INVESTIGATING MERCURY:

A GUIDE TO ENVIRONMENTAL MONITORING

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2014

DEPARTMENT OF STATE
UNITED STATES OF AMERICA

BAN TOXICS!

ABOUT BAN TOXICS

BAN Toxics is an independent, non-profit, non-governmental, environmental organization that seeks to:

1. Promote environmental justice in the Philippines and the Southeast Asian region, ensuring that developing countries in the region do not bear a disproportionate burden of pollution coming from developed countries.
2. Prevent toxic trade in products, wastes, and technologies, particularly trade from developed to developing countries in the Southeast Asian region through the promotion of self-sufficiency in waste management, clean production, toxics-use reduction, and other sustainable and equitable practices or methodologies.
3. Reach out and work in solidarity and partnership with allied groups locally and regionally in Southeast Asia, striving to instill a broader consciousness of the interrelatedness of each community, each country within the region and to uphold our collective fundamental human right to life and to live in a healthy and peaceful environment.
4. Promote a new earth economics that accounts for nature's services, and the disservices from pollution, that internalizes all costs including those

transferred to the global commons, disenfranchised communities, the environment and the future.

5. Develop local and regional initiatives through research, investigation, and policy dialogue with government and grassroots organizations in order to actively share information and expertise through workshops, conferences, newsletters, reports, films, web features, and through other similar or as yet undeveloped media.

BAN Toxics works closely with local, national and international environmental NGOs, intergovernmental organizations, and academic institutions using both local and international campaigning, capacity-sharing and bridge-building between activists in Asia, and throughout the world.

BAN Toxics is a duly registered non-profit, non-governmental organization with the Philippine Securities and Exchange Commission.
We are based in Quezon City, Philippines.

ABOUT THE POLICY PAPER

Investigating Mercury: A Guide to Environmental Monitoring was co-authored by Richard Gutierrez, *JD. Ll.M.*, founder and Executive Director of BAN Toxics, and Myline Macabuhay, Global Chemicals Programme Assistant Coordinator at BAN Toxics.

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DISCLAIMER

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OBJECTIVES OF THE MANUAL

This manual serves as a reference material for training community stakeholders and individuals in conducting mercury concentration measurements in different mediums in suspected high-risk areas particularly in artisanal and small-scale gold mining sites, dental clinics, and waste dumpsites and landfills. It includes:

1. Information about mercury, mercury compounds and mercury toxicity;
2. Guidelines on developing mercury monitoring project plans;
3. Standard operating procedures in collecting samples in different mediums; and,
4. Interpreting mercury measurement results and its possible use in the development of mercury exposure policies and interventions at the community level.

The manual also looks at the importance of the scientific method in minimizing bias or prejudice by providing an objective, standardized approach to conducting research investigations and improving results by eliminating possible sources of errors. Moreover, it highlights the importance of using science-based and empirical information on advancing efforts and initiatives to eliminate toxics use, production and management. Since mercury is harmful not only to the environment but also to human health, determining actual mercury concentration by which the community is exposed to is a big step in capacitating local policymakers and stakeholders to develop and implement sound policies on mercury.

BAN Toxics aims to contribute in achieving this goal by sharing its practices on the field. Monitoring mercury concentration in different mediums is a continuous and progressive undertaking of the organization, and is coupled with the following strategies:

- ✓ Educating individuals and communities about the risks of mercury exposure;
- ✓ Presenting alternative methods and products, as well as providing access to affordable and safe technologies;
- ✓ Demonstrating behaviors that reduce and eliminate the risk of mercury poisoning to community members and stakeholders; and,
- ✓ Bridging stakeholders such as local government units, government agencies, private and public sectors towards the creation of intervention mechanisms.

BAN Toxics' training program further inculcates important values relating to scientific investigations, toxics-elimination campaigning and environmental sensitivity to its field investigators by embedding them in the local community context. This is done by working with various sectors in the impacted community to achieve a holistic and effective development in the line of work.

LIST OF ACRONYMS/TERMS

ADEQ	Arkansas Department of Environmental Quality
ASGM	Artisanal and Small-scale Gold Mining
AO	Administrative order
AOC	Area of contamination
ATSDR	Agency for Toxic Substances and Diseases Registry
BT	BAN Toxics
CFLs	Compact fluorescent lamps
CSOs	Civil society organizations
CV AAS	Cold vapor atomic absorption spectrometry
DENR	Department of Environment and Natural Resources
DL	Detection limit
DOH	Department of Health
DQO	Data quality objectives
HASP	Health and Safety Plans
IDW	Investigation-derived waste
IUPAC	International Union for Pure and Applied Chemistry
LGUs	Local government units
MENRO	Municipal Environment and Natural Resources Office

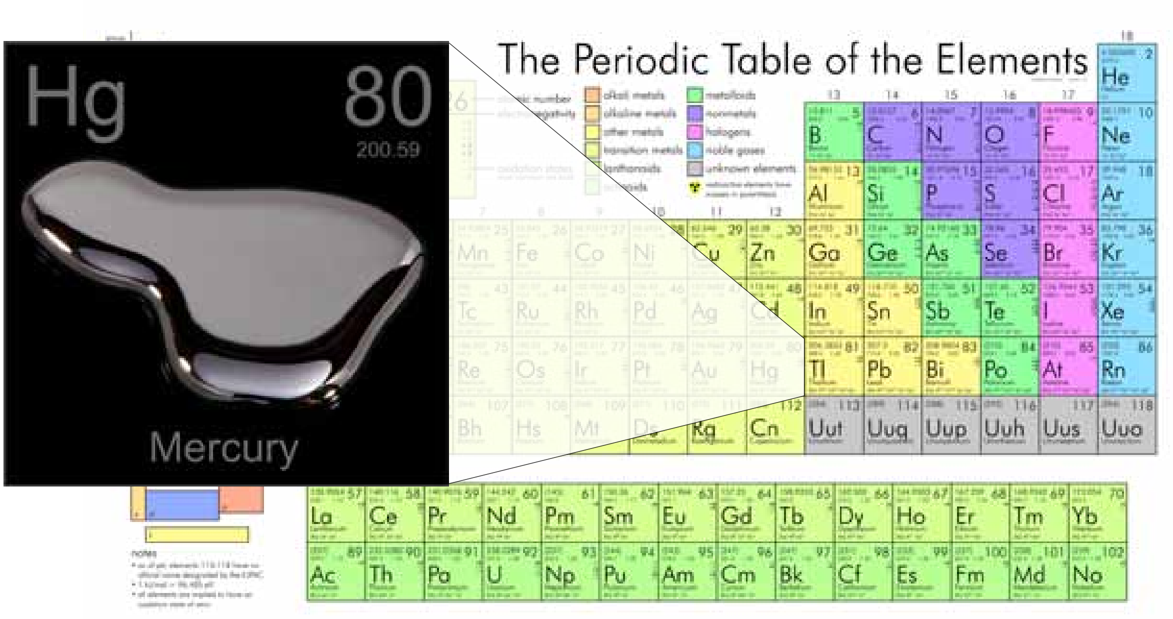
MGB	Mines and Geosciences Bureau
PAGASA	Philippine Atmospheric, Geophysical and Astronomical Services Administration
PARCCS	Precision, accuracy, representativeness, completeness, comparability and sensibility
PENRO	Provincial Environment and Natural Resources Office
POs	People's organizations
ppb	parts per billion
ppm	parts per million
QAPP	Quality Assurance Plan
QA/QC	Quality assurance/ quality control
RSD	Relative standard deviation
SAP	Sampling and Analysis Plan
SD	Standard deviation
TDU	Treatment/ disposal unit
UNEP	United Nations Environment Program
US EPA	United States Environmental Protection Agency
WHO	World Health Organization

CHAPTER 1: UNDERSTANDING MERCURY

This section provides a brief overview of mercury its characteristics, speciation, and routes of exposure to humans. The section also discusses in brief the linkage of mercury in society, where it is found and how it is used, in order to provide the reader a quick understanding of the impacts of mercury use to human health and the environment.

1.1 WHAT IS MERCURY?

Mercury is a silvery, d-block element with an atomic number of 80. Commonly known as quicksilver, it is represented by the symbol “Hg”, which originates from its former name *“hydrargynum”* from the Greek words *“hydr”* (water) and *“argyros”* (silver) [1].



d-block elements, also known as the transition metals, include elements whose atom has an incomplete d sub-shell.

Mercury is part of the 12th group of elements under the International Union for Pure and Applied Chemistry (IUPAC) numbering, together with zinc (Zn), cadmium (Cd) and copernicium (Cn)-- also known as volatile metals [2].

