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Setting Up of Risk Based Remediation Goal for Remediation of Persistent Organic Pesticides (Pesticide-POPs) Contaminated Sites

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1. Introduction

1.1 Persistent Organic Pollutants (POPs)

Persistent Organic Pollutants (POPs) is a common name of a group of pollutants that are semi-volatile, bioaccumulative, persistent and toxic. POPs comprising of pesticides, industrial chemicals and unintentionally produced POPs are toxic chemicals that adversely affect human health and the environment around the world (Vallack et al.,1998; Mocarelli &Tallman,1998 & Jones &de Voogt,1999). Since these pollutants can be transported by wind (natural ,human barriers and perturbation , grass in the desert ,cities and thermal updrafts, etc), water (ssurface, rain, ground, pumped and/or anthropogenically modified chemicals) and human intervention (waste-water conduits, drainage ditches, roadways, railways, irrigation, ponding, physical transformation physical collection and concentration, human species transformation) (Sw-846,USEPA,2007) , most POPs generated in one country can affect people and wildlife far from where they are used and released. These chemicals persist for long periods of time in the environment and can accumulate and pass from one species to the next through the food chain.

POPs can be deposited in marine and freshwater ecosystems through effluent releases, atmospheric deposition, runoff, and other means. As POPs have low water solubility, they bond strongly to particulate matter in aquatic sediments. As a result, sediments can serve as reservoirs or "sinks" for POPs. When sequestered in these sediments, POPs can be taken out of circulation for long periods of time. If disturbed, however, they can be reintroduced into the ecosystem and food chain, thereby potentially becoming a source of local, and even global contamination.

To address this global concern, there exists a groundbreaking United Nations' treaty in Stockholm, Sweden (May 2001). Under the treaty, known as the Stockholm Convention, countries agree to reduce or eliminate the production, use, and/or release of 12 key POPs (UNEP Tookits on POPs,1999,2001,2003,2005) which are shown in **Table 1**.

The Convention specifies a scientific review process that could lead to the addition of other POPs chemicals of global concern. The list of nine new POPs added to the Stockholm Convention in May, 2009 is shown in **Table 2**.

Sr. No.	POPs Identified
POPs-Pesticides	
1	Aldrin [1]
2	Chlordane [1]
3	Dichlorodiphenyl trichloroethane (DDT)[1]
4	Dieldrin[1]
5	Endrin[1]
6	Heptachlor[1]
7	Hexachlorobenzene [1,2]
8	Mirex[1]
9	Toxaphene[1]
POPs-nonpesticides	
10	Polychlorinated biphenyls (PCBs) [1,2]
11	Polychlorinated dibenzo-p-dioxins[2](dioxins)
12	Polychlorinated dibenzofurans[2] (furans)

1. Intentionally produced.
2. Unintentionally Produced - Result from some industrial processes and combustion.

Table 1. List of 12 POPs identified by the Stockholm Convention of May 2001

POPs	Usage
Alpha hexachlorocyclohexane	Pesticide, produced as byproduct of lindane
Beta hexachlorocyclohexane	Pesticide, produced as byproduct of lindane
Chlordecone	Pesticide, agricultural use
Hexabromobiphenyl ether	Flame retardant
Hexabromodiphenyl ether and heptabromodiphenyl ether	Flame retardant, recycling of articles containing these chemicals is allowed
Lindane (Gamma hexachlorocyclohexane)	Pesticide, for control of head lice and scabies as second line treatment
Pentachlorobenzene	Pesticide, unintentionally produced POPs
Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride	Industrial chemical: Photo-imaging, photo-resist and anti-reflective coatings for semi-conductor and liquid crystal display (LCD) industries, etching agent for compound semi-conductors and ceramic filters, aviation hydraulic fluids, metal plating (hard metal plating and decorative plating), certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio-opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters), fire-fighting foam, insecticides for control of fire ants and termites, electric and electronic parts for some colour printers and colour copy machines, chemically driven oil production, carpets , leather and apparel, textiles and upholstery, paper and packaging, coatings and coating additives, rubber and plastics
Tetrabromodiphenyl ether and pentabromodiphenyl ether	Flame retardant, recycling of articles containing these chemicals is allowed

Table 2. Nine new POPs added to the Stockholm Convention in May, 2009

An attempt is now being made to include endosulfun in the list of POPs.

1.2 Remediation requirement for obsolete pesticides stockpiles and contaminated sites

Obsolete pesticide stocks refer to pesticides that have been banned or whose shelf life has expired. Many international organizations are working on the issue of obsolete pesticide stocks. These include FAO, UNEP Chemicals and the Secretariat of the Basel Convention, UNIDO (United Nations Industrial Development Organization), industry associations and NGOs (non-governmental organisations) dealing with environment. Approximately 20,000 tons of obsolete pesticides are located in Africa and in the Middle East, often in containers that leak toxic waste into the environment (Fitz,2000). While exact quantities are unknown, large stockpiles also exist in Central Eastern European Countries (CEEC) and the New Independent States (NIS) (UNEP GEF Draft Report, 2002). The risks associated with large-scale storage of compounds pose a particular environmental risk. The principal uncertainly in terms of these obsolete stocks is characterization in terms of POP content. Little is known of the composition of the waste materials and it must be recognized that, within the 'cocktail' of possible chemicals, a variety of substances will be present in unknown amounts. These could represent locally and regionally important on-going primary source inputs of compounds to the environment.

