without deleterious effects. Excursions above the criterion maximum concentration are permitted occasionally (once in 3 years) because it is believed that most aquatic ecosystems can recover from such excursions within 3 years.

Freshwater chronic criteria depend on continuous exposure testing over 4 days and lead to a *final chronic value*, which is an estimate of the concentration of a chemical that is lower than chronic toxicity values for 95 % of the genera that have been chronic-toxicity tested. Excursions above the final chronic value are treated in the same way as excursions above the criterion maximum concentration.

Saltwater acute and chronic criteria are derived from tests on marine aquatic organisms and are interpreted in the same way as the freshwater criteria.

Selections of EPA ambient water-quality criteria for aquatic organisms are listed in Table 5.

Pesticide,	Fres	hwater	Sal	twater
metabolite	Acute, μg/l	Chronic, µg/l	Acute, μg/l	Chronic, μg/l
Azinphos-methyl		0.01		0.01
Camphechlor	0.73	0.0002	0.21	0.0002
Chlordane	2.4	0.0043	0.09	0.004
Chlorpyrifos	0.083	0.041	0.011	0.0056
p,p'-DDT	1.1	0.001	0.13	0.001
Demeton		0.1		0.1
Dieldrin	0.3595	0.0651	0.6594	0.1194
Endosulfan	0.22	0.0056	0.034	0.0087
α-Endosulfan	0.22	0.056	0.034	0.0087
β-Endosulfan	0.22	0.056	0.034	0.0087
Endrin	0.19	0.061	0.033	0.011
Heptachlor	0.52	0.0038	0.053	0.0036
Heptachlor epoxide	0.52	0.0038	0.053	0.0036
Hexachlorobenzene	6	3.68		
Lindane	2	0.08	0.16	
Malathion		0.1		0.1
Methoxychlor		0.03		0.03
Mirex		0.001		0.001
Parathion	0.065	0.013		
Pentachlorophenol	20	13	13	7.9

**Table 5** EPA ambient water-quality criteria for aquatic organisms. Data are summarized from Nowell and Resek [11].

#### New Zealand

The New Zealand Ministry of Health [9] defines maximum acceptable values for determinands (analytes) in drinking water.

Maximum acceptable value (MAV): the concentration of a determinand below which the presence of the determinand does not result in any significant risk to a consumer over a lifetime of consumption of 2 l/day of drinking water. For carcinogenic chemicals, the MAVs set in these Standards generally represent a risk of 1 additional incidence of cancer per 100 000 people ingesting the water (2 l/day) at the concentration of the MAV for 70 years. For other chemicals, MAVs are calculated from the TDI. Most of the MAVs are based on WHO values.

MAV values are set to take into account lifetime consumption; the quality of drinking water should not, however, be degraded to the MAV level. New Zealand MAVs for pesticide residues in drinking water are summarized in Table 6.

Pesticide	μg/l	Pesticide	μg/l	Pesticide	μg/l
Alachlor	20 <sup>a</sup>	1,3-Dichloropropene	20 <sup>a</sup>	Oxadiazon	200 <sup>b</sup>
Aldicarb	10	Dichlorprop	100	Pendimethalin	20
Aldrin/dieldrin	0.03	Diquat	10	Pentachlorophenol	10 <sup>b</sup>
Atrazine	$2^{b}$	Diuron	$20^{\mathrm{b}}$	Permethrin	20
Azinphos methyl	4 <sup>b</sup>	Fenoprop	10	Picloram	$20^{\mathrm{b}}$
Bentazone	$400^{b}$	Heptachlor and	0.04	Pirimiphos methyl	100
		heptachlor epoxide			
Bromacil	$400^{b}$	Hexachlorobenzene	1 <sup>a</sup>	Pirimisulfuron methyl	900
Carbofuran	8	Hexazinone	$400^{b}$	Procymidone	700
Chlordane	0.2	Isoproturon	10	Propanil	20
Chlorpyrifos	70	Lindane	2	Propazine	70 <sup>b</sup>
Chlortoluron	40	MCPA	2	Pyridate	100
Cyanazine	0.7	Mecoprop	10	Simazine	$2^{\mathbf{b}}$
2,4-D	40	Metalaxyl	100 <sup>b</sup>	2,4,5-T	10
2,4-DB	100	Methoxychlor	20	Terbuthylazine	8
DDT + isomers	2	Metolachlor	10	Thiabendazole	$400^{b}$
Diazinon	10	Metribuzin	70 <sup>b</sup>	Triclopyr	100 <sup>b</sup>
1,2-Dibromo-3-chloropropane	$1^a$	Molinate	7	Trifluralin	30
1,2-Dichloropropene	$2^{b}$	Oryzalin	400 <sup>b</sup>	1080	3.5 <sup>b</sup>

Table 6 Maximum acceptable values (MAVs) for pesticide residues in drinking water in New Zealand [9].

Guidance is provided by the New Zealand Ministry of Health [9] on interpretation of a deviation above an MAV. Transgression of the MAV by a single sample does not necessarily result in the water supply failing to comply with the Standards. A small number of transgressions are permitted without breaching compliance, but immediate action must be taken, involving advice to the Medical Officer, resampling of the supply, and investigating the cause of the transgression. Weekly sampling should follow until the MAV is not exceeded in three successive analyses. Persistent transgressions will raise questions about suitability of the supply for drinking water.

#### Japan

Ozawa [25] described measures taken in Japan to control water pollution, including *environmental quality standards* and *effluent standards*.

Environmental quality standards for water are the target levels of water quality to be desirably achieved and maintained for public water areas and are established for the protection of human health and for the conservation of the natural environment. The standard is listed as "not detectable" for organic phosphorus compounds (parathion, parathion-methyl, demeton-methyl, and EPN) and relates to the protection of human health.

Effluent standards are set in terms of permissible quantity of each harmful substance for protecting human health and preserving the living environment. Effluent permissible limits for organic phosphorus compounds (parathion, parathion-methyl, demeton-methyl and EPN) are set at  $1000 \,\mu\text{g/l}$ , based on protection of human health.