Mercury is unique among heavy metals for possessing a high vapor pressure of 0.001201 Torr at 20°C [3]. This means that the saturation concentration of mercury in air increases dramatically with increasing temperature (Table 1).

TABLE 1. VAPOR PRESSURE AND SATURATION CONCENTRATIONS OF MERCURY IN AIR AT SELECTED TEMPERATURES: MERCURY CONCENTRATIONS IN AIR INCREASE RAPIDLY WITH INCREASING TEMPERATURE

Temperature (°C)	Temperature (°F)	Vapor pressure (Torr)	Vapor pressure (mg/m³)
0	32	0.000185	2.2
10	50	0.000490	5.9
20	68	0.001201	13.2
30	86	0.00277	29.5
40	104	0.006079	62.6

At 20°C, the saturation concentration of Mercury in air is 132 times the Occupational Safety and Health Agency (OSHA) exposure limit.

Alchemists believed that mercury was the most important of all substances because it encompasses solid and liquid, earth and heaven, and life and death [4]. In China and Tibet for instance, mercury use was thought to prolong life and maintain good health. The first emperor of China, Qín Shî Huáng Dì, died from religiously drinking a mercury and jade mixture formulated by Qín alchemists, and is allegedly buried in a tomb with rivers of flowing mercury on a model of the land he once ruled [5]. *See Annex 2.*

1.2 FORMS OF MERCURY [6]

Mercury occurs naturally in the environment, and as a heavy metal, is a constituent element of the earth. It exists in a large number of forms, the pure form is known as *elemental* or *metallic* mercury and expressed as Hg(0) or Hg^0. However, mercury is rarely found in nature as the liquid metal, but rather within compounds and inorganic salts. Mercury forms compounds through its monovalent or divalent mercury forms, expressed as Hg(I) or Hg^{1+} and Hg(II) or Hg^{2+} respectively. Most inorganic and organic compounds are formed from the divalent form.

1. **Elemental mercury**. Elemental mercury is a shiny, silver-white metal and is in liquid state at room temperature.

Mercury occurs naturally in the environment in the form of mercuric sulphide or *cinnabar* ores, which have been the source ores for the commercial mining of metallic mercury industry through history. The metallic form is refined by heating the mercuric sulphide ore to temperatures above 540°C. This condition allows the vaporization of the mercury from the ore, the vapors are then captured and cooled to form the liquid metal mercury.

2. **Inorganic mercury**. Inorganic mercury compounds, generally known as *mercury salts*, include mercuric sulphide (HgS), mercuric oxide (HgO) and mercuric chloride ($HgCl_2$). Most inorganic mercury compounds are white powders or crystals, except for mercuric sulphide which is red and turns to black upon exposure to light.

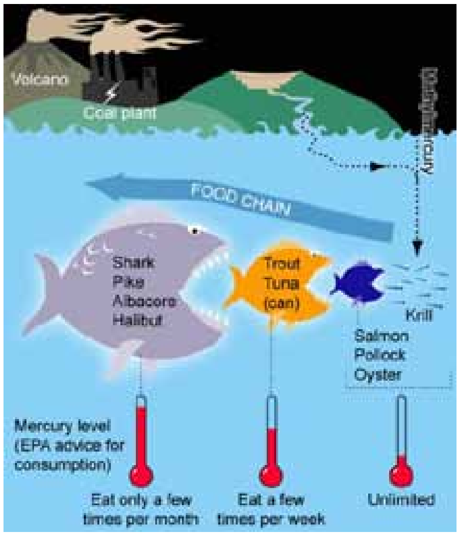
Though the mercury in this form occurs as a component of a compound, some mercury salts such as $HgCl_2$ are sufficiently volatile to exist as an atmospheric gas. The divalent state of mercury lends these mercury gases inherent water solubility and chemical reactivity which lead to much more rapid deposition from the atmosphere than for elemental mercury. This result in significantly shorter atmospheric lifetimes.

3. **Organic mercury**. When mercury combines with carbon, organic mercury compounds or *organomercurials* are formed. There is a potentially large number of organic mercury compounds, sych as dimethylmercury, phenylmercury, ethylmercury, however, the most common in the environment is methylmercury.

1.3 NATURAL SOURCES OF MERCURY

The most common natural forms of mercury found in the environment are mercuric sulphide (*cinnabar)*, mercuric chloride and methylmercury. Natural sources of mercury include volcanoes and forest fires, while some microorganisms and natural processes change mercury in the environment from one form to another. Volcanic contribution alone is responsible for approximately 20 to 40% of atmospheric mercury emissions [7].

Methylmercury is generated from conversion of other forms of mercury by microorganisms through natural processes. It is of particular concern because it can bioaccumulate in the bodies of many edible freshwater and saltwater fish, and biomagnify in the food chain to levels that increases the risk of mercury exposure for human consumption [8].



As an element, mercury cannot be created nor destroyed by any chemical means. It can only change between the different states and species in its cycles. Once mercury has been liberated from either its natural or anthropogenic sources and released into the biosphere, its high mobility can impact its biospheric sinks-- earth's surface soils, water bodies and bottom sediments.

1.4 ANTHROPOGENIC SOURCES OF MERCURY

Anthropogenic sources of mercury remain to be the leading source of mercury in the environment. Mercury levels have historically increased due to discharge from mining, pulp and paper industries, incineration of municipal and medical wastes and emissions from coal-fired power plants.

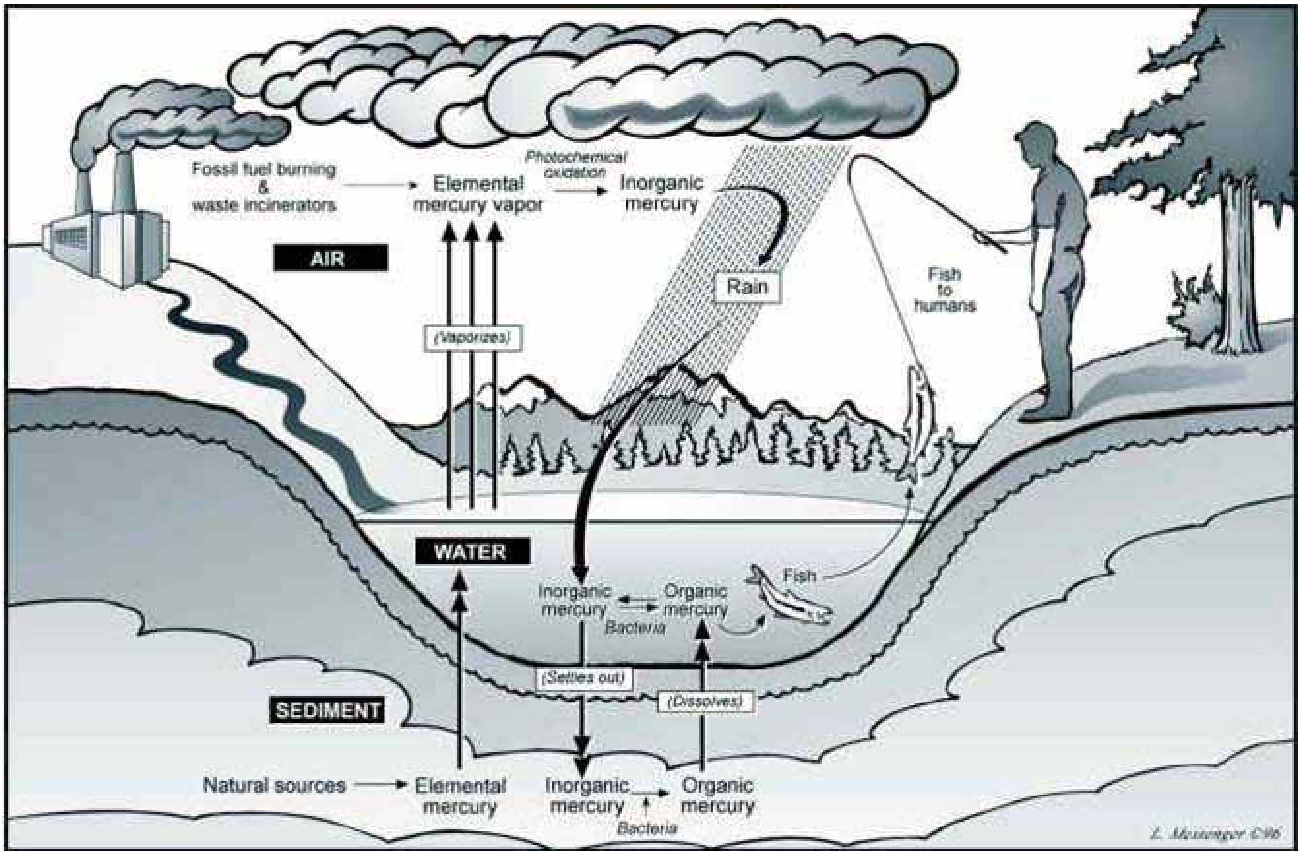
The study is based on the Level-1 Toolkit for Identification and Quantification of Mercury Releases provided by UNEP, which uses a spreadsheet with default input factors/ distribution factors, and provides a general overview of the mercury inventory.