A contaminated site can be defined as an area of the land in which the soil or any groundwater lying beneath it, or the water or the underlying sediment, contains a hazardous waste, or another prescribed substance in quantities or concentrations exceeding prescribed risk based or numerical criteria or standards or conditions.

Article 6 of the Stockholm Convention describes measures to reduce or eliminate releases from stockpiles and contaminated sites.

This chapter will focus on the risk assessment prior to remediation of sites contaminated with persistant organic persticides [DDT, aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, and hexachlorohexane (HCH)]. The pesticide contaminated sites include pesticide manufacturing sites, pesticide formulation sites and other sites, including storage facilities and aerial application facilities (Fitz,2000;NNEMS,2000). Due to the complexity of these sites, it is difficult to make generalizations regarding the risk assessment for the types of contamination present and the remediation activities that were/ are being chosen.

The readers of this chapter are suggested to go through the UNIDO document titled "Persistent Organic Pollutants: Contaminated Site Investigation and Management Toolkit (2010) available on UNIDO site for free download (Contaminated Site Ttoolkit, 2010). This Toolkit aims to aid developing countries with the identification, classification and prioritization of POPs-contaminated sites, and with the development of suitable technologies for land remediation in accordance with best available techniques/best environmental practices (BAT/BEP). The Toolkit focuses exclusively on the 12 POPs listed in **Table 1**. The nine POPs recently added to the Stockholm Convention (listed in **Table 2**) are not included because there are still significant scientific challenges and unknowns associated with them. The Toolkit could be used both as a training tool and as a self-directed manual and resource document for decision-makers, practitioners and a range of other stakeholders. Pertaining to POPs contaminated site management

The readers may also peruse the Alberta Tier 1 Soil and Groundwater Remediation Guidelines (Alberta Tier 1, 2010) encompassing generic remediation guidelines for achieving equivalent land capability. Site-specific guidelines for achieving equivalent land capability can be developed using a Tier 2 approach (Alberta Tier 2,2010).

2. Site prioritization for risk assessment

2.1 Contaminated site prioritization

The purpose of the site prioritization is to classify contaminated sites based on risk assessment. In this section, two semi-quantitative tools are presented that allow the user to determine which sites should be assessed and then to prioritize sites based on their potential for causing unacceptable risks to humans and/or to natural environment. These are pre-screening tool and prioritization tools.

The pre-screening tool determines, through inventorization approach, as to whether the site has a history of activity leading to pesticide-POPs contamination or whether there are other reasons to believe that contaminants have been present at the site

The tool aims to gather contaminant characteristics, off-site migration potential, exposure and socio-economic factors. Then, based on the information obtained , the sites should be classified into the following categories:

- Class 1 – High priority for risk assessment
- Class 2 – Medium-high priority for risk assessment
- Class 3 – Medium priority for risk assessment
- Class 4 – Low priority for risk assessment
- Class N – Not a priority for risk assessment

The site prioritization tools are based on principles derived from the Canadian National Classification Tool for contaminated sites (CCME 2008).

The following web resources are helpful for designing a sampling program: http://www.ccme.ca/assets/pdf/pn_1101_e.pdf (PDF file) .

While the tools are applicable to any contaminated site, a greater emphasis has to be put on pesticide- POP's related contaminant issues.

2.2 Setting up of risk-based standards by regulatory agency

2.2.1 Risk based approach

The assessment before procedures and of contaminated sites is to follow the human health and environmental risk based approaches delineated in the Procedures for the Use of Risk Assessment under Part XV.1 of the Environmental Protection Act ,Ontario Ministry of the Environment, Canada. The Contaminated Sites Monograph Series, The Health Risk Assessment and Management of Contaminated Sites, and Australian Standard AS4482 — Guide to the sampling and investigation of potentially contaminated soil and the equivalent National Environment Protection Measure (NEPM) Guidelines(a,b,c,d,e,f and g,1999) are some of the important references for consultants carrying out contaminated site investigations.

Land becomes contaminated when there is spillage, leakage or disposal of pesticide POPs to the ground. Soil at or below the ground surface, and sometimes groundwater, as well, may be contaminated depending on the subsurface conditions. To determine objectively if a piece of land is contaminated, certain standards would need to be put in place. Generally developing countries have no locally-derived standards for land contamination assessment. These countries adopt standards from developed country(ies) which has/have very different conditions. Therefore there is a need to develop contaminated land standards that are tailor-made for local conditions.

The United States (US) Environmental Protection Agency (USEPA) pioneered the application of chemical risk assessment principles and procedures to evaluate contaminated

sites under their Superfund Program in the 1980s. Other countries (mainly Canada, Australia and some European countries including the Netherlands) followed the US footsteps and began developing their own risk-based standards in the 1990s by making reference to the US approach. http://www.epd.gov.hk/epd/english/boards/advisory_council/ files/ACE_Paper_18-2006.pdf)

The risk-based approach means that contaminated land will be managed by considering the nature and extent of the potential risk it poses as a result of the receptors' exposure to chemicals in the soil and/or groundwater. This basically acknowledges that there is an acceptably low level of exposure to contaminants, which poses negligible risk. Choosing the level of negligible risk is a very important decision in the derivation of risk-based standards. The risk levels usually considered for protection of public health are:

- An excess lifetime cancer risk of 1 in 10^6 for carcinogens
- Actual intake must be less than the safe dose for non-carcinogens.

