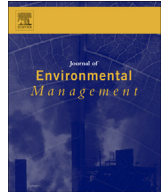




Contents lists available at ScienceDirect

## Journal of Environmental Management

journal homepage: [www.elsevier.com/locate/jenvman](http://www.elsevier.com/locate/jenvman)

Research paper

## Residential surface soil guidance applied worldwide to the pesticides added to the Stockholm Convention in 2009 and 2011

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## ARTICLE INFO

## Article history:

Received 19 November 2014  
 Received in revised form  
 5 June 2015  
 Accepted 8 June 2015  
 Available online xxx

## Keywords:

Stockholm Convention  
 Surface soil contamination  
 Regulatory guidance values  
 Persistent organic pollutants  
 Pesticides  
 $\alpha$ -HCH  
 $\beta$ -HCH  
 $\gamma$ -HCH  
 $\delta$ -HCH  
 Chlordane  
 Kepone  
 Endosulfan  
 Endosulfan I  
 Endosulfan II  
 Endosulfan sulfate

## ABSTRACT

Due to the widespread use of agricultural and residential pesticides, the potential for pesticide soil contamination is a worldwide concern. In response, regulatory jurisdictions in at least 54 nations have promulgated guidance values to specify the maximum allowable concentration of pesticides in soils. Guidance values may be found for more than 700 pesticides. A previous analysis examined the values applied to the original “dirty dozen” persistent organic pollutant (POP) pesticides that were addressed in the 2001 Stockholm Convention (Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Mirex, and Toxaphene). Results are presented here for the “new POP” pesticides that were added to the Stockholm Convention in 2009 and 2011 (isomers of Hexachlorocyclohexane, Chlordecone, and isomers of Endosulfan). The guidance value extremes used worldwide for these pesticides vary by as much as 8.5 orders of magnitude and the randomness in their distributions resembles that of lognormal random variables. However, there are nonrandom value clusters in some distributions that may identify values around which consensus are forming. The current value distributions imply that a wide range of human health risks are being accepted. Hopefully, the results presented will help regulatory jurisdictions and the regulated communities identify values that should be revised to be adequately protective of human health.

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## 1. Introduction

Many environmental regulatory jurisdictions promulgate values that specify the maximum amount of a pollutant that may be present in air, water, food, or soil without prompting a regulatory response. For soil, there is no standard terminology for these values, but they are often referred to as remediation standards, screening levels, cleanup objectives, exposure criteria, limit values, or intervention values. They specify the maximum allowable “concentration” (in units of mg/kg) of a pollutant that may be present. Here, all of these values are referred to as regulatory guidance values (RGVs). In many jurisdictions, RGVs are developed for several types of exposures. Some jurisdictions provide values based on human health or environmental quality, but the majority are developed based on

human health risk considerations in scenarios such as residential, commercial, or industrial exposures. The highest levels of concern yielding the lowest, most restrictive values are often applied to residential soil where children often come into direct contact with surface soils and experience contamination by ingestion, inhalation, and dermal sorption. The analysis presented here concentrates on the RGVs applied worldwide to control residential exposures to contaminated surface soil.

Previous studies have identified surface soil RGVs promulgated in at least 72 United Nations member states, although the number and type of regulated pollutants varies from a few well-known inorganics such as Cd or Pb, to hundreds of organic compounds common in manufacturing and agriculture. Previous studies have also demonstrated that there is little agreement on the magnitude of the guidance values applied to pollutants. Chemicals have been identified for which the worldwide surface soil guidance value extremes vary by as much as 10 orders of magnitude (Jennings and Li, 2014). Variations of five or six orders of magnitude are common.

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The work presented here is the product of an ongoing effort to analyze variability in the surface soil RGVs applied worldwide to important classes of soil contaminants. Work on this subject has previously addressed RGVs applied to BTEX (benzene, toluene, ethylbenzene, and xylenes) (Jennings, 2009), naphthalene (Jennings, 2012a), chlorinated methanes, ethanes, and ethenes (Jennings, 2011a,b,c), chlorinated benzenes (Kowalsky and Jennings, 2012), polycyclic aromatic hydrocarbons (Jennings, 2012b,c) and the 20 most frequently regulated elements (Jennings, 2010, 2013a,b). Several other research groups have also examined RGV variability (see Jennings and Li, 2014), but have not considered the scope of jurisdictions or the set of pesticides considered here.

Recently, Jennings and Li (2014) examined the extent to which worldwide jurisdictions have promulgated surface soil RGVs for pesticides. More than 19,400 pesticide RGVs from 174 jurisdictions in 54 United Nations member states were identified. This effort required translating guidance documents from 29 languages and identifying compounds from numerous nomenclature descriptions and product name variations used for pesticide products. Jennings and Li (2015) then examined the RGVs applied to the persistent organic pollutant (POP) pesticides (Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Mirex, and Toxaphene) that were among the 12 “dirty dozen” pollutants banned or seriously restricted by the Stockholm Convention of 2001 (Secretariat of the Stockholm Convention, 2008). With the exception of Mirex, all of these are among the 20 most frequently regulated pesticides worldwide (Jennings and Li, 2014). Mirex is not among the top 20 because its most common use was for fire ant control in the southern United States (U.S.), so it is less frequently regulated by other nations.