Evident in the results of the UNEP toolkit inventory are the significant contributions of the mercury use in artisanal and small-scale gold mining (ASGM) operations, the release of mercury as a by-product in the combustion of coal for power generation, and the application of mercury in a wide array of industries such as cement, lime, pulp and paper production, measuring devices, electric and electronic equipment, etc. [9]

MAIN SOURCE CATEGORY	TOTAL HG OUTPUT (KG HG/YEAR)						
	Air	Water	Land	Impurity in products	General waste	Treatment disposal	TOTAL
Extraction and use of fuels/ energy sources	31,886	0	0	0	53.90		31,940
Primary (virgin) metal production	39,507	13,171	13,197	2,610	0	2,610	71,095
Production of other minerals and materials with Hg impurities	241	0	0	241	0	0	482
Intentional use of Hg in industrial processes	105	11	200	53	0	158	527
Consumer products with intentional use of Hg	943	20	1,120	0	1,082	0	3,165
Other intentional product/ process use	7,064	1,331	1,326	266	17,179	532	27,698
Production of recycled metals (secondary) metal production	0	0	0	0	0	0	0
Waste incineration	0	0	0	0	0	0	0
Waste deposition/ landfilling and waste water treatment	48	1,161	595	0	0	0	1,804
Crematoria and cemeteries	38	0	344	0	0	0	382
TOTAL	**78,628**	**15,694**	**16,782**	**3,170**	**18,314**	**3,300**	**137,093**

Artisanal and small-scale gold mining	- Elemental mercury is used in the process of gold extraction through amalgamation
Medicine and medical devices 	- Used in thermometers and sphygmomanometers - Used as a preservative in vaccines (*thiomersal/ thimerosal*) - Used as a topical antiseptic for minor cuts and scrapes (merbromin or mercurochrome) - Used as a chief component (~50%) of dental amalgam or silver fillings [10]
Laboratory devices 	- Used in thermometers and barometers, especially those used to measure high temperatures - Found in liquid mirror telescopes
Lighting, electric and electronic gadgets 	- Used in fluorescent lighting, mercury-vapor lamps, “neon-sign” type advertising and fluorescent lamps - Can be used in germicidal lamps, and in skin tanners - Present in electric and electronic products with lamps such as camcorders, laptops, LCD TVs, scanners, LCD projectors, among many others
Cosmetics	- Used as a preservative in mascara (thiomersal/ thimerosal) [11]
Paint	- As a high-grade pigment (mercuric sulfide or vermillion)

1.5 IMPACTS TO THE ENVIRONMENT



Mercury in the environment is constantly cycled and recycled through a biogeochemical process. The cycle has 6 major steps [12]:

1. Degassing mercury from rocks, soils and surface waters, or emissions from volcanoes and human activities;
2. Movement in gaseous form through the atmosphere;
3. Deposition of mercury on land and surface waters;
4. Conversion of the element into insoluble mercuric sulphide;
5. Precipitation or bioconversion into more volatile forms or soluble forms such as methylmercury; and
6. Re-entry into the atmosphere or bioaccumulation in food chains.

Both natural and human activities release mercury vapor (Hg(0)) into the atmosphere. Once in the atmosphere, mercury vapor can circulate for years and is widely dispersed. This airborne mercury can fall to the ground in raindrops, dust, or simply due to gravity known as *dry deposition*. Once in soil, the mercury accumulates until a physical event causes it to be released again, as the case with forest fires. In water, inorganic mercury have two end results [13]:

1. It can be converted into insoluble mercury sulfide which settles out of the water and into the sediment; or,
2. It can be converted by bacteria that process sulfate into methylmercury. The conversion of inorganic mercury to methylmercury is important because the latter is more toxic than the former, and organisms require a long time to eliminate methylmercury, which leads to bioaccumulation.

Methylmercury accumulates in fish at levels that may harm the fish and other animals that eat them. The amount of methylmercury in different water bodies is influenced by a number of factors: the amount of mercury deposited from the atmosphere, local non-air releases of mercury, naturally-occurring mercury in soils, the physical, biological and chemical properties of different water bodies and the age, size and types of food the fish eats [14]. This explains why fish from lakes with similar local sources of methylmercury can have significantly different methylmercury concentrations.

Birds and mammals that eat fish are more exposed to methylmercury than any other animals in water ecosystems. Similarly, predators that consume fish-eating animals are also at-risk. According to the United States Environmental Protection Agency (US EPA), some highly-exposed wildlife species are harmed by methylmercury [15]. The effects include muscle and nervous disorders, reduced or altered mating habits, and the abilities to reproduce, raise offspring, catch food and avoid predators have been demonstrated to affect individual animal viability and overall population stability. Moreover, research shows that the endocrine system of fish, which plays an important role in fish development and reproduction may be altered by methylmercury exposure.

1.6 IMPACTS TO HUMAN HEALTH [16]

There are a number of factors that determine whether an exposure to a specific form of mercury will harm a person's health. Trace amounts of methylmercury is present in tissues of almost everyone, a reflection of methylmercury's widespread presence in the environment and people's exposure through the consumption of fish and shellfish. People may be exposed to mercury in any of its forms under different circumstances. However, the factors that determine the severity of the health impacts include:

- Chemical form of mercury
- Dose
- Age of the person exposed (the fetus being the most susceptible)
- Duration of exposure
- Route of exposure (through inhalation and ingestion)
- Health status of the person exposed

The table below summarizes the health impacts caused by the three forms of mercury, as well as their routes and/or sources of exposure:

FORM OF MERCURY	SOURCE/S OF EXPOSURE	ROUTES OF EXPOSURE	IMPACTS TO HUMAN HEALTH
Elemental mercury	Mercury released from: - (broken) thermometers - (broken) sphygmomanometers - (improperly disposed) light switches - (improperly disposed) batteries - preparation of tooth fillings Laboratory-grade mercury Mercury used in artisanal and small-scale gold mining (ASGM)	Inhalation of vapor leading to absorption in the lungs	Symptoms - Tremors - Emotional changes (e.g. mood swings, irritability, nervousness, excessive shyness) - Insomnia - Neuromuscular changes (weakness, muscle atrophy, twitching) - Headaches - Disturbances in sensations - Changes in nerve responses - Performance deficits on tests of cognitive function High exposure may lead to kidney effects, respiratory failure and death
Inorganic mercury	Some types of: - Cosmetics - Skin lightening creams - Antiseptic creams - Chemical reagents	Contact with skin Ingestion	Symptoms of high exposures: - Skin rashes and dermatitis - Mood swings - Memory loss - Mental disturbances - Muscle weakness May result in damage to the gastrointestinal tract, the nervous system and the kidneys
Organic mercury	Contaminated fish and shellfish	Ingestion	Symptoms: - Impairment of the peripheral vision - Disturbances in sensations ("*pins and needles*" feelings usually in the hands, feet and around the mouth - Lack of coordination of movements - Impairment of speech, hearing and walking - Muscle weakness For fetuses, infants and children, the primary effect is impaired neurological development. Impacts on cognitive thinking, memory, attention, language and fine motor and visual spatial skills have been seen in children exposed to methylmercury in the womb.

CHAPTER II: DEVELOPMENT OF A SAMPLING AND ANALYSIS PLAN (SAP)

Monitoring mercury contamination in the environment involves conducting periodic sampling activities to determine the spatial and temporal spread of the substance, considering the identified pollution source. Though the definitions of sampling and monitoring are different, these terms are often used interchangeably. In this case, developing a sampling and analysis plan (SAP) for mercury monitoring implies that the plan will be implemented multiple times within specific time intervals.

A SAP is the systematic and rational integration of the technical and quality aspects of a sampling project, which encompasses the planning, implementation and assessment stages. [18] The main objective of SAP is to provide a project-specific "blueprint" in obtaining the type and quality of environmental data for a specific decision or use. For example, determining mercury concentrations in fishes to obtain basis for health advisories will have a different blueprint compared to investigating the impacts of the occupational exposure of dentists when doing dental amalgam procedures. Thus, SAP documents how sampling principles are applied to an environmental data operation.