These risk limits are in line with the international practice and are at the conservative end of the range of risk limits adopted worldwide. For example, it is noted that the risk limit of 1 in 10^6 has also been adopted by some countries such as the US, the Netherlands and Canada, etc. while the UK has used a higher risk of 1 in 10^5.

2.2.2 Health risk assessment

Establishment of Base Line Human Health Risk Assessment (BHRA)

The risk assessment procedures, developed and documented by US EPA, are still subject to improving, especially concerning human health (US EPA 1989; 1991a; 1995; 1996a; 1996b; 2001a; 2001b; 2002).

Generally, the purpose of base line human health risk assessment (BHRA) is to:

- Assess potential risks to human health
- Determine the need for remedial action
- Determine measures needed to eliminate or mitigate health and environmental effects.

BHRA is an analysis of the potential adverse health effects caused by exposure to hazardous substances released from a site in the absence of actions to control or mitigate these releases (i.e., under an assumption of no action) (US EPA 1989).

To estimate BHRA, the following steps are undertaken:

- Data collection and evaluation
- Selection of indicator chemicals
- Exposure assessment
- Toxicity assessment
- Risk characterization.

Data collection and evaluation

An objective of the data collection and evaluation step is to produce data that can be used to assess risks to human health. This step includes:

- Review of available site information
- Consideration of modeling parameter needs
- Collection of background data (samples not influenced by site contamination)
- Preliminary identification of potential human exposure

- Development of an overall strategy for sample collection
- Identification of analytical needs
- Collection and evaluation of data
- Development of a data set that is of acceptable quality for the risk assessment.

Human health implications of POPs

The implications of chronic and acute exposures to POPs are not fully understood. Laboratory investigations and environmental impact studies in the natural environment have indicated that POPs exposure can result in endocrine disruption, reproductive and immune dysfunction, brain and nervous system disorders, developmental disorders and cancer. Some organochlorine chemicals are likely carcinogenic by promoting the formation of tumors. Six of the 9 pesticide-POPs, identified in the *Stockholm Convention* , are classified as *possibly* carcinogenic to humans. The remaining three - endrin, dieldrin and aldrin are classified by WHO as highly hazardous (class 1b) on the basis of their acute toxicity to experimental animals.

Fetuses and infants are particularly vulnerable to pesticide POPs exposure due to the transfer of these POPs from the mother during critical stages of development. Exposure during development has been linked to reduced immunity (and increased infections), developmental abnormalities, brain and nervous system impairment, and cancer and tumor induction or promotion in infants and children. There may also be a link to human breast cancer.

Cancer risk

The International Agency for Research on Cancer identifies most of the 12 POPs targeted by the Stockholm Convention as presenting a potential carcinogenic risk to humans, as described in the **Table 3** below.

Sr. No.	**IARC Classification**	**POPs**
1	**Group 1**: The agent (mixture) is carcinogenic to humans	• 2,3,7,8-Tetrachlorodibenzo-para-dioxin (TCDD)
2	**Group 2A**: The agent (mixture) is probably carcinogenic to humans	• Mixtures of polychlorinated biphenyls (PCB)
3	**Group 2B**: The agent (mixture) is possibly carcinogenic to humans	• Chlordane • DDT • Heptachlor • Hexachlorobenzene • Mirex • Toxaphene (mixtures of Polychlorinated camphenes)
4	**Group 3**: The agent (mixture or exposure circumstance) is unclassifiable as to carcinogenicity in humans	• Aldrin, Dieldrin and Endrin • Polychlorinated dibenzo-para-dioxins (other than TCDD) • Polychlorinated dibenzofuran

Source: http://www.chem.unep.ch/gpa_trial/02healt.htm

Table 3. POPs posing potential carcinogenic risk to humans

Possible human exposure pathways

Humans can be exposed to pesticide-POPs through diet, occupation, accidents and both the indoor and outdoor environments. Exposure to these POPs can either be a short-term exposure to high concentrations (acute) or long-term exposure to lower concentrations (chronic).

Acute exposure to pesticide-POPs can occur during production and application and industrial accidents. In addition, exposure to chlorinated pesticides can occur both from accidental ingestion of treated seeds or via poor handling or application processes. Presently, pesticide poisoning is mainly attributable to aldrin, dieldrin, HCB and chlordane.

Chronic exposure occurs most commonly via dietary exposure pathways. Due to their tendency to bio-accumulate, longer-term human exposure to the pesticide- POPs identified in the Stockholm Convention is generally via food. Foods containing the greatest concentrations of POPs include the fatty tissues of animals and edible oils. The contamination of food, including breast milk, by POPs is of worldwide concern (Stober,1998).