The drinking-water standard in Japan is based on the ADI, and 10 % of the ADI is allocated to drinking water [26].

The regulatory limits for tap water are calculated by assuming that a 50-kg person drinks 2 l/day water (Table 7).

<sup>&</sup>lt;sup>a</sup>For excess lifetime cancer risk of 10<sup>-5</sup>.

<sup>&</sup>lt;sup>b</sup>Provisional maximum acceptable value.

**Table 7** Standards for agricultural chemicals relating to water quality [26]. (Katayama, personal communication, 2001).

Agricultural chemical		standards for tap rater, µg/l		al pollution control. average over a year), µg/l	Water pollution law standards for effluent water, µg/l
	Value	Note	Value	Note	Effluent from specified facilities
Bensulide			100	guideline	
Bromobutide			40	guideline	
Buprofezin			10	guideline	
Butamifos			4	guideline	
Carbaryl			50	guideline	
Chlornitrofen	0.1	surveillance	0	surveillance	
Chlorothalonil	40	surveillance	40	surveillance	
Chlorpyrifos			30	guideline	
Diazinon	5	surveillance	5	surveillance	
Dichlorofenthion			6	guideline	
1,3-Dichloropropene	2	standard	2	standard	20
Dichlorvos	10	surveillance	10	surveillance	
Edifenphos			6	guideline	
EPN	6	surveillance	6	surveillance	1000
Esprocarb			10	guideline	
Etofenprox			80	guideline	
Fenitrothion	3	surveillance	3	surveillance	
Fenobucarb	20	surveillance	20	surveillance	
Flutolanil			200	guideline	
Fthalide			100	guideline	
Imidacloprid			200	guideline	
Iprobenfos	8	surveillance	8	surveillance	
Iprodione			300	guideline	
Isoprothiolane	40	surveillance	40	surveillance	
Isoxathion	8	surveillance	8	surveillance	
Malathion	O	Sur vernance	10	guideline	
Mefenacet			9	guideline	
Mepronil			100	guideline	
Molinate			5	guideline	
Oxine copper			40	surveillance	
Pencyuron			40	guideline	
Pendimethalin			100	guideline	
Pretilachlor			40	guideline	
Probenazole			50	guideline	
Propyzamide Propyzamide	8	surveillance	8	surveillance	
Pyridafenthion	o	survemance	2	guideline	
Simazine	3	standard	3	standard	30
Simetryne	3	stanuaru	60	guideline	30
Thiobencarb	20	standard	20	standard	200
Thiram		standard standard		standard standard	
Tolclofos-methyl	6	stanuaru	6 200		60
•			200	guideline	
Trichlorfon			30	guideline	
Tricyclazole			100	guideline	

The Japanese Environment Agency sets limits for residues in rice paddy discharge water by allowing for a 10-fold dilution in river water and applying the drinking-water limit (Table 8).

**Table 8** Guidelines for agricultural chemicals concerning water quality–effluent from paddy fields (average over 150 days) (Katayama, personal communication, 2001).

Pesticide	μg/l	Pesticide	μg/l	Pesticide	μg/l
Acephate	800	Ethoxysulfuron	1000	Paclobutrazole	1000
Acibenzolar-s-methyl	1000	Etobenzamid	1000	Pencyuron	400
Azimsulfuron	2000	Etofenprox	800	Pentoxazone	2000
Azoxystrobin	5000	Fenobucarb	200	Permethrin	1000
Benfuresate	700	Fenthoate	70	Piperophos	9
Bensulfuron-methyl	4000	Ferimzone	200	Pretilachlor	400
Bensultap	900	Fipronil	5	Probenazole	500
Bentazone	2000	Fluazifop-butyl	300	Procymidone	900
Benzofenap	40	Flutolanil	2000	Prohexadione-ca	5000
Bispyribac-Na	300	Fthalide	1000	Prometryn	700
Bromobutide	400	Furametpyr	200	Propanil	400
Buprofezin	100	Furathiocarb	80	Propaphos	10
Butachlor	300	Glyphosate	4000	Pymetrozine	300
Butamifos	100	Hydroxyisoxazole	1000	Pyrazolynate	30
Cafenstrole	80	Imazosulfuron	2000	Pyrazosulfuron-ethyl	1000
Carpropamid	400	Imidacloprid	2000	Pyrazoxyfen	40
Cartap	3000	Iminoctadine triacetate	60	Pyributacarb	200
Chlorpyrifos-methyl	8	Inabenfide	3000	Pyriminobac-methyl	200
Chromafenozide	7000	Indanofan	90	Pyroquilon	400
Cinosulfuron	2000	Iprobenfos	80	Quinoclamine	50
Clomeprop	200	Iprodione	3000	Quizalofop-ethyl	200
Cumyluron	300	Isoprocarb	100	Sethoxydim	4000
Cycloprothrin	80	Isoprothiolane	400	Silafluofen	3000
Cyclosulfamuron	800	Isoxathion	80	Simetryn	300
Cyhalofop-butyl	60	Linuron	200	Tebufenozide	200
Cynmethylin	1000	Malathion	100	Teclofthalam	1000
2,4-D	300	MCPA	50	Tetrachlorvinphos	100
Daimuron	8000	Mefenacet	90	Thenylchlor	2000
Dichlobenil	100	Mepronil	1000	Thifluzamide	500
Dichlocymet	100	Metalaxyl	500	Thiobencarb	200
Dichlomezine	500	Metominostrobin	400	Thiocyclam	300
Dichlorvos	80	Molinate	50	Thiophanate-methyl	3000
Dimepiperate	30	Monocrotophos	20	Trichlorfon	300
Dimethylvinphos	100	<i>N</i> -Dimethyldithiocarbamate	2000	Tricyclazole	800
Dithiopyr	80	Naproanilide	200	Trinexapac-ethyl	200
Edifenphos	60	Nitenpyram	13 000	Uniconazole	400
EPN	60	Oxaziclomefone	200	Vamidothion	200
Esprocarb	100	Oxolinic acid	600		

#### Canada

In Canada, an *MAC* in drinking water is established for a substance known or suspected to cause adverse effects on health [19]. MACs have been derived to safeguard health on the basis of lifelong consumption. Short-term excursions above the MAC do not necessarily mean that the water poses an undue health risk. The use of drinking water for all domestic purposes has been considered in their derivation. However, water of higher quality may be required for some special purposes (e.g., renal dialysis).