The SAP template that will be presented in this chapter is based on the template provided for by the US Environmental Protection Agency (US EPA), with additional guidelines from the Agency for Toxic Substances and Diseases Registry (ATSDR) and Arkansas Department of Environmental Quality (ADEQ), and illustrative examples from the experiences in the field of BAN Toxics (BT) [19, 20, 21]. It is usually accompanied by a Quality Assurance Project Plan (QAPP) and Health and Safety Plans (HASP). Templates for both documents can be acquired through the websites of said sources.

2.1 COMPONENTS OF THE SAP

The SAP is composed of standardized, recognizable elements covering the entire project from planning, through implementation, to assessment. These elements are presented in that order and have been arranged for convenience into eight general groups.

2.1.1 PROJECT MANAGEMENT

This section enumerates the specific individuals and organizations that are involved in the project, together with their roles and responsibilities. Ideally, a concise organizational chart showing the relationships and the lines of communication among the project proponents should be provided. This chart should also identify any subcontractor's relationship relevant to the environmental data operations, including the laboratories and couriers providing analytical and delivery services, respectively.

2.1.2 BASELINE INFORMATION

Baseline information is needed to provide rationale on the specificity of the sampling or monitoring activity to be conducted. Pertinent [baseline data] site information may be gathered by gaining a basic understanding of the site, identifying data needs and sources, conducting a site visit, communicating with community members and other stakeholders, critically reviewing site documentation, identifying data gaps and compiling and organizing relevant data to support the monitoring. The table below enumerates the checklist of information needed to be included in the SAP:

INFORMATION SCOPE	CHECKLIST
SITE BACKGROUND INFORMATION Includes site operations and history, physical environment, relevant regulatory actions, area land use and natural resources, tribal resource uses and demographics	1. Site description - Site name(s) and address, include coordinates - Site boundaries - Site maps— current and historical (e.g., site plans, aerial photographs, topographical maps), photographs that depict site conditions, areas of contamination, proximity to populated areas, and site use - Physical hazards 2. Site operations and history - Current and past site-related activities (dates of operation, process description, significant events, and estimated number of people involved). - Current and past mercury waste treatment, storage and disposal practices - Current and past site use (industrial, military, energy facility, landfill, surface impoundment) 3. Regulatory history and activities - Site investigation results - Permit and compliance information - Site remedial activities (past, current and future) and actions taken to address contaminant releases - Types of institutional controls planned or in place 4. Land use and natural resources information - Types of barriers or signs to prevent public access - Residential, commercial, and industrial land use on or near the site, including schools. - Estimated frequency of recreational activities on or near the site - Children's play areas on or near the site, both designated playgrounds and informal play areas - Planned or proposed future land use or development - Location and purveyors of public water supplies (groundwater and surface water, including number of users) - Location of nearby private drinking water wells - Surface water uses downstream of the site - Drainage systems on and in the vicinity of the site - Agriculture, aquaculture, animal husbandry, hunting, fishing and tribal activities near the site 5. Demographic information - Types, sizes, locations and levels of activities of the population residing on or near the site (worker, residential, recreational) - Indicators of sensitive populations in the vicinity of the site (e.g., schools, nurseries, hospitals, retirement homes) - Ethnic identity, age, gender distribution, and socioeconomic status of potentially-affected population

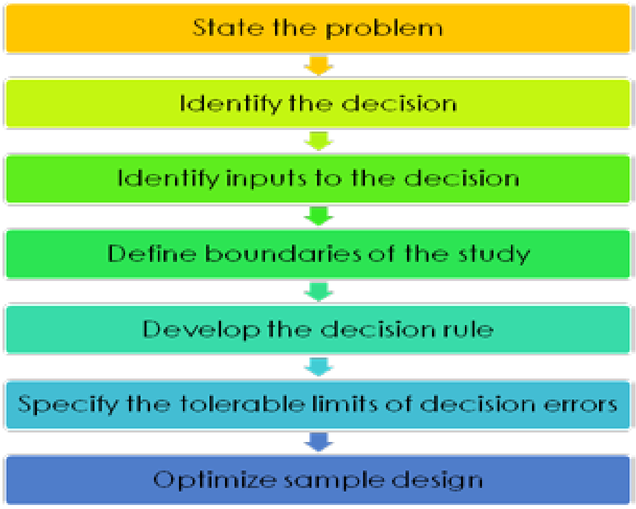
COMMUNITY HEALTH CONCERNS Includes the nature of the concerns and the populations affected and other community-supplied information, such as surveys	1. Records of health and environmental complaints by the public about the site (e.g., petition letters, public meetings, and public availability sessions) 2. Logs of actions taken by local or national agencies at or near the site in response to health concerns, complaints, or community issues 3. Information from the community, gathered during meetings or health studies 4. Environmental justice, tribal member concerns, or cultural issues
ENVIRONMENTAL CONTAMINATION INFORMATION Includes chemical data, as well as documentation, where possible, on the quality and reliability of the data	1. Summary of current and historical sampling data for all media 2. List of other hazardous substances analysed for, tested for and not found (data gap analysis), and detected (by medium) 3. Range of detected concentrations, date and location of maximum concentration 4. Sampling and analytical methods used, including detection limits 5. Quality assurance (QA) and/or quality control (QC) documentation
EXPOSURE PATHWAY INFORMATION Includes the information on how people come in contact with the contamination	1. Contaminant sources (e.g., landfills, drums, spills, effluents, air emissions from operations) 2. Description of physical barriers to prevent pollutant transport (e.g., pollution control equipment, point of entry treatment systems on drinking water supplies) 3. Topography, geology and hydrogeology information 4. Description of upstream (surface water) or nearby off-site activities that may contribute to contamination 5. Affected medium 6. Exposure point (e.g. drinking water supplies, residences, recreational areas, workplace) 7. Exposure route
SUBSTANCE-SPECIFIC INFORMATION Includes the chemical and physical properties that may affect the substance's (mercury) fate in the environment or within the human body	1. Information on chemical and physical properties 2. Toxicologic and epidemiologic data 3. Biologic and physiologic data
HEALTH EFFECTS DATA Includes the toxicologic, epidemiologic, medical and health outcome data	1. Relevant health outcome databases (e.g. morbidity/ mortality data, cancer incidence, birth defects data) 2. Any site-specific community health records and/or health studies

Site-specific circumstances will drive the amount of information that may be available. At some sites, a diverse range of documentation is available, while environmental and health data may be limited in others. However, it must be emphasized that the more specific the knowledge about the site and its potential hazards is, the more accurate and definitive the conclusions will be.

2.1.3 DATA QUALITY OBJECTIVES (DQOS) [22]

The DQO process is a seven-step planning approach to develop sampling designs for data collection activities that support decision making. The DQO process is an application of the scientific method, which involves designing and experiment (sampling and analysis processes) to support the hypothesis (decision) developed to answer a problem. DQOs are qualitative and quantitative statements that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decision-making.

THE SEVEN STEPS OF THE DQO PROCESS



The seven steps of the DQO process are discussed below:

1. *State the problem*. The problem is the situation that needs to be investigated or investigated further. It is developed at the beginning of site characterization using known information about the site, such as the location of known areas of elevated mercury or potential contaminant sources, types of contaminants expected, types of media potentially contaminated (e.g., soil, surface water, air), potential migration pathways, and potential human and ecological targets or receptors. The output from this step may be in the form of a simple statement that describes the

contamination problem or potential contamination problem that may present a threat or unacceptable risk to human health and the environment.