Toxicity assessment

Toxicity assessment is based on available scientific data on potential adverse health effects of the contaminants in humans, which are usually compiled in the form of a toxicological profile for each contaminant. This step also includes also identification of important measures of toxicity, i.e., reference doses (RfDs) to evaluate non- carcinogenic effects, and cancer slope factors (CSFs) for carcinogenic effects.

RfDs and CSFs have been developed by the US EPA and published in the Integrated Risk Information System (IRIS) (IRIS 2003), and Health Effects Assessment Summary Tables (HEAST) databases. IRIS is recommended as a preferred source of toxicity information. HEAST is used when data are not available in IRIS (US EPA 1989; 2003).

The US EPA has also developed provisional values of RfDs and CSFs, which are used for specific purposes (US EPA 2003). If no RfDs and CSFs are available, the chemicals can be evaluated only qualitatively.

Exposure assessment

The exposure assessment stage estimates the magnitude of actual and/or potential human exposure, the frequency and duration of exposure, and pathways by which humans are potentially exposed (USEPA 1989).

The exposure assessment proceeds with the following steps:

Step 1. Characterization of exposure setting - the physical environment of the site and the potentially exposed populations are characterised.

Step 2. Identification of exposure pathways - chemical sources and mechanism of chemical release, transport media (e.g., soil, air, groundwater), exposure points as well as exposure routes (e.g., ingestion, inhalation, dermal contact) are identified in this step; an exposure pathway describes the course a chemical or physical agent takes from the source to the exposed individual (e.g., ingestion of contaminated schoolyard soil by children).

Step 3. Quantification of exposure - exposure concentrations of contaminants are estimated and pathway-specific intakes are calculated.

During this step, site-specific exposure scenarios are developed for both current and/or intended future land use patterns (e.g., residential, commercial/industrial, recreational).

Results of the exposure assessment are pathway-specific contaminant intakes, under developed exposure scenarios. Standard intake equations and suggested values of exposure parameters are provided by the US EPA; however, site-specific factors and expert judgment can influence the final selection thereof.

In the classical approach, exposure parameters, such as body weight, exposure duration, ingestion or inhalation rates, can be selected to estimate "reasonable maximum exposure" (RME), defined as the highest exposure that is reasonably expected to occur at a given site (US EPA 1989). The goal of RME is to combine upper-bound and mid-range exposure factors in the equation so that the result represents an exposure scenario that is both protective and reasonable, not the worst possible case (US EPA 1991b).

The quantification of exposure is based on an estimate of the average daily intake, i.e., the average amount of the contaminant entering the receptor's body per day.

The considered human receptors are strictly related to defined land use patterns, e.g., adult receptors under the industrial land use, and children and adults under residential/recreational land uses.

The generic equation for calculating chemical intakes is as follows:

$$DI = C \times (IR / BW) \times (EF \times ED / AT) \quad (1)$$

where:

DI = daily intake of chemical (mg/kg-d)

C = concentration of chemical in an environmental medium (e.g., mg/kg for soil or food, mg/L for water, mg/m^3 for air)

IR = intake rate of the environmental medium (e.g., kg/day for food or soil, L/day for water, m^3/day for air)

BW = body weight (kg)

EF = exposure frequency (days/yr)

ED = exposure duration (years)

AT = averaging time (days)

It may be noted that the term IR/BW is a description of the basic contact rate with a medium (e.g., L of water per kg body weight per day) and the second term (EF×ED/AT) adjusts for cases where exposure is not continuous. For example, if a person was exposed for 50 days/year for 20 years of a lifetime (70 years), the value of this term would be $50/365 \times 20/70 = 0.039$.

There is often wide variability in the amount of contact between different individuals within a population. Thus, human contact with an environmental medium is best thought of as a distribution of possible values rather than a specific value. Usually, emphasis is placed on two different points of this distribution:

Average or Central Tendency Exposure (CTE)

CTE refers to individuals who have average or typical intake of environmental media.

Upper bound or Reasonable Maximum Exposure (RME)

RME refers to people who are at the high end of the exposure distribution (approximately the 95th percentile). The RME scenario is intended to assess exposures that are higher than average, but are still within a realistic range of exposure.

As the calculations of CTE and RME risk are done using single numbers (point estimates) for each input value, this approach is usually referred to as the point estimate method. In

some cases, the risk assessor may wish to describe each exposure parameter not by a single number but as a distribution. This is referred to as probabilistic risk assessment (PRA). In this case, computations require computer-based methods (Monte Carlo simulation) and the output is also a distribution rather than a point estimate. This approach provides a more complete description of the range of exposures that occur in the exposed population and also helps increase the accuracy of combining exposure levels across different pathways.
In some cases, human exposure may be measured directly (biomonitoring) rather than calculated based on assumed exposure parameters. For example, exposure to lead is often evaluated by measuring the amount of lead in blood, and exposure to arsenic is often evaluated by measuring the amount of arsenic in urine or in hair. While direct measurement bypasses many of the uncertainties associated with calculating human exposure, this approach is limited by providing data only on current conditions. In addition, if exposure is occurring from more than one source, direct measurement does not distinguish between the sources.
Equations for exposure pathway to contaminated soil for outdoor and indoor workers are in the Tables published by USEPA (USEPA, BJC/OR-271, 2006.) URL: http://rais.ornl.gov/homepage.