The MAC for a pesticide is derived from its ADI in a procedure analogous to that of the WHO drinking-water guideline values. In Canada the derivation is generally based on an average daily intake of 1.5 l drinking water by a 70-kg adult, although in specific cases the MAC may be based on intake by the most sensitive subpopulation. Human exposure from other sources is taken into account with a default 20 % of ADI assigned to drinking water.

The *maximum acceptable concentration* must be achievable by treatment methods and measurable by existing analytical methods. Where this is not achievable, an *interim maximum acceptable concentration* (IMAC) is established, and improvements in treatment or analysis are recommended. An IMAC may also be established in some cases where there are toxicology data gaps or data of poor quality and inadequate for an ADI. Canadian drinking-water-quality MAC and IMAC values are summarized in Table 9.

	U		•					
Parameter	MAC μg/l	IMAC μg/l	Parameter	MAC μg/l	IMAC μg/l	Parameter	MAC μg/l	IMAC μg/l
Aldicarb	9		Diazinon	20		Metribuzin	80	
Aldrin + dieldrin	0.7		Dicamba	120		Paraquat (as dichloride)		10
Atrazine + metabolites		5	Diclofop-methyl	9		Parathion	50	
Azinphos-methyl	20		Dimethoate		20	Pentachlorophenol	60	
Bendiocarb	40		Dinoseb	10		Phorate	2	
Bromoxynil		5	Diquat	70		Picloram		190
Carbaryl	90		Diuron	150		Simazine		10
Carbofuran	90		Glyphosate		280	Terbufos		1
Chlorpyrifos	90		Malathion	190		Trifluralin		45
Cyanazine		10	Methoxychlor	900				
2,4-D		100	Metolachlor		50			

**Table 9** Canadian drinking-water quality MAC and IMAC values [19].

A goal of the Canadian water-quality guidelines for the protection of aquatic life is the protection of all life stages of all species [27]. Standard laboratory testing on species such as *Daphnia magna*, rainbow trout, and fathead minnows produces an LOEL for the most sensitive species. A safety factor allowing for differences in sensitivity among species, extrapolation from laboratory to field, and the chosen test endpoints converts the effect level to a long-term no-effect concentration.

Guidance is provided on the use of the water quality guidelines, suggesting incorporation of an understanding of the chemical, physical, and biological characteristics of the water body as well as the behavior of the substance once it is introduced into the aquatic environment. In practice, however, no specific quantitative guidance exists for the incorporation of these site-specific characteristics into the interpretation, and resource managers typically adopt the guidelines directly to assess and manage water quality.

Environment Canada [28] has issued three protocols for the derivation of water-quality guidelines: protection of aquatic life, irrigation water, and livestock water. Pesticide residues in those guidelines are summarized in Table 10. An interim guideline value is derived in the same way as a full guideline value, but on a data set insufficient for the full guideline.

Guidelines for aquatic life are set at such values as to protect all forms of aquatic life and all aspects of aquatic life cycles. Each GV is based on a long-term no-effect concentration and applies to the total concentration in an unfiltered sample. The LOEL from a chronic exposure study on the most sensitive Canadian species is multiplied by a safety factor of 0.1 to arrive at the final guideline concentra-

tion. Alternatively, the lowest  $LC_{50}$  or  $EC_{50}$  from an acute exposure study is multiplied by a suitable factor to produce the final guideline concentration.

**Table 10** Canadian and interim guidelines for pesticide residue levels in irrigation water, livestock water, freshwater, and marine water [28].

Pesticide	Irrigation v	vater µg/l	Livestock v	water µg/l	Freshwa	ter µg/l	Marine w	ater µg/l
	Guideline	Interim	Guideline	Interim	Guideline	Interim	Guideline	Interim
Aldicarb	54.9		11			1		0.15
Atrazine		10		5	1.8			
Bromacil		0.2		1100		5		
Bromoxynil	0.33			11	5			
Captan				13		1.3		
Carbaryl			1100		0.2			0.32
Carbofuran			45		1.8			
Chlorothalonil		5.8		170		0.18		0.36
Chlorpyrifos				24	0.0035			0.002
Cyanazine		0.5		10		2		
Deltamethrin				2.5	0.0004			
Dicamba	0.006		122			10		
Diclofop-methyl	0.18			9	6.1			
Dimethoate				3		6.2		
Dinoseb	16		150		0.05			
Endosulfan					0.02			
Glyphosate				280		65		
Hexachlorobenzene				0.52				
Lindane			4		0.01			
Linuron		0.071				7		
MCPA	0.025			25		2.6		4.2
Metolachlor		28		50		7.8		
Metribuzin		0.5		80		1		
Pentachlorophenol					0.5			
Phenoxy herbicides			100		4			
Picloram			190			29		
Simazine		0.5		10	10			
Tebuthiuron		0.27		130		1.6		
Triallate				230		0.24		
Tributyltin			250			0.008	0.001	
Trifluralin				45		0.2		

Irrigation water quality guidelines are based on the most sensitive crops grown in Canada. Dose–response data for sensitive crops allow the calculation of the acceptable soil concentration or acceptable application rates of the toxicant. An acceptable soil concentration multiplied by unit area soil mass and divided by the maximum irrigation rate (volume per unit area per year) provides a *species maximum acceptable toxicant concentration* (SMATC). The irrigation water guideline is obtained by selecting the lowest SMATC in each crop group. Alternatively, where irrigation study data are available, an SMATC may be derived from the LOAEL and NOAEL with an appropriate safety factor.