2. *Identify the decision.* Identifying the decision entails stating the possible decision(s) or hypothesis that will address the problem. For example, a decision may be made to determine whether or not concentrations of contaminants are present above the mercury advisory level or above average background concentrations.
3. *Identify inputs to the decision*. This step identifies the information that is needed to support the decision(s) identified in Step Two. Much like a literature review, the type of information that may be required will depend on the site and the information available. The output from this step is a list of information inputs required to resolve the decision statement.
4. *Define the boundaries of the study*. This step defines the spatial (physical and geographical), temporal (time period), demographic and regulatory boundaries for the investigation. The scope of investigation encompasses the area(s) and depth to be investigated, the media to be investigated (e.g., surface soil, air, biota, surface water or sediment), the timeframe of the investigation, and the potential population (human, plant, animal) that could be affected. Moreover, defining the scope of the SAP involves considering the practical constraints that could interfere with the investigation. For instance, locations for sediment sampling in an ASGM community can be limited by the ease of access to the site. Thus, the boundaries of the study may either expand or be reduced as more information about the site is obtained.
5. *Develop a decision rule.* The decision rule is a logical "if… then" statement that describes and serves as a guideline in creating interventions in response to the findings of the investigation. The rule is commonly applied to the necessary actions to be taken if standards or action levels are found to be extensive.
6. *Specify the tolerable limits on decision errors*. This step establishes the degree of uncertainty (decision errors) that is acceptable to the decision makers because it is impossible to sample and investigate an entire medium. Collecting samples and assigning analytical process to be

used are critical in ensuring that the results are deemed representative of the concerned medium. For instance, if 3, 100 mL water surface represents a 10-hectare lake and the water samples collected has mercury concentrations exceeding an action level, the entire area represented by the samples will be considered contaminated. Thus, the more samples that are collected, the more likely the concentrations recorded can be used to accurately represent conditions in the area and the likelihood of an incorrect decision is decreased. To determine the limit of uncertainty acceptable, factors such as the substance's risks to human health and the environment and the potential remediation cost can be used.

7. *Optimize sample design*. Improve sample design based on the target problem and scope of the study.

ILLUSTRATIVE EXAMPLE: BT DQO FOR AN ASGM SITE	
1. State the Problem	The monitoring activity aims to check whether there is decline in mercury levels in ambient air in the project site, as a function of the decrease in use of mercury in ASGM operations. A reduction in mercury levels will indicate the success of the interventions introduced.
2. Identify the decision	Decision statement: Mapping of sampling points versus suspected emissions source will determine whether the particular ASGM operation continues to use mercury. Alternative actions: Extended sampling hours will be organized to pinpoint sources of emission of releases, in case the decision stated above fails.
3. Define the boundaries of the study	Sample population: The study will be conducted within the areas of which 5 percent of total ASGM operations in the municipality are conducted. Spatial boundaries: 10 sampling points downwind of each ASGM operation will be chosen Sampling time frame: Sampling will be conducted for 5 days (1 ASGM operation per day), starting from 12 NN to 6 PM. Time stamps per sampling point will be the same for all ASGM operations Practical constraints for collecting data: i.e., Weather changes, distance of ASGM operations from each other.
4. Develop a decision rule	Decision rule: ASGM operations that are found to have mercury levels beyond the US EPA standards will be put under probation of the Provincial Environment and Natural Resources Office (PENRO).

2.1.4 FIELD ASSESSMENT/ SAMPLING METHODOLOGY

This section contains the bulk content of the plan and it enumerates the sampling procedures needed to evaluate the extent of environmental contamination in the project site. The environmental sampling data indicates the levels of contaminants in the water, air, soil and food chain. An in-depth discussion on environmental sampling in different mediums can be found in the next chapter.

Generally, this section includes:

- Identified areas of concern, or the proposed sampling locations illustrated by a lay-out adequately depicting the site;
- Field instrumentation, or the equipment to be used;
- Sampling procedures, which include the field materials and equipment that will be used in the collection of all media samples. The preparation of the samples will be dependent on the analytical procedure to be utilized. It is important to pre-identify and contact the laboratory with whom the organization/proponents will be working with to know sample requirements for the analysis, such as the amount of sample material that needs to be submitted, type of container, preservation method and allowable holding time. These information should be presented in a table format:

TABLE 3
CONTAINERS, PRESERVATIVES AND HOLDING TIMES FOR MEDIA SAMPLES

Analysis	Matrix	Analytical Method	Sample Container Size/ Type	Preservation	Holding Time

REMINDER

While most analytical methods only need a certain amount of sample material, some laboratories require the submission of samples with amounts greater than what is required. For example, analysis of mercury concentration in soils using cold vapour atomic absorption spectrometry (CVAAS) can be undertaken using 1 g of dried soil sample. However, a laboratory can require as much as 10 g of dried sample per replicate.

- Quality assurance/ quality control (QA/QC) measures should also be specified. As a general rule, 10 percent of samples should be QC samples, such as [23]:
    - Field blanks. These are "clean" samples produced in the field that are used to detect analytical problems which occurred during the duration of the investigation (sampling, transport, and laboratory analysis). For instance, a field blank for water sampling can be created by taking clean sampling containers with distilled or deionized water to the sampling site. Except for the type of water in these containers, the field blanks and all site-collected samples will be treated and handled in the same manner.
    - Equipment or rinsate blanks. Also considered as "clean" samples, these are used to check the cleanliness of sample collection equipment. In a water sampling scenario, a sample of distilled water will be collected in a sample container using the regular collection equipment used with the actual water samples. This blank will be analysed as a sample and should not register any readings in the equipment.
    - Split samples. Done after the sampling activity, one sample will be divided equally into two or more sample containers and sent to different analysts or laboratories. This QC sample is used to measure precision of the study.
    - Replicate samples. These are obtained when two or more samples are taken from the same site, at the same time, using the same method. However, these are independently analyzed in the same manner.
    - Spiked samples. Used to measure accuracy, these samples contain a known concentration of the substance for analysis. If done in the field, the results reflect the effects of preservation, shipping, laboratory preparation, and analysis.
- Equipment decontamination procedures.

2.1.5 SAMPLE DOCUMENTATION AND SHIPMENT

Record keeping is as important as the actual data collection in any sampling activity. This includes not only noting the results of the analysis but also the procedures and events encountered in the field. Information to be maintained, at a minimum, is provided in the table below, together with several examples of record-keeping procedures:

DOCUMENTATION TOOL	MINIMUM INFORMATION
FIELD LOGBOOKS Should be used to document where, when, how and from whom any vital project information was obtained. Logbook entries should be complete and accurate enough to allow reconstruction of field activities. All entries should be legible, written in blue or black ink and signed by the individual making the entries. Only factual and objective language should be used	- Sample location and description - Site or sampling area sketch showing sample location and measured distances - Sampler's name(s) - Date and time of each sample collection - Designation of sample as composite or grab - Type of sample (e.g., soil, sediment, or water) - Type of sampling equipment used to collect each sample - Field instrument readings and calibrations - Field observations and details related to analysis or integrity of samples (e.g., weather conditions, noticeable odors, colors) - Sample preservations - Lot numbers of sample containers, sample identification numbers and any explanatory codes, and chain-of-custody form numbers - Shipping arrangements (overnight air bill number) - Name(s) of recipient laboratory(ies) In addition to the sampling information listed above, the following specific information will also be recorded in the field logbook for each day of sampling - Tem members and their responsibilities; - Time of arrival/ entry on site and time of site departure - Other personnel on site - Summary of any site meetings or discussions with contractors, agency personnel, and site personnel - Deviations from sampling plans and site safety plans - Changes in personnel and responsibilities with reasons for the changes - Levels of safety protection
PHOTOGRAPHS Will be taken at the sampling locations and at other areas of interest on site or sampling area. Photographs will serve to verify information entered in the field logbook.	For each photograph taken, the following information will be written in the field logbook or recorded in a separate field photography log: - Time, date, location, direction and weather conditions - Description of the subject photographed - Name of the person taking the photograph and name of the person witnessing the photograph.
LABELING All samples collected will be labeled in a clear and precise way for proper identification in the field and for tracking in the laboratory. The samples will be pre-assigned, identifiable and unique numbers	- Station location - Date of location - Analytical parameter(s) - Method of preservation, if applicable
SAMPLE CHAIN-OF-CUSTODY FORMS AND CUSTODY SEALS Used to document sample collection and shipment to laboratories for analysis	A sample is considered to be in someone's custody if it is either in someone's physical possession, in someone's view, locked up or kept in a secured area that is restricted to authorize personnel. - Date, time and airbill number - Type of shipping container used - History of custody of the samples, from collection to analysis, with dated signatures and seals

2.1.6 INVESTIGATION-DERIVED WASTE (IDW)

Sampling activities may result in the production of waste materials that may pose a risk not only to the health of the fieldworkers, but also to the health and the environment of the community with which the sampling activity is being conducted. Thus, procedures on the management of these investigation-derived wastes must be included in the SAP. The table below summarizes some of the different types of IDWs, their generation processes, as well as the management options as prescribed by the US EPA [24]:

TYPE OF IDW	GENERATION PROCESSES	MANAGEMENT OPTIONS
Soil	- Well/ test pit installation - Borehole drilling - Soil sampling	- Return to boring, pit or source immediately after generation - Spread around boring, pit or source within the area of contamination (AOC) - Send to on-site or offsite treatment/ disposal unit (TDU) - Store for future treatment and/or disposal
Sludges/ sediment	- Sludge pit/ sediment sampling	- Return to boring, pit, or source immediately after generation - Send to on-site or offsite TDU - Store for future treatment and/or disposal
Aqueous liquids (groundwater, surface water, drilling fluids, other wastewaters)	- Well installation/ development - Well purging during sampling - Groundwater discharge during pump tests - Surface water sampling	- Discharge to surface water - Pour onto ground close to well (non-hazardous waste) - Send to on-site or offsite TDU - Store for future treatment and/or disposal - Send to publicly-owned treatment works
Disposable PPEs	- Sampling procedures or other on-site activities	- Send to on-site or offsite TDU - Store for future treatment and/or disposal - Place in on-site industrial dumpster

2.1.7 Reporting

A reporting system for both internal and external systems must be in place to provide more contexts to the investigation. A report should include all analytical data and sampling locations that can be rendered in a visual and/ or graphical formats, as well as the conclusions and recommendations identified by the proponents. This should be submitted within the timeframes agreed by the proponent(s) and its (their) partner(s).