The POP pesticides of the “dirty dozen” addressed by the Stockholm Convention of 2001 were “first generation” formulations that emerged shortly after the end of World War II. By 2001, the potential consequences of these pesticides were well-known, and their use was declining. Without manufacturers advocating for their continued production and nations arguing for their continued use, they were relatively easy targets for elimination. Unfortunately, the first “dirty dozen” POP pesticides do not represent a very comprehensive list of problematic formulations, and several attempts have been made to extend the provisions of the Stockholm Convention to other pesticides. These efforts resulted in pesticides that were added in 2009 and 2011.

This manuscript presents analysis of the RGVs applied to the POP pesticides that were added to the Stockholm Convention in 2009 (Chlordecone and isomers of Hexachlorocyclohexane) and in 2011 (Endosulfan and its related isomers) (Secretariat of the Stockholm Convention, 2014a). These are often referred to as the “new POP” pesticides. Pentachlorobenzene was also added in 2009 as an industrial chemical, pesticide, and manufacturing by-product, but has been omitted from the analysis presented here. Analysis of Pentachlorobenzene RGVs may be found in Kowalsky and Jennings (2012). Like the first POP pesticides, the “new POP” additions were also first generation pesticides introduced in the 1950's and used extensively in residential and agricultural applications around the world. Also, similar to the first POP pesticides, by the time the “new POPs” were added, most of their uses had been eliminated. One might then wonder if their regulation is still an important issue. The answer is almost certainly YES.

The “new POP” pesticides entered the market early in the era when people were enthusiastic about their potential and naive about their consequences. They were generously applied with little regulatory oversight. Today, it is not difficult to find soils with high concentration of “new POP” pesticides. In the U.S. as in many other nations, as suburban developments spread into former agricultural lands, residential exposures to these residuals can be surprisingly

high. In addition, as discussed in Jennings and Li (2015), there are large stockpiles of “obsolete” pesticides in at least 93 nations totaling nearly 300,000 metric tons (Food and Agricultural Organization of the United Nations, 2014). Much of this total is made up of POP pesticides.

The three most common “new POP” isomers of hexachlorocyclohexane ( $\alpha$ -,  $\beta$ - and  $\gamma$ -) and Endosulfan are among the 20 most frequently regulated pesticides worldwide (Jennings and Li, 2014). Less common isomers or technical grade formulations of Hexachlorocyclohexane, Chlordecone (also known as Kepone) and Endosulfan isomers are not as frequently regulated. Technical Hexachlorocyclohexane appears at number 105,  $\delta$ -Hexachlorocyclohexane appears at number 112, and Chlordecone appears at #147 on the list of most frequently regulated pesticides. The Endosulfan I and II isomers and Endosulfan Sulfate are found at numbers 227, 244, and 274 respectively (Jennings and Li, 2014).

Although 179 nations have ratified the 2001 Stockholm Convention and the list continues to expand (recent additions include Montenegro, Palau, the Russian Federation, and Suriname in 2011, Saudi Arabia and Zimbabwe in 2012, Afghanistan, and Estonia in 2013) and the signatories represent the majority of industrial and agricultural nations, there are noteworthy exceptions. As of 2014, Israel, Italy, Malaysia and the U.S. had not ratified the convention (Secretariat of the Stockholm Convention, 2014b). Nevertheless, Italy, Malaysia, and the U.S. provide guidance values for many of the new POPs.

## 2. Materials

The “materials” of this work are the pesticides that were added to the 2001 Stockholm Convention in 2009 and 2011. The following sections provide descriptions of each. Comprehensive summaries of toxicology data for these pesticides may be found in the National Library of Medicine, Hazardous Substances Data Bank (2014), the U.S. Environmental Protection Agency Integrated Risk Information System (USEPA/IRIS) (2014a), and in Agency for Toxic Substances and Disease Registry (ATSDR) (2014) publications. This material is not reproduced here. Rather, following brief descriptions of the origin and use of each pesticide, the descriptions concentrate on how their potential health impacts have been assessed by organizations such as the American Conference of Governmental Industrial Hygienists (ACGIH), the International Agency for Research on Cancer (IARC), Safe Work Australia (SWA), the International Labour Organization (ILO), Deutsche Forschungsgemeinschaft (DFG, the German Research Foundation), the World Health Organization International Program on Chemical Safety (WHO/IPCS) and the U.S. Environmental Protection Agency (USEPA). These organizations are responsible for synthesizing toxicology data and making risk determinations. It is their determinations that appear to have the greatest impact on the RGVs developed by regulatory jurisdictions.

Hereafter, the “new POP” pesticides will be referred to by their common names, or common abbreviations, but Table 1 summarizes their International Union of Pure and Applied Chemistry (IUPAC) name, elemental composition, and National Institute of Standards and Technology (NIST) Chemical Abstract Service number (CAS No.) for unambiguous identification.

Table 2 provides an indication of how often the new POP pesticides have been recognized as important pollutants by their addition to compilations such as the United Kingdom Red List (Environment Agency, 2012), the European Union European Commission (2014) Priority Substances List, the U.S. Priority Pollutant List (USEPA, 2013) and the Agency for Toxic Substances and Disease Registry (2013b) Substance Priority List. Table 2 also provides data on how often these pesticides have been identified at U.S. National Priority List soil contamination sites (USEPA

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