Livestock water-quality guidelines are derived from chronic or acute exposure studies that consider the most sensitive life stages and endpoints for Canadian livestock. A TDI is calculated from the lowest- and no-observed-effect-doses (LOEDs and NOEDs) with an appropriate safety factor. The TDI, with daily livestock water consumption and body weights, provides the final livestock water-quality guideline.

#### European Union

An EU document [6] cited principles for establishing standards of water quality for human consumption in Europe, among which are the statements:

"The parametric values are based on the scientific knowledge available, and the precautionary principle has also been taken into account; those values have been selected to ensure that water intended for human consumption can be consumed safely on a life-long basis, and thus represent a high level of health protection."

"A balance should be struck to prevent both microbiological and chemical risks; to that end, and in the light of a future review of the parametric values, the establishment of parametric values applicable to water intended for human consumption should be based on publichealth considerations and on a method of assessing it."

The document [6] allows relaxation of enforcement of the standards in those situations where there is no potential health risk and there is no alternative drinking-water supply.

EU Member States are authorized to grant derogations from the Directive under certain conditions, provided they do not constitute a potential danger to human health and provided that the supply of water intended for human consumption in the area concerned cannot otherwise be maintained by any other reasonable means.

The document [6] also disallows water pollution causing deterioration of the present quality but still meeting the new standards. It recognizes the need to protect drinking-water sources as well as the drinking water itself:

"Member States shall ensure that the measures taken to implement this Directive in no circumstances have the effect of allowing, directly or indirectly, either any deterioration of the present quality of water intended for human consumption so far as that is relevant for the protection of human health or any increase in the pollution of waters used for the production of drinking water."

In Europe, procedures have been introduced for integrated standard setting based on various ecotoxicological levels. The aim is to evaluate the data on acute and chronic toxicity, provided by the pesticide registrant and available in the open scientific literature, to establish MPCs. MPC values indicate at which concentration no unacceptable risks are to be expected in the ecosystem under consideration. The methodology allows the determination, according to certain rules, of an MPC for the aquatic (water and sediment phase) and the terrestrial ecosystem. Finally, the data may be taken together to give the combined overall MPC for the whole ecosystem for which the lowest compartmental MPC is used as a matter of definition. The method has been described in detail by Kalf et al. [29].

In the direct method for determining an MPC, at least four no-observed-effect-concentration (NOEC) values are necessary for different taxonomic groups. The method assumes that the NOEC values for a chemical substance are lognormally distributed and calculates the safety factor that assures a protection level of 95 % for all organisms in the ecosystem. The indirect method for MPC determination is used, for example, when there are no toxicity data for the terrestrial ecosystem. In that case, the equilibrium partitioning method is used for the compartments soil and sediment, where MPCs for other compartments are calculated from the MPC for water and the respective partition coefficients. For strongly fat-soluble substances, i.e.,  $\log P_{\rm ow}$  greater than 5, or substances with low excretion or highly accumulating properties the possibility of secondary poisoning is also assessed. ( $P_{\rm ow}$  is octanol—water partition coefficient).

Policy for protecting water in the European Union is still evolving with the Water Framework Directive recently coming into force [30]. This Directive (2000/60/EC) aims to bring a coordinated ap-

proach by establishing a framework to protect inland surface waters, transitional waters, coastal waters, and ground water. Under the Directive, European-wide environmental quality standards (EQSs) are to be set, defined as "the concentration of a particular pollutant or group of pollutants in water, sediment or biota which should not be exceeded in order to protect human health and the environment". These EQSs will be set using, where possible, both acute and chronic data for the following: algae and/or macrophytes, daphnia or representative organisms for saline waters and fish; persistence and bioaccumulation will also be taken into account.

Under the Directive, the European Community identified in November 2001, using a combined monitoring- and modeling-based priority-setting process—COMMPS [31], 32 priority substances for EU-wide control [32,33]. Of the 32 substances, 11 have been identified as "priority hazardous substances" and another 11 as "priority substances under review"—this latter group being reviewed to see if they also should be classified as priority hazardous substances. Included in these 22 substances are several pesticides. With the backing of the European Parliament, the aim of the Directive is to "phase out certain hazardous substances" within 20 years of their inclusion on the priority list [34].

The Water Framework Directive is also committed to achieving the objectives of relevant international agreements, including those which aim to prevent and eliminate pollution of the marine environment. This is consistent with the aims of the Convention for the Protection of the Marine Environment of the North-East Atlantic—OSPAR [35]. This convention, which came into force in 1998, has been ratified by all of the contracting parties to the previous conventions (Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, the Netherlands, Norway, Portugal, Spain, Sweden, and the United Kingdom, plus Luxembourg, Switzerland and the European Union.

The Convention strategy is to prevent pollution of the maritime area by continuously reducing discharges, emissions, and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment close to zero for man-made synthetic substances. The Convention has identified a list of chemicals for priority action based on simple exposure-potential estimates, and cut-off criteria for persistence, liability to bioaccumulate and toxicity using a procedure known as DY-NAMEC [36]. The list includes pesticides, and if they remain on the priority action list, the threshold concentration allowed in the marine environment will be "close to zero" and they may well be required to be phased out over the coming years.

A similar initiative for the Baltic Sea is covered by the Convention on the Protection of the Marine Environment of the Baltic Sea area. The governing body of the Convention, which is supported by Denmark, Estonia, Finland, Germany, Latvia, Lithuania, Poland, Russia, Sweden and the European Union is the Baltic Marine Environment Protection Commission, the Helsinki Commission—HEL-COM [37]. The Commission recognizes that the procedures for priority setting described above are valuable but are not directly applicable to the Baltic Sea [38]. So far, the priority substances regarding pesticides have focused on older and obsolete pesticides [39].

In the above instances, the review of substances is in a relatively early phase, and it remains to be seen how the threshold concentrations of these substances in water are estimated and, indeed, how a "level close to zero" will be measured experimentally.