ILLUSTRATIVE EXAMPLE

Insert BT MeMo report template

2.1.8 SCHEDULE OF IMPLEMENTATION

This section outlines the anticipated time schedule for operations related to the SAP activities at the site. Information regarding this section may be presented in a table format:

TABLE 4
ESTIMATED TASK-BASED TIME SCHEDULE

Tasks	Start Date	End Date	Duration (days)
Task 1:			
Task 2:			
Task 3:			
Etc.			

2.2 EVALUATING ENVIRONMENTAL SAMPLING SCOPE [25]

As highlighted in the DQO process, the determination of whether the environmental sampling data collected from the field is sufficient to provide a picture of the extent of mercury contamination in the environment is an important component of the mercury monitoring process. Since the environmental sampling data is collected to elucidate the extent of exposure, or exposure assessment in a target project site, the two questions below are critical in evaluating the sampling scope of the study:

- Are the collected or measured data of sufficient quality and quantity to evaluate the exposure pathways?; and
- If critical data gaps are identified, how should they be filled?

Thus, all defined aspects of the data collection process must be assessed using the PARCCS (precision, accuracy, representativeness, completeness, comparability and sensibility) tool, which considers the expected variability of natural systems. For example, temperature, flow, sunlight and other factors are never constant in the field and thus may affect systems and the living components that inhabit them.

Moreover, variability is inherent in the monitoring process itself, such as the differences brought about by the monitoring efforts, types of equipment used, among others. Thus, measuring for PARCCS helps in evaluating the sources of variability and error and thereby increases confidence in the data.

2.2.1 PRECISION

Precision provides information on how consistent and reproducible the field and laboratory methods are by computing how close the measurements are to each other. It provides information on how consistent and reproducible the field and laboratory methods are by showing how close the measurements are to each other.

Typically, precision is monitored through the use of replicate samples or measurements, discussed in the last chapter. These replicate samples are samples that were taken from the same place at approximately the sample time. To compute for the range of variation between multiple replicate samples, identifying the standard deviation (SD) can be used. Another method for computing for precision is the determination of the relative standard deviation (RSD), or coefficient of variation. The RSD expresses the standard of deviation as a percentage, which makes it generally easier to understand. It must be noted that the smaller the relative standard deviation is, the more precise is the measurement.

ILLUSTRATIVE EXAMPLE

A study was conducted to determine the concentration of mercury in the sediments found in the riparian area along a river downwind of an ASGM operation. The ASGM operation has been in existence for almost 10 years, and tailing dusts are blown by the north and northeastern winds. The investigator took sediment samples in 10 sampling points with 50-meter intervals from each other. Three replicates for each sampling point were taken. Subsequent analysis of the samples showed the following results. Compute for the SD and RSD using the formula given below. The first answer for the first sampling point is already provided for.

SAMPLING POINT	DISTANCE FROM POLLUTION SOURCE, M	MERCURY CONCENTRATION, PPM				SD	RSD
		1	2	3	AVERAGE		
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
AVERAGE							

To determine the SD (s), use the following formula:

$$S = \sqrt{\frac{\Sigma(X - \overline{X})^2}{N}}$$

where S = the standard deviation of a sample,
Σ means "sum of,"
X = each value in the data set,
$\overline{X}$ = mean of all values in the data set,
N = number of values in the data set.

To determine the RSD, use the following formula:

$$\text{RSD}(\%) = \frac{(100)(s)}{\overline{X}}$$

What are the average SD and RSD? If the SAP guidelines indicate an 85 percent RSD, will the samples and sampling method usable for decision-making?

If there are only two replicate samples, the relative percent difference (RPD) of the two samples can be used to determine precision. To determine the RPD, use the following formula:

$$\boxed{percent\ \ difference = \frac{\left|measured_1 - measured_2\right|}{\left(\dfrac{measured_1 + measured_2}{2}\right)} \times 100\%}$$

Similar to SD and RSD, the smaller the relative percent different, the more precise are the measurements.

2.2.2 ACCURACY

The term “accuracy” is at times used interchangeably with “precision”, however, these two characteristics refer to different things. While the latter is focused on determining the extent of agreement between the samples collected under similar conditions, the former aims to know if the sample results actually reflect the true or expected value. Thus, accuracy is a measure of confidence in measurement. The smaller the difference between the measurement of a parameter and its true or expected value, the more accurate the measurement is. The more precise or reproducible result is, the more reliable or accurate the result is.

Measuring accuracy can be determined by comparing a sample that has a known value, such as a standard reference material or a performance evaluation sample, to the investigator’s measurement of that sample. For example, if there are concerns regarding other components of the sample matrix (e.g. soil or sludge) that may cause interference with the analysis of a parameter, addition of a known concentration of the parameter to a portion of the sample can be done. The difference between the original measurement of the parameter in the sample and the measurement of the spiked sample should equal (or be close to) the added amount. The difference will reflect the ability to obtain accurate measurement.

low accuracy
but high precision

Higher accuracy
but low precision

High accuracy and
high precision

ILLUSTRATIVE EXAMPLE

CVAAS was used in determining the mercury concentrations in the soil samples collected in the study described in Section 2.2.1. To measure the accuracy of the samples, a spiked sample (Sample 11) with the known concentration of 300 ppm of mercury was added in the samples analysed. The results of the laboratory analyses are presented in the graph below:

Based on the graph, how accurate is the analysis? *(Key: how close is the result of the analysis to the known concentration of the spiked sample?)* Compute for the percent difference between the sample result and the expected value using the result in the spiked samples. The answer for the first row is provided below:

SAMPLING POINT	**DISTANCE FROM POLLUTION SOURCE, M**	**MERCURY CONCENTRATION, PPM**				**SD**	**RSD**
		1	**2**	**3**	**AVERAGE**		
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
AVERAGE							

It must be noted, however, that there are parameters that have no standard reference or performance evaluation. Examples of these are the depth of the flowing rivers or abundance of invertebrates in the area. In these cases, results of a previous sampling study can be used as the reference value to which other studies on the same site will be compared to. If there were no sampling studies available, the current sampling study will be used.

2.2.3 REPRESENTATIVENESS

Representativeness is the extent to which measurements depict the true environmental conditions or populations that are being evaluated. Given the variability in natural systems, no investigations can fully review a site and collect sampling data that characterize all possible exposures. Typically, the data available for a site characterizes the levels of contamination at very specific locations and for very specific time frames. For example, mercury levels measured from urine samples of 5 ASGM miners do not necessarily mean that all of the 1000 workers will have the same level of exposure. Factors such as differing work responsibilities, dietary consumption, and length of employment will influence the degree of exposure of individuals.