Risk characterization

Risk characterization combines toxicity assessment with exposure assessment, in order to quantify risks posed by a contaminated site under a given set of conditions.
Risk characterization is considered separately for carcinogenic and non-carcinogenic effects, and includes identification of sources of uncertainty. Chemicals, which produce both non-carcinogenic and carcinogenic effects are evaluated in both groups.
Risks are quantified under the present site conditions for present and/or future exposure scenarios relevant to the land use pattern. Risk characterization should also include a discussion on accompanying uncertainties.

Non-cancer risk

Potential non-cancer risks are evaluated by comparison of the estimated contaminant intakes from each exposure route (oral, dermal, inhalation) with the relevant RfD to produce the hazard quotient (HQ), defined as follows (US EPA 1989):

HQ-ingestion and dermal = CDI/RfD
HQ-inhalation = CDI/RfC

where:
HQ:Hazard Quotient (unitless),
CDI: Chronicl Daily Intake (mg/kg/day),
RfD: Reference Dose (mg/kg/day).
RfC : Reference Concentration

The hazard quotient assumes that there is a level of exposure (i.e., RfD/RfC) below which it is unlikely to experience adverse health effects, even for sensitive populations. If the HQ exceeds unity (a value of 1), there may be a concern for potential non- carcinogenic effects.
To assess the overall potential for non-carcinogenic health effects posed by more than one chemical, the HQs calculated for each chemical are summed (assuming additivity of effects), and expressed as a Hazard Index (HI) (US EPA 1989).

$$HI = HQ1 + HQ2 + ... + HQn \quad (2)$$

In cases where the non-cancer HI does not exceed unity (HI<1), it is assumed that no chronic risks are likely to occur at the site (US EPA 1989). If the HI is higher than unity, as a consequence of summing several hazard quotients, the compounds are segregated by effects, target organs, and by mechanism of action and separate HIs are derived for each group.

Because of the potential for different health effects/target organs via oral/dermal and inhalation exposures, these exposures are evaluated separately (US EPA 2002). To assess the overall potential for non-carcinogenic effects, posed by several exposure pathways, HIs for each exposure pathway contributing to exposure of the same individual or subpopulation are summed up and expressed as a total hazard index (HI Tot). When HI Tot exceeds unity, there may be concern for potential non-cancer health effects.

Quantitative risk assessment

Under the residential and recreational scenarios, i.e., scenarios which refer to different group receptors (children, adults), HIs are generated separately for children and adults.

Cancer risk

Cancer risks are estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen (i.e., incremental or excess individual lifetime cancer risk). The following linear low-dose carcinogenic risk equation is used for each exposure route (US EPA 1989):

$$\text{Excess Lifetime Cancer Risk (ELCR)-ingestion \& dermal} = \text{CDI} \times \text{slope factor (CSF)} \quad (3)$$

$$\text{Excess Lifetime Cancer Risk (ELCR) - inhalation} = \text{CDI} \times \text{unit risk factor (URF)} \quad (4)$$

$$\text{Cancer Risk} = \text{CDI} \times \text{CSF} \quad (5)$$

where:

CDI: Chronic Daily Intake averaged over 70 years (mg/kg/day),

CSF/URF:: Cancer Slope/Unit Risk Factor (mg/kg/day) 1 ; a plausible upper-bound estimate of the probability of a response per unit intake of a chemical over a lifetime.

CDI and CSF/URF represent the same exposure route (i.e. oral, dermal and inhalation CDIs are multiplied by oral, dermal and inhalation CSFs/URF, respectively). The risk number represents the probability of occurrence of additional cancer cases. For example, if it is expressed as 1E-06, it means that one additional case of cancer is expected in a population of one million people exposed to a certain level of a given chemical over their lifetime.

If a site has multiple carcinogenic contaminants, cancer risks for each carcinogen are added (assuming additivity of effects), and the cancer risk for each exposure pathway is calculated.

For multiple exposure pathways, the total cancer risk is calculated by summing up the pathway-specific cancer risks:

Risks in the range of 1E-06 to 1E-04 are generally accepted by regulatory agencies, e.g., US EPA (US EPA 1990; 1991a; 1991c). A risk-based remedial decision can be superseded by the presence of a non-carcinogenic impact or environmental impact requiring action at the site. Remedial action is generally required at a site, when a cumulative carcinogenic risk exceeds 100 in a million (1E-04, excess cancer risk) or the cumulative non-carcinogenic HI exceeds 1, based on RME assumptions (US EPA 1991a; 1991c). If the cumulative risk is less than 1E-04, action generally is not required, but may be warranted if a risk-based chemical-specific

standard (e.g., drinking water standards) is violated. Setting up 1E-06 risk level for individual chemicals and pathways should generally lead to cumulative site risks within the range of 1E-06 to 1E-04 for the combinations of chemicals.
Under the scenarios, which refer to both receptors – a child and an adult (i.e., residential and recreational), cancer risks are calculated separately for these receptors, and then summed up to yield the total cancer risk for the aggregate resident/recreational user.