#### Taiwan

Tang et al. [40] summarized the effluent limits, including maximum effluent limits for pesticide residues, applying in Taiwan. The limits for pesticide residues in effluent from industries, sewage systems and sewage treatment facilities are summarized in Table 11.

Effluent characteristic	Maximum effluent limitations, μg/l	Effluent characteristic	Maximum effluent limitations, μg/l
Aldrin, dieldrin	not detectable	Herbicides (such as butachlor, paraquat, 2,4-D, etc.)	1000
Captafol	not detectable	Lindane	not detectable
Captan	not detectable	Pentachloronitrobenzene	not detectable
DDT and its derivatives	not detectable	Pentachlorophenol and its salts	not detectable
Endosulfan	30	Total aminomethylcarbamate (such as carbofuran, BPMC, etc.)	500
Endrin	not detectable	Total organophosphorus compounds (such as parathion, diazinon, etc.)	500
Folpet Heptachlor and its derivatives	not detectable not detectable	Toxaphene	not detectable

**Table 11** Taiwan effluent standards showing the quality characteristics and limitations of effluent from industries, sewage systems, and sewage treatment facilities [40].

#### 7.2 "Good practices" limit

When a pesticide is used directly on water (e.g., a herbicide for control of weeds in reservoirs or mosquito control in drinking-water tanks), it is possible to set a limit based on the approved use on the water. Such uses should only be approved after risk assessments that parallel the risk assessments for pesticide uses on food crops.

Where a pesticide is approved for use in water or water catchment areas in Australia, the guideline value is set at a level consistent with good management practice and which would not result in any significant risk to the health of the consumer over a lifetime of consumption [7]. Temephos is registered for the control of mosquito and midge larvae by aerial treatment of breeding areas. It is applied as a granular formulation (50 g/kg temephos) at a rate of 1–2 kg product per hectare of open water, swamps, marshes, dams, and breeding areas. No more than 6 g of granules are to be applied per 1000 l of treated water [41]. The temephos GV is based on the maximum concentration of temephos expected in water if the label instruction is followed.

#### 7.3 "Zero residue (LOD or LOQ)" limit

In Australia, pesticides that are not approved for use in water or water catchment areas should not be present in drinking water, which in practical terms means they should not exceed the limit of determination (LOD) specified in the guidelines (Table 3). Action should be taken to determine the source and prevent further contamination if a pesticide level exceeds the LOD [7]. The LOD in this context has the same meaning as the LOQ.

In the United States, the MCL (is the maximum permissible level of a contaminant in water that is delivered to any user of a public water system and is set as close to the MCLG as possible [11]. The MCL is an enforceable standard. In those cases where the MCLG was set at zero (known or probable human carcinogen), the MCL was formerly set at the LOD. However, the capabilities of analytical methods have continued to improve, and detection limits have now generally been pushed substantially lower than the required MCL values (Table 4).

#### 7.4 Legislative limit

In the European Union, water intended for human consumption must meet minimum specified requirements, including for pesticides a maximum level for each pesticide of 0.1 µg/l and a maximum of 0.5

μg/l for total pesticides, except for aldrin, dieldrin, heptachlor, and heptachlor epoxide, which are each limited to maximum levels of 0.03 μg/l [42].

Because of the general public perception that pesticides should not be present in drinking water a precautionary principle is often applied in setting standards as low as reasonably achievable [43]. The European Union established limit values for individual pesticides of  $0.1 \mu g/l$  in drinking water as being as low as reasonably achievable, which was taken as the generally accepted LOD for all pesticides.

#### 8. INTERPRETATION OF RESIDUE-MONITORING DATA

A 1988 WHO consultation [20] noted that an excursion above a GV is the signal to investigate the cause prior to remedial action.

Carter [44] pointed out that identifying the cause is not always straightforward because pesticides have a wide range of uses in agriculture and elsewhere (e.g., in human and animal hygiene, timber treatments, anti-fouling paints, and surface biocides). Interpretation of water-monitoring data must allow for the range of potential contamination sources. Diffuse sources of water contamination are: spray drift, volatilization and precipitation, surface runoff, leaching, through-flow or interflow, drain flow, and base flow seepage. Point sources of water contamination include: tank filling, spillages, faulty equipment, washings and waste disposal, sumps and drainage, direct contamination by over-spray, and consented discharges.

A significant portion of the organochlorine residues in water may be sorbed to particulates, and the bioavailability of this sorbed portion as well as the level of the dissolved portion should be considered when using aquatic life criteria to assess the potential for adverse effects on aquatic organisms [12]. The criteria were mostly developed using whole-water concentrations without distinguishing the total concentrations and the bioavailable fraction. It is also inappropriate to compare the concentrations in filtered water (concentration in dissolved phase) with the criteria, which are based on total concentrations without regard for the fraction in the dissolved phase.

#### 9. DISCUSSION

Regulatory limits and guidelines for pesticide residue limits in water are derived from various criteria and are difficult to understand and interpret for experts, administrators, and the general public. What are the implications when a pesticide residue in water exceeds the standard or guideline? The answer is not always clear.

More attention has been paid to residues in drinking water than other situations, and more information is available.

Limits and GVs for pesticide residues in drinking water are compared in Table 12. Clearly, the values may be quite different from one authority to another even when apparently they should be the same. A number of possible explanations come to mind.

- The same terminology may have different meanings in different systems, for example, GV in WHO means a value calculated from a toxicology parameter (TDI or ADI), whereas in Australia, a GV is at or about the analytical determination or a maximum level that might occur if good practices are followed and in New Zealand, the GV is the concentration where aesthetic significance is influenced. The Australian HV or is conceptually the same as the WHO GV. The New Zealand MAV and the Canadian MAC are also conceptually the same as the WHO GV.
- WHO does not include metabolites and environmental degradation products in its residue. WHO
  GVs refer only to parent compound. Some authorities provide no definition of the residue, but
  sometimes specify a value for an identified metabolite (e.g., aldicarb sulfoxide or heptachlor
  epoxide), and so, by inference, all the others should be parent compound only.