The challenge in determining how representative a measured level of contamination is lies in considering conditions in other locations and other time frames. Though assessing the representativeness of data can be considered a subjective task, a technical understanding of the fate and transport of the environmental contaminant is useful. The following questions, and associated examples, serve as a guide in determining whether the environmental sampling data, from specific locations and times, can be assumed to be representative of exposure point concentrations which may be at other locations and other times. These questions should be viewed as examples of thought processes to be undertaken when interpreting environmental sampling data and not a complete guide for evaluating data representativeness [34]:

ILLUSTRATIVE EXAMPLES:

- Were enough samples taken to understand the spatial extent of potential exposure?
  - At sights with groundwater contamination, the investigator should ask whether the number and placement of monitoring wells are sufficient for characterizing the spatial extent of contamination to which people are most likely exposed and whether an adequate number of residential and municipal water supply wells have been tested.
- How are the contaminants distributed? Are there “hotspots”?
  - Mercury is used in the amalgamation stage of the ASGM process, where the gold-mercury amalgam is burned in improvised chimneys to sequester the gold. In this stage, the application of heat enables the transformation of mercury from its liquid form into vapor, thus resulting in high emission levels measured by a mercury vapor analyzer. For such sites, there is a need to examine whether sampling locations were selected specifically to identify such areas of elevated contamination.
- Were samples taken in areas most likely impacted by site contamination?
  - The nearest ambient air monitoring station to a large municipal landfill is approximately 1 kilometer downwind. Is this proximity close enough to capture the highest ground level (or breathing zone) impacts of the landfill’s emissions? Knowing that the passive releases from landfills tend to have their highest impacts closer to the source would help in such evaluations.
  - Dental institutions are typically divided into separate rooms for different fields of dentistry. In order to determine releases from the use of mercury in dental amalgam, ambient air monitoring can be conducted inside the restorative department/ section of the school/ clinic, as well as near identified exit points in the room (doors, exhaust systems, etc.).
- Are the sampling data grab samples or long-term sampling efforts?
  - At some sites, the only environmental data available are from a single sampling event, such as one water sample collected downstream from a ASGM tailings drainage. Is this one sample representative of the water quality of the area through time? It is important to remember that lone grab samples only give a “snapshot” of the overall trends in environmental contamination.
  - For example, if the objective of the study aims at knowing occupational exposures for professions that use mercury, the length of sampling time must be at least 8 hours to correspond to a typical day’s work.
- Were samples collected over time taken to understand the temporal extent of contamination?
  - For an ASGM operation that has discharged tailings in the river for over 5 years, having data for only the last 2 years may not be representative of the previous levels of pollution. Changes in the facility’s production levels and tailings treatment over the years would be important to consider.
- Is the frequency of sampling adequate to characterize the public health threat?
  - Mercury levels are often measured in ambient air as the element’s characteristic volatility dictates its most common pathway for exposure (inhalation). However, ambient air conditions are influenced by the temperature, humidity, wind direction, etc. of weather, thus resulting to the increase or decrease of values in a span of a few minutes. If ASGM operations occur within the vicinity of the community, how often/ frequent does sampling need to be conducted to characterize potentially hazardous acute exposures?
  - In the case of contamination of biota, how often do sampling and analysis of mercury (methylmercury) content in fishes be done? Since coastal resources often serve as the source of food and livelihood of the people, the frequency of sampling is relevant in undertaking interventions to address these concerns.
- Based on knowledge of the site, does the pattern of contamination make sense?
  - ASGM operations are often conducted on-site, thus, high levels of mercury in different mediums may be expected. However, if high concentrations of the substance are reported in residential areas, additional research must be conducted to understand why. In this case, knowing whether there are gold buyers (who act as smelters) are located in the area would help the evaluation.

In addition to the above concerns, there are numerous media-specific concerns for evaluating the representativeness of sampling data. This is because samples collected in some media might be representative of contamination over very small areas, while other media-specific samples might be representative of the contamination over broad ranges. These medium-related considerations will be discussed in the next chapter.

2.2.4 COMPLETENESS

While SAP indicates the targeted number of samples that needs to be collected to have a viable analysis of mercury contamination in the area, field realities often hinder data collection activities. Completeness is thus measured to know the number of samples that must be taken to be able to use the information, as compared to the number of samples that were originally proposed to be taken. Since there are many reasons why fieldworkers or investigators may not collect as many samples as planned, as a general rule, investigators should try to take more samples than what is needed.

To calculate percent completeness, divide the number of measurements considered valid by the total number of measurements originally planned to be taken, then multiply by 100. If extra samples are factored into the project, the completeness requirements can be lowered. The extra samples, in turn, increase the likelihood of more representative data.

ILLUSTRATIVE EXAMPLES

The BT team planned to collect 30 soil samples (10 sampling points multiplied by 3 replicates) in a forest adjacent to a special hazardous waste landfill. However, one of the fieldworkers fell ill and a severe storm is approaching the area only 27 samples were collected. Furthermore, of these, two samples were judged invalid because too much time elapsed between sample collection and laboratory analysis. Thus, of the 30 samples planned, only 25 were judged valid. The following formula is used to determine percent completeness (%C):

$$\%\ \text{Completeness} = \frac{\text{number of valid measurements}}{\text{total number of planned measurements}} \times 100$$

In this example, $v = 25$ and $T = 30$. %C would be 83.3 percent. Is this enough information to be useful?

2.2.5 COMPARABILITY

Comparability is the extent to which data from one study can be compared directly to the data collected by other studies. For example, in terms of monitoring with defined periodicity, data collected in 22 May 2014 can be compared to the data collected 10 years ago on the same date by other investigators.

However, it must be noted that comparability is applicable only if the sampling and analytical methods used in both studies are standardized, as well as the units of reporting and site selection procedures help ensure comparability. It is also important to keep in mind that some types of monitoring rely heavily on best professional judgment and that standard methods may not always exist.

2.2.6 SENSITIVITY

Analytical measurements are heavily dependent on the equipment's detection limits. The detection limit is described as the lowest level of a contaminant that analytical equipment can discern from the "noise" inherent to scientific measurements. When laboratories report that a contaminant was not detected in a sample, it does not mean that the contaminant was not present. Rather, it means the contaminant levels present in the samples are not sufficient enough to be reliably measured by the analytical method. Thus, the only conclusion that can be drawn is that the actual concentration is somewhere between zero and the reported detection limit (e.g. < DL). In statistical analyses of environmental sampling data, one common practice is to replace non-detect observations with surrogate concentrations of one-half the detection limit.

ILLUSTRATIVE EXAMPLE

Jerome and Lumex are two of the portable analyzers used to detect mercury vapour in ambient air. Jerome takes advantage of gold's inherent electrical conductivity and affinity for elemental mercury to calculate for the mass of mercury vapour taken from a known volume of air. Whereas, Lumex takes advantage of a light source with a known wavelength and intensity to gain an indirect measurement of how many mercury atoms were present.

Jerome	3000 ng/m3	999,000 mg/m3
Lumex	2 ng/m3	20,000 ng/m3

Additionally, some analytical equipment has specific measurement ranges. The measurement range is the range of reliable measurements of an instrument or measuring device.

ILLUSTRATIVE EXAMPLE

The Jerome 431-X mercury vapor analyzer has a measurement range of 0.003-0.999 mg/m^3. If the objective of the sampling activity requires monitoring levels lower than 3000 ng/m^3 there is a need to use another equipment or analytical method that is sensitive to lower mercury levels.

CHAPTER III:
SAMPLING PROCEDURES FOR DIFFERENT MEDIUMS (22)

The broad objective of mercury monitoring activities is to determine how widespread mercury contamination is in a particular site. This degree of contamination can be measured in a variety of medium (i.e., air, soil and sediments, water, and biota). As described in the previous chapter, gathering information from the project site is useful in optimizing the sampling procedures, as this will allow investigators to design a study that can: (1) maximize resources, and; (2) achieve the most complete review of the baseline and anthropogenic loading of mercury in various mediums.

The sampling protocols described in the following sections are based on the draft mercury source protocol prepared for the Utah Division of Solid and Hazardous Waste by TechLaw, Inc. Illustrative examples of sampling activities by BAN Toxics, as well as PARCCS assessment questions, are also presented to guide in the design and development of sampling designs.

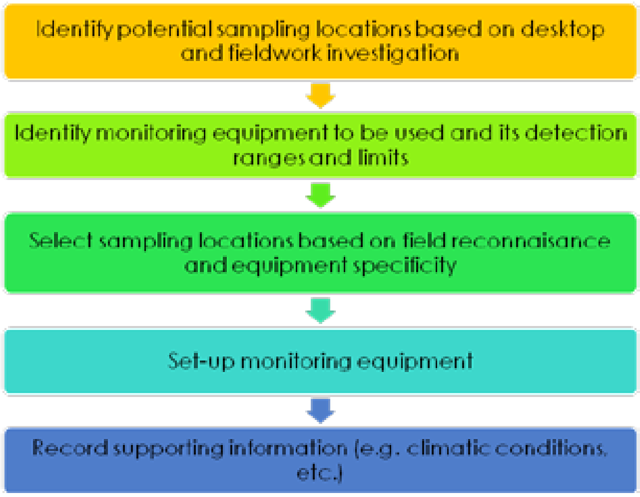
3.1 AMBIENT AIR

Monitoring mercury levels in ambient air is important since one of the main routes of exposure of mercury for humans is through inhalation. Particularly for workspace settings, monitoring through this medium will provide the necessary data for occupational exposures and the subsequent mercury intoxication diagnoses. However, conducting an air sampling program requires an understanding of the great variability that is inherent to the medium, as free-flowing air can easily diffuse in a wide range of area and is affected by climatic conditions. As such, PARCCS of the data collection process must be considered carefully in order to make well-founded decisions for interventions.