2.3 Dealing with biased data

The basic unit of a risk assessment is an exposure unit, and the key description of exposure is the arithmetic mean concentration within an exposure unit. If the data collected from within an exposure unit are either random or systematic, the methods for computing the mean (and confidence limits around the mean) are relatively straightforward. However, in some cases, the data available are not random or systematic, but are biased. That is, more samples are collected from areas with high concentrations than with low concentrations. This unequal sampling density poses a difficulty in computing the mean, but techniques are available for adjusting for this issue. Important guidance documents on how to make these adjustments include the following:
Spatial Analysis and Decision Assistance (SADA) Software Home Page GeoSEM Software (Syracuse Research Corporation)

2.4 Probabilistic Risk Assessment (PRA)

Equations for computing human exposure contain a number of terms that are inherently variable. For example, not all people have the same body weight. Rather, there is a distribution of body weights across different people. The same is true for intake rates, exposure frequencies, and exposure durations. If data are available to describe the distribution of each of these terms, then a mathematical method is needed to combine the distributions.
While there are a number of different methods available, the most common and convenient is Monte Carlo simulation. In this approach, each term in the exposure model is described by a distribution rather than a single value. The computer draws a value at random from each distribution, computes the exposure, and saves the value. This process is repeated many times, resulting in a distribution of exposure values. This distribution provides a more complete description of exposure than the point estimate approach and helps ensure that values selected for CTE and RME exposures are realistic. Key guidance documents dealing with PRA include the following:

- RAGS III Part A: Process for Conducting Probabilistic Risk Assessment (OSWER 9285.7-45, December 2001)
- Note: In particular, see Chapter 3 - Using Probabilistic Analysis in Human Health Assessment (PDF) (27 pp, 2MB).
- Guiding Principles for Monte Carlo Analysis (EPA/630/R-97/001, March 1997)
- Policy for Use of Probabilistic Analysis in Risk Assessment at the U.S. Environmental Protection Agency (May 1997)

2.5 Biomonitoring

In some cases, biomonitoring may be a useful tool to help evaluate current exposure levels at a site. This requires that a population of humans are present at the site and that there is a

method available for measuring the level of exposure in the population. In general, the results of the biomionitoring may be compared to other (reference) populations to help understand the magnitude of the site-related exposure, and/or may be compared to health-based guidelines for the maximum level of exposure that is considered acceptable. Important guidance documents on planning, performing, and interpreting biomonitoring studies are presented below.

- Criteria for Evaluating Blood Lead (PDF) (Region 8 Guidance RA-07, September 1995) (22 pp, 1.6MB)
- Sample Analysis and Quality Assurance Plan for Urinary Arsenic and Blood Lead Among Residents of VBI70 Neighborhoods (PDF) (Region 8, June 2002) (27 pp, 333K)
- Experience Using Filter Paper Techniques for Whole Blood Lead Screening in a Large Pediatric Population (PDF) (8 pp, 187K) (J.A. Collins and S.E. Puskas, MEDTOX Laboratories, Inc., Saint Paul, MN)

3. Development of site-specific Health-based Remedial Goals (HBRGs)

3.1 HBRGs

Health-based remedial goals (HBRGs), termed also risk-based concentrations [RBCs,(http://www.image-train.net/products/papers/ASC3_EW_RBA.pdf)], are concentration levels for individual chemicals that correspond to target risk (TR), i.e., a specific cancer risk level (e.g., $1E^{-06}$) or hazard quotient (HQ) or hazard index (HI) (e.g., less than or equal to 1) (US EPA 1991a). RBCs are usually calculated under all developed scenarios for the purpose of guiding remedial activities at a site; they are used during analysis and selection of remedial alternatives.

There are two methods for calculating RBCs. The first method (Method 1) is a simplified method based on site- specific exposure data (US EPA 1995). This method uses the ratio between the target risk and calculated risk due to a specific chemical in a given medium:

$$\frac{C}{\text{Calculated Risk}} = \frac{RBC}{\text{Target Risk}} \tag{6}$$

where:

C: Chemical Concentration in soil or groundwater

RBC: Risk-Based Concentration (oral/dermal or inhalation).

Rearranging this equation, RBC is calculated as follows:

$$RBC = C \frac{\text{Target Risk}}{\text{Calculated Risk}} \tag{7}$$

RBCs are calculated for both carcinogenic and non-carcinogenic substances, and only for those contaminants for which the calculated site-specific risk is above acceptable risk levels (target risk). For carcinogens, RBCs can be calculated for target cancer risks of 1E-06, 1E-05 or 1E-04. Concerning non-carcinogenic risk,target HQs of 0.1 or 1 can be substituted for target risk, and the calculated HQs substituted for calculated risks.

Under industrial scenario, RBCs are estimated for adult receptors, and under the residential/recreational scenarios - separately for child and adult receptors for non-carcinogenic effects, and for an aggregate resident/recreational user for carcinogenic

effects. According to the US EPA recommendations, RBCs are calculated separately for oral/dermal and inhalation exposures, because of the potential for different health effects (target organs) via these routes (US EPA 2002). If both carcinogenic and non-carcinogenic RBCs are calculated for a given contaminant, and for both oral/dermal and inhalation exposures, then lowest of these values should be applied as the preliminary remedial goal.