- Limits set by the same methodology at different times might be different just because the starting points for the estimation might be different as the science develops and new information comes to hand. For example, a GV based on a TDI or the LOQ of an analytical method will obviously change with time if the TDI or LOQ changes and the GV is reassessed.
- The choice of safety factors and other related assumptions are somewhat arbitrary. For example, in the WHO calculation of GVs for drinking water, either 1 or 10 % of the ADI (or TDI) is used in the calculation; Australia, in a similar calculation for the HV, usually uses 10 % of the ADI; Japan uses 10 % of the ADI in the drinking-water standard; the United States uses 20 % of the ADI in the lifetime health advisory; in Canada, the MAC usually takes 20 % of the ADI. Harmonizing percentage of ADI assigned to drinking water is unlikely because there is no logical reason to prefer one over another.

**Table 12** Comparison of standards and guideline values for pesticide residues in drinking water. Pesticides are listed where there are standards or guidelines from 3 or more authorities (WHO and national governments).

Pesticide	WHO GV	USA MCL	USA MCLG	USA Health	USA 10 <sup>-4</sup>	NZ MAV	Japan std,	Aust GV	Aust HV	Canada MAC
				advisory,	cancer		surv			
				lifetime	risk					
	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l
Alachlor	20	2	0		40	20 <sup>a</sup>				
Aldicarb	10	7	7	7		10		1	1	9
Aldicarb sulfone		7	7	7						
Aldicarb sulfoxide		7	7	7						
Aldrin					0.2					
Dieldrin					0.2					
Aldrin/dieldrin	0.03					0.03		0.01	0.3	0.7
Atrazine	2	3	3	200		2 p		0.5	20	5 I <sup>b</sup>
Azinphos-methyl						4 p		2	3	20
Bentazone	300			200		400 p			30	
Bromacil				90		400 p		10	300	
Carbaryl				700				5	30	90
Carbofuran	7	40	40	40		8		5	10	90
Chlordane	0.2	2	0		1	0.2		0.01	1	
Chlorothalonil					150		40 surv	0.1	30	
Chlorpyrifos				20		70				90
Cyanazine	0.6			1		0.7				10 I
2,4-D	30	70	70	70		40		0.1	30	100 I
DDT	2									
DDT + isomers						2		0.06	20	
Diazinon				0.6		10	5 surv	1	3	20
1,2-Dibromo-3- chloropropane	1	0.2	0		3	1 <sup>a</sup>				
Dicamba				200					100	120
1,3-Dichloropropene	20				40	20 <sup>a</sup>	2 std			
Diquat	10	20	20			10		0.5	5	70
Diuron				10		20 p			30	150 I
EDB	0.4-15	0.05	0		0.05	-		1	1	
Fenoprop (2,4,5-TP)	9	50	50	50		10			10	
Glyphosate	unnec	700	700	700				10	1000	280 I
Heptachlor		0.4	0		0.8					

(continues on next page)

Table 12 (Continued).

Pesticide	WHO GV	USA MCL	USA MCLG	USA Health	USA 10 <sup>-4</sup>	NZ MAV	Japan std,	Aust GV	Aust HV	Canada MAC
				advisory,	cancer		surv			
				lifetime	risk					
	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l
Heptachlor + epoxide	0.03					0.04		0.05	0.3	
Heptachlor epoxide		0.2	0		0.4					
Hexachlorobenzene	1	1	0		2	1 <sup>a</sup>				
Hexazinone				400		400 p		2	300	
Lindane	2	0.2	0.2	0.2		2		0.05	20	
Malathion				100					50	190
MCPA	2			4		2				
Methoxychlor	20	40	40	40		20		0.2	300	900
Metolachlor	10			100		10		2	300	50 I
Metribuzin				200		70 p		1	50	80
Molinate	6					7		0.5	5	
Paraquat				30				1	30	10 I <sup>c</sup>
Pendimethalin	20					20			300	
Pentachlorophenol	9	1	0		30	10 p		0.01	10	60
Permethrin	20					20		1	100	
Picloram		500	500	500		20 p			300	190 I
Propanil	20					20		0.1	500	
Propazine				10		70 p		0.5	50	
Simazine	2	4	4	4		2 p	3 std	0.5	20	10 I
2,4,5-T	9			70		10		0.05	100	
Terbufos				0.9				0.5	0.5	1
Trifluralin	20			5	500	30		0.1	50	45 I

Abbreviations: p: provisional MAV; std: standard; surv: surveillance; I: interim MAC.

Drinking-water residue limit values calculated from the ADI or other toxicological measure may be slightly different from one country to another, even with exactly the same methodology, because body weights (e.g., 60 or 70 kg) or daily water consumption (1.5 or 2 l) are different.

Each of the possible ways of defining the residues has its merits. The sum of parent pesticide and important metabolites expressed as parent has usually constituted residue definitions in food, which is the residue we need in the risk assessment step. A residue limit in water would also be best expressed in this way where it is derived directly from a toxicological property such as an ADI. For monitoring purposes, where it is best to keep the residue definition as simple as possible for the sake of economy, the parent or a marker residue is preferable. In water, it is also possible that parent and degradation products (hydrolysis and photolysis products and metabolites) become physically separated as the water moves through soil strata, which suggests that separate limits should be set for parent and important degradation products.

The consumer risks from pesticide residues and other contaminants in drinking water should be viewed in the same context to minimize the overall risk. Regulations encourage ozone treatment of raw water to reduce pesticide residue levels below a maximum level for drinking water. The ozone treatment generates bromate, reported to be carcinogenic, but it is allowed in the water by the regulations. The

<sup>&</sup>lt;sup>a</sup>Excess lifetime cancer risk of 10<sup>-5</sup>.

<sup>&</sup>lt;sup>b</sup>Atrazine + metabolites.

<sup>&</sup>lt;sup>c</sup>Paraquat as dichloride.

treatment, where it is only removing low levels of pesticide residues, would apparently increase consumer risk.