The air monitoring protocol described in the subsections of this manual will focus on the use of mercury vapour analyser equipment, specifically that of RA 915+ Lumex Mercury Vapor Analyzer. This equipment employs atomic absorption spectrometry and Zeeman effect, and has a detection limit ranging from 2 ng/m^3 to 20,000 ng/m^3. The actual procedures in using and handling the Lumex, and other related equipment, can be found in the accompanying user's manual provided by the manufacturers. These handling and usage procedures should be followed thoroughly, particularly for the calibration and maintenance of the equipment.

It must be noted that there are also other methods for sampling and analysis of mercury species in air such as wet and dry mercury deposition sampling. However, due to the complex interactions of mercury species in the atmosphere and the relatively low levels involved, these methods are often expensive. Consequently, sampling and analysis protocols are strict and laboratories with capabilities to successfully analyze low levels of mercury are limited. Alternatively, some studies were reported to show success using biological monitors (i.e., mosses and lichens, for atmospheric mercury deposition).

3.1.1 FLOW CHART FOR SAMPLING



3.1.2 SAMPLING POINTS

When conducting air monitoring, consideration should be given to suspected point sources for contamination. If there is a suspected or known point source, such as an ASGM facility employing whole ore amalgamation, air dispersion modelling or mapping of site emissions can be conducted to determine locations of sampling points. Air dispersion mapping can also help identify areas of the site where the majority of the population resides. These areas can be used as sampling points to determine exposure levels of the people.

Due to the factors which affects mercury levels in ambient air, climatic conditions and spatio-temporal characteristics should be considered. Additionally for the former, data on previous temporal durations can be collected from the local Philippine Atmospheric, Geophysical and Astronomical Services Administration (PAGASA) weather station. Collecting past information on climatic conditions can help in inferring mercury dispersion in the atmosphere.

CLIMATIC CONDITIONS	SPATIO-TEMPORAL DATA
Temperature Humidity Wind direction	GPS coordinates Altitude Time and duration of sampling

ILLUSTRATIVE EXAMPLES (OUTDOOR)

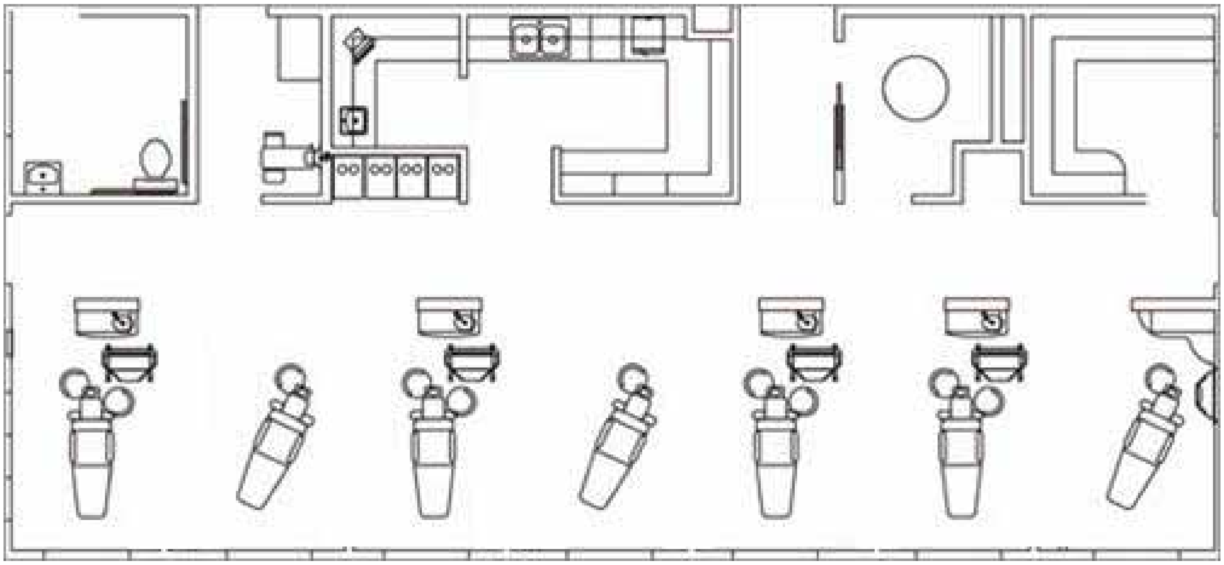
Artisanal and small-scale gold mining is one of the anthropogenic sources of mercury in the atmosphere. A gold smelting facility located in the commercial and residential center of municipality X processes gold-mercury amalgam. Residents of municipality X requested their Environment and Natural Resources Office (MENRO) to determine the extent of mercury emissions in air of the gold smelting facility. The MENRO proposed setting up 4 sampling points (north, south, east and west) located 500 meters away from the facility.

Insert map with 4 sampling points

Monitoring activity was conducted over 24 hours for 7 days, and is repeated after a 3-month interval. Concurrently, data on climatic conditions were also collected. These information are then present through a stakeholders' consultation participated by civil society organizations (CSOs), the local government unit (LGUs), peoples' organizations (POs), the owner of the gold smelting facility, and the DENR.

ILLUSTRATIVE EXAMPLE (INDOOR)

Prior to the implementation of an Administrative Order (AO) on the phasing out of dental amalgam restoration in the Philippines, a dental school that trains/ teaches dental students on dental amalgam restoration procedures is being checked for occupational exposure to mercury. This is in line with the provision of the AO which aims to change the dentistry curriculum by scrapping the practice of conducting actual dental amalgam restoration procedures to either typhodonts or live patients. The layout of the clinics in the dental school, together with its dimensions are shown below:



While actual restoration procedures are conducted in the restorative department, storage, and preparation of the amalgam material is done in other sections of the school. Given the limited financial resources and the logistical constraints, the team from the Department of Health (DOH) proposed an 8-hour monitoring activity in the school for 7 days, which will be done 3-months before the change in the dental curriculum and repeated 3-months after implementation. The 8-hour monitoring will be done in sync with the operation hours of the restorative section.

Together with the climatic conditions, data on the number of mercury-based restoration procedures during the pre-AO implementation phase will also be recorded to check if spiked mercury levels will be detected. The occupational exposure data will be presented in a graphical format contrasting mercury levels with the time of the day. The time in which restoration procedures were conducted will be highlighted.

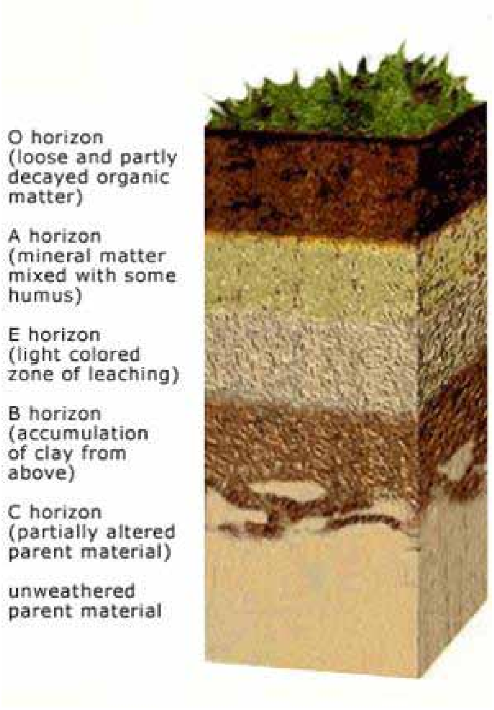
PARCCS ASSESSMENT

The number and location of sampling points can be determined by answering the following guide questions:

- What was the time span when the samples were collected (e.g. 1-hour average, 24-hour average, or longer)? How frequently were these samples collected?
- Were samples collected at locations upwind and downwind from the source?
- Was the source of concern operating at full capacity when the samples were collected?
- Were the ambient air sampling devices placed in close proximity to a source that may bias the results?
- Are stationary monitors located in areas representative of pathway exposures?
- Were the data generated by a one-time air sampling event or a long-term ambient air monitoring program?

3.2 SOIL