Concerning non-carcinogens, if more than one chemical affects the same target organ/system, RBCs calculated for those chemicals should be divided by the number of chemicals present in the group. In that way, RBCs are adjusted to reflect the potential for additive risks:

$$ARBC = RBC/n \quad (8)$$

where:

ARBC: Risk-Based Concentration adjusted for exposure to multiple contaminants with the same target organs/effects

RBC: Risk-Based Concentration for an individual non-carcinogen

n: Number of contaminants with the same target organs/effects.

RBCs can also be calculated by rearrangement of standard risk equations, separately for combined oral and dermal exposures, and for inhalation exposure by a receptor within the used scenario (US EPA 2002).

In summary, application of risk-based approach to contaminated land assessment and remediation allows to:

- Determine the needs for remedial action, aimed at reducing risk,
- Determine preliminary remedial goals based on the protection of human health,
- Provide a basis for the selection of an appropriate remedial option
- Facilitate making decision on appropriate corrective actions at the site.

3.2 Health concerns

Persistent pesticides pose a threat to the well-being of the environment and to human health. The solid organochloride insecticides are known to accumulate in human adipose tissue. Some of these insecticides, including chlordane, can even be absorbed dermally. Other health problems caused by exposure to the solid organochloride insecticides are convulsions, a hyperexcitable state of the brain and a predisposition to cardiac arrhythmia. Eating wheat treated with hexachlorobenzene, another organochloride insecticide, has been associated with human dermal toxicity, which can result in blistering of the skin. Although not all organochlorine insecticides are considered POPs, many of them are among the compounds on the UNEP's list of persistent organic pollutants, including aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzenes, mirex and toxaphene.

The assessment of health effects of contamination is to be made with reference to the human health-based investigation levels for various settings described in Contaminated Sites Monograph Series No 5, 1996 as incorporated in Appendix 9. The assessment of environmental impacts is to include reference to the ANZECC/NHMRC Environmental Investigation Thresholds in Appendix 9.1.

In urban residential settings where sensitive ecological receptors are not present, assessment should address:

- Potential health risks to occupants
- The capacity of the soil to support a normal ornamental domestic garden without significant phytotoxic effect.

In this process, reference may be made to the contemporary background metal levels for Queensland horticultural soils determined in studies by the Department of Natural Resources (full reference in Appendix 9.2). The chemical form of the contaminant and its mobility characteristics will be essential components of assessments.

Complex health risk assessments are to be undertaken by qualified professionals using nationally accepted health risk assessment methodology when a significant exposure risk exists. A suitable module on Site-Specific Health Risk Assessment and Management of Contaminated Sites is to be refererred to, if available.

Environmental risk assessment is to be conducted on a site-specific basis when contamination levels exceed background. The characteristics of the contaminant (including chemical form, mobility, leachability and bioavailability) and the exposure routes to local receptors should be identified.

4. Integrating risk assessment with contaminated site management

Risk is governed by the contaminants present on the site, pathways through which these contaminants reach the receptors and the receptors who are usually the site users. A conceptual site model, encompassing all the three site attributes , usually helps to focus on risk. Construction of a contaminant-pathway-receptor model is the first step of risk assessment.

Since remediation through risk management deals with eliminating or controlling one or more of the three risk components: (i) contaminant, ii) exposure pathway, and iii) receptor, remediation becomes the proactive risk management solution. The remediation measures include:

- Source control
- Site stabilization and decontamination to the extent required by the Regulatory Agency for a specific site-use purpose(s).
- Alternative forms of risk management on a contaminated site, such as exposure barriers, administrative controls and/or partial remediation, may be acceptable to a regulatory agency in certain cases.

Remediation , either on-site (in-situ) or off-site (ex-situ) can employ one method, or a combination of the available physical, chemical and biological methods.Sometimes, it is not possible to remove the contaminants or exposure routes due to technical or economic or environmental constraints, the last resort is to control the receptor's accessibility by relocations and imposing land use restrictions.

Long-term remediation strategies are intended to implement a comprehensive monitoring program that properly characterizes the baseline (pre-remediation) condition and monitors improvements to be achieved through targeted remediation. Long-term remedial measures focus on compliance with all regulatory standards applicable to all contaminated media (e.g., groundwater, soil, and soil vapour) present at the site.

The readers of this chapter are suggested to go through the UNIDO document titled "Persistent Organic Pollutants: Contaminated Site Investigation and Management Toolkit (2010) available on UNIDO site for free download. This Toolkit aims to aid

developing countries with the identification, classification and prioritization of POP-contaminated sites, and with the development of suitable technologies for land remediation in accordance with best available techniques/best environmental practices (BAT/BEP).

5. References

Alberta Tier 1 Soil and Groundwater Remediation Guidelines Alberta Environment December 2010

Alberta Tier 2 Soil and Groundwater Remediation Guidelines Alberta Environment December 2010

Contaminated Site Toolkit (2010)

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National Environment Protection Measure (NEPM) Guidelines

a. Schedule B(4): Health Risk Assessment Methodology - Dec 1999

This Guideline incorporates aspects of the *ANZECC Guidelines for the Laboratory Analysis of Contaminated Soil 1996*, which were prepared in response to a recognised need for consistent procedures of soil analysis for environmental assessment of contaminated land.