Canadian pesticide residue guidelines for irrigation water take into account the phytotoxicity of the residues to sensitive crops. For nonherbicides or nonphytotoxic residues, an additional basis for guidelines would be the accumulation of residues in crops. For a systemic pesticide such as aldicarb, residues in irrigation water could be taken up to produce a residue level in the crop exceeding the MRL. The maximum guideline limit would be set so that residues in the crop would not exceed the MRL.

Canadian livestock water-quality guidelines are derived from animal toxicity studies. An additional concern, as with residues in crops from irrigation water, is the resulting residues in food commodities, in this case, residues in meat, milk, and eggs. Farm animal feeding studies provide information on the relation between residue levels in the animal diet and the resulting residue levels in the animal tissues, milk, and eggs. The feeding studies would allow calculation of the maximum residue intake from livestock drinking water before residues in animal commodities exceeded MRLs.

An analytical method must be available to measure the residue at a standard or guideline limit designed for surveillance or regulatory enforcement. The specified limit should be no lower than the method LOQ, which is the lowest concentration where suitable recoveries are achieved (usually, mean recoveries of between 70 and 110 %).

#### 10. CONCLUSION

The Commission, after reviewing a number of national systems, has made 12 recommendations for regulatory limits for pesticide residues in water. Standard terminology is needed to improve the general understanding of pesticide residue limits in water. The recommendations will act as a checklist for authorities introducing or revising limits or guidelines for pesticide residues in water.

#### 11. ACKNOWLEDGMENT

The authors gratefully acknowledge the funding support for this project provided by IUPAC and ICSU (International Council for Science).

#### 12. REFERENCES

- 1. N. Aharonson, S. Z. Cohen, N. Drescher, T. J. Gish, S. Gorbach, P. C. Kearney, S. Otto, T. R. Roberts, J. W. Vonk. "Potential contamination of ground water by pesticides", *Pure Appl. Chem.* **59**, 1419–1446 (1987).
- 2. H. Greim. "Scientific justification of setting limits", Food Chem. Toxicol. 38, S107–S110 (2000).
- 3. B. Jiménez, J. Ramos, I. L. Quezada. "Analysis of water quality criteria in Mexico", *Water Sci. Technol.* **40** (10), 169–173 (1999).
- 4. A. M. Van Dijk-Looijaard, J. Van Genderen. "Levels of exposure from drinking water", *Food Chem. Toxicol.* **38**, S37–S42 (2000).
- 5. EU. Directive 2000/60/EC of the European Parliament and of the Council of 23 Oct 2000 establishing a framework for Community action in the field of water policy. Official Journal L 327, 22/12/2000, pp. 0001–0072 (2000).
- 6. EUR-Lex. Council Directive 98/83/EC of 3 Nov 1998 on the quality of water intended for human consumption. Official Journal L 330, 05/12/1998, pp. 0032–0054. Community legislation in force document 398L0083 (1998).
- National Health and Medical Research Council. Australian drinking water guidelines. Agricultural and Resource Management Council of Australia and New Zealand. Commonwealth of Australia (1996).

- 8. D. T-C. Tang, R. J. Ferris, H-H. Tsai. Drinking Water Management Act. Environmental Protection Administration of the Republic of China on Taiwan (1997). <a href="https://www.epa.gov.tw/english/-LAWS/drinkwater.htm">www.epa.gov.tw/english/-LAWS/drinkwater.htm</a>
- 9. Ministry of Health, NZ. Drinking-water standards for New Zealand (2000). <www.moh.govt.nz>
- 10. EPA. Part 141—National primary drinking water regulations. Section 141.2. Definitions. U.S. Environment Protection Agency. Federal Register. 40 CFR Ch. (7-1-00 Edition) (2000).
- 11. L. H. Nowell and E. A. Resek. "National standards and guidelines for pesticides in water, sediment, and aquatic organisms: application to water-quality assessments". *Rev. Environ. Contam. Toxicol.* **140**, 1–164 (1994).
- S. J. Larson, P. D. Capel, M. S. Majewski. "Analysis of key topics—environmental significance", Chap. 6 in *Pesticides in Surface Waters. Distribution, Trends, and Governing Factors*, Vol. 3 of the series Pesticides in the Hydrologic System, R. J. Gilliom, Series Ed., U.S. Geological Survey, National Water Quality Assessment Program, Ann Arbor Press, Chelsea, MI (1997).
- 13. K. S. Sidhu. "Standard setting processes and regulations for environmental contaminants in drinking water: State versus Federal needs and viewpoints". *Regul. Toxicol. Pharmacol.* **13**, 293–308 (1991).
- J. E. Barbash and E. A. Resek. "Pesticides in the hydrologic system—environmental significance", Chap. 10 in *Pesticides in Ground Water. Distribution, Trends and Governing Factors*, Vol. 2 of the series. R. J. Gilliom, Series Ed., U.S. Geological Survey, National Water Quality Assessment Program, Ann Arbor Press, Chelsea, MI, (1996).
- 15. M. Younes and H. Galal-Gorchev. "Pesticides in drinking water—a case study". *Food Chem. Toxicol.* **38**, S87–S90 (2000).
- 16. European Union. Guidelines and Criteria for the Evaluation of Dossiers and the Preparation of Reports to the European Commission by Rapporteur Member States relating to the Proposed Inclusion of Active Substances in Annex I of Directive 91/414/EEC, Document 1654/VI/94, Rev. 6.4, (31 October 1997).
- 17. EU Guidance Document on Relevant Metabolites, Draft Working Document, October 1999, adopted by The Netherlands by the Board on the Registration of Pesticides, p.15 (1999).
- 18. ECPA proposal for defining and assessing the relevance of metabolites. European Crop Protection Association, Brussels, 1 September 1998. Document D/98/GRG/3260 (1998).
- 19. Environmental Health Directorate. Summary of guidelines for Canadian drinking water quality. Prepared by the Federal-Provincial Subcommittee on Drinking Water of the Federal-Provincial Committee of Environmental and Occupational Health (April 1999).
- 20. WHO. Revision of the WHO guidelines for drinking-water quality. Report of a consultation in Rome from 17–19 October 1988. Document WHO/PEP/89.4 (1988).
- 21. European Commission, SANCO/825/00 rev. 6, Guidance document on residue analytical methods (2000).
- 22. EPA. Part 141—National primary drinking water regulations. Section 141.24. Organic chemicals, sampling and analytical requirements. U.S. Environment Protection Agency. Federal Register. 40 CFR Ch. (7-1-00 Edition) (2000).
- 23. WHO. Second Consultation on Herbicides in Drinking-Water, Rome, 13-18 July 1987. Document ICP/CWS 012A(S) (1987).
- 24. EPA. Drinking water standards and health advisories. U.S. Environment Protection Agency. Office of Water 4304. EPA 822-B-00-001 (2000).
- 25. M. Ozawa. "Water pollution control administration in Japan". Water Sci. Technol. 20, 1–11 (1988).
- Ministry of Public Health and Welfare (Japan). Various standards for agricultural chemicals concerning water quality. (Information from Norio Kurihara) (1997).
- 27. S. L. Walker and F. A. P. C. Gobas. "An investigation of the application of the Canadian water quality guidelines". *Environ. Toxicol. Chem.* **18**, 1323–1328 (1999).

- 28. Environment Canada. Canadian Environmental Quality Guidelines. Protocols for the derivation of water quality guidelines (2001). <www2.ec.gc.ca/ceqg-rcqe/prot.htm>
- D. F. Kalf, B. J. W. G. Mensink, M. H. M. M. Montforts. Protocol for Derivation of Harmonised Permissible Concentrations (MPCs). RIVM report 601506 001, Bilthoven, The Netherlands, p. 73 (1999).
- 30. EC. Directive 2000/60/EC of the European Parliament and of the Council of 23 October establishing a framework for Community action in the field of water policy. Official Journal L 327, 22/12/00 P.1 (2000).
- 31. EC. Study on the prioritisation of substances dangerous to the aquatic environment. Office for Official Publications of the European Communities (1999).
- 32. Commission of the European Communities. Proposal for a decision of the European Parliament and Council establishing the list of priority substances in the field of water policy. COM (2001) 17 final, Brussels (2001).
- 33. Commission of the European Communities. Amended proposal for a European Parliament and Council decision establishing the list of priority substances in the field of water policy. COM (2000) 47 final, Brussels (2000).
- 34. European Commission DG XI, Water policy: Commission identifies priority substances and proposes to phase out eleven hazardous substances. Press release, Brussels, 18 January (2001). <a href="https://www.waternunc.com/gb/dg11en44.htm">www.waternunc.com/gb/dg11en44.htm</a>
- 35. OSPAR Commission. Commission for the Protection of the Marine Environment of the North-East Atlantic, Annual Report 2000–2001, London (2001). <a href="https://www.ospar.org">www.ospar.org</a>>
- 36. OSPAR Commission. Briefing document on the work of DYNAMEC and the DYNAMEC mechanism for the selection and prioritisation of hazardous substances, Publication 104 (2000). <a href="https://www.ospar.org">www.ospar.org</a>
- 37. Helsinki Commission. Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1992 (in force 17 January) (2000). <a href="https://www.helcom.fi/helcom/convention.html">www.helcom.fi/helcom/convention.html</a>>
- 38. Helsinki Commission. Baltic Marine Environment Protection Commission, Harmonisation of HELCOM recommendations with EU directives and OSPAR decisions and recommendations, final report (2001). <www.helcom.fi/a/publications/harmon\_recomm.pdf>
- 39. Helsinki Commission. Baltic Marine Environment Protection Commission, the pesticides selected for immediate priority action. (2001) <www.helcom.fi/a/hazardous/-Final\_Pesticide.Report.pdf>.
- 40. D. T.-C. Tang, R. J. Ferris, H-H. Tsai. Effluent Standards. Environment Protection Administration of the Republic of China on Taiwan (2000) <a href="https://www.epa.gov.tw/english/LAWS/Effluent.htm">www.epa.gov.tw/english/LAWS/Effluent.htm</a>.
- 41. Abate<sup>®</sup> 50SG label, Directions for use on registered label (2000).
- 42. European Union. Common position (EC) 12767/97. Adopted by the Council on 16 December 1997 with a view to the adoption of Council Directive on the quality of water intended for human consumption. Interinstitutional file 95/0010 (SYN) (1997).
- 43. F. X. R. Van Leeuwen. "Safe drinking water: the toxicologist's approach". *Food Chem. Toxicol.* **38**, S51–S58 (2000).
- 44. A. Carter. "Pesticide contamination of water sources and the monitoring data across the EU", XI Symposium on Pesticide Chemistry, Cremona, Italy, September 1999, pp. 11–20 (1999).

#### 13. GLOSSARY OF ACRONYMS

ADI acceptable daily intake

DWEL drinking-water equivalent level (USA)
EPA U.S. Environmental Protection Agency
EQS environmental quality standard (EU)

EU European Union

GV guideline value (WHO, Australia)

HV health value (Australia)

IMAC interim maximum acceptable concentration (Canada)

LOAEL lowest-observed-adverse-effect-level

LOD limit of determination LOED lowest-observed-effect-dose LOQ limit of quantification

MAC maximum acceptable concentration (Canada)

MAV maximum acceptable value (NZ)
MCL maximum contaminant level (USA)
MCLG maximum contaminant level goal (USA)
MPC maximum permissible concentration (EU)

MRL maximum residue limit

NOAEL no-observed-adverse-effect-level NOEC no-observed-effect-concentration

NOED no-observed-effect-dose NOEL no-observed-effect-level

OECD Organization for Economic Cooperation and Development SMATC species maximum acceptable toxicant concentration (Canada)

TDI tolerable daily intake