The Guideline covers the philosophy behind the methods selected, it also comprises guidelines on the quality assurance procedures and techniques for sample preparation and describes methods for the analysis of physico-chemical properties, inorganics and organics in soil.

filename: ASC_NEPMsch__03_Lab_Analysis_199912.pdf

This document provides an approach to site-specific health risk assessment. Due to the complexity and scale of the health risk assessment process a concise 'cookbook' is not practicable. Similarly, the site-specific issues are often sufficiently complex and 'site-specific' for a particular site that a manageable and complete algorithm for decision-making cannot be drafted. The document provides a series of guidelines (and prescriptions) to assist the decision-making process. Where possible, the document is prescriptive about certain aspects of risk assessment.

filename: ASC_NEPMsch__04_Health_Risk_Assessment_199912.pdf

b. Schedule B(5): Ecological Risk Assessment - Dec 1999

The overall aim of this guideline is to promote a consistent, rational approach to ecological risk assessment of site contamination throughout Australia. Specifically, this document aims to provide a clear framework for ecological risk assessment for chemically contaminated soils that can be readily and consistently used by jurisdictional environmental agencies and risk assessors.

filename: ASC_NEPMsch__05_Ecological_Risk_Assessment_199912.pdf

c. Schedule B(6): Risk Based Assessment of Groundwater Contamination- Dec 1999

The purpose of this draft Guideline is to provide a framework for the risk based assessment of groundwater that may have been affected by site contamination. The general processes outlined for the assessment of contaminated groundwater are compatible with the Policy Framework and the site assessment processes shown in Schedule A of the NEPM. The aim of this process is to minimise the risk of adverse human health and environmental impacts arising from contaminated groundwater.

filename: ASC_NEPMsch__06_Groundwater_199912.pdf

d. Schedule B(7a): Health-Based Investigation Levels - Dec 1999

e. This guideline was published jointly with the National Environmental Health Forum (NEHF) and is part of a series of NEHF monographs.

This guideline discusses the general principles for deriving guidance values for health-based investigation levels and also explores the process applied to develop health-based investigation levels for soils.

filename: ASC_NEPMsch__07a_Health_Based_Investigation_Levels_199912.pdf

vvvSchedule B (7b): Exposure Scenarios and Exposure Settings - Dec 1999

This guideline was published jointly with the National Environmental Health Forum (NEHF) and is part of a series of NEHF monographs.

This paper focuses on the component of exposure scenarios which may be seen as exposure settings (or standard land uses), with some reference to the characteristics of the populations potentially exposed in those settings. The intention is to define more clearly a standard range of exposure settings which regulators and risk assessors could use as baseline cases, to improve consistency of assessments, and provide a sound basis for land use/planning and remediation decisions based upon such risk assessments.

filename: ASC_NEPMsch__07b_Exposure_Scenarios_199912.pdf

f. Schedule B(8): Community Consultation and Risk Communication-Dec. 1999

This guideline provides a systematic approach to effective community consultation and risk communication in relation to the assessment of site contamination. It is not intended to be prescriptive but is intended to be used as a tool for effective consultation by consultants and regulators and should also provide a useful reference for all stakeholders including industry, government, landholders and the wider community. It should be noted that, in addition to this Guideline, each State or Territory has its own regulatory requirements regarding notification of pollution to the appropriate regulatory agency.

filename: ASC_NEPMsch__08_Community_Consultation_199912.pdf

g. Schedule B(9): Protection of Health & the Environment During the Assessment of Site Contamination Dec 1999

NNEMS (2000) The Bioremediation and Phytoremediation of Pesticide-contaminated Sites Prepared by Chris Frazar National Network of Environmental Studies (NNEMS) Fellow Compiled June - August 2000).

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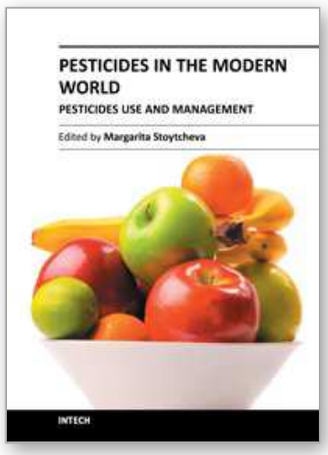

Pesticides in the Modern World - Pesticides Use and Management
Edited by Dr. Margarita Stoytcheva

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This book brings together issues on pesticides and biopesticides use with the related subjects of pesticides management and sustainable development. It contains 24 chapters organized in three sections. The first book section supplies an overview on the current use of pesticides, on the regulatory status, on the levels of contamination, on the pesticides management options, and on some techniques of pesticides application, reporting data collected from all over the world. Second section is devoted to the advances in the evolving field of biopesticides, providing actual information on the regulation of the plant protection products from natural origin in the European Union. It reports data associated with the application of neem pesticides, wood pyrolysis liquids and bacillus-based products. The third book section covers various aspects of pesticides management practices in concert with pesticides degradation and contaminated sites remediation technologies, supporting the environmental sustainability.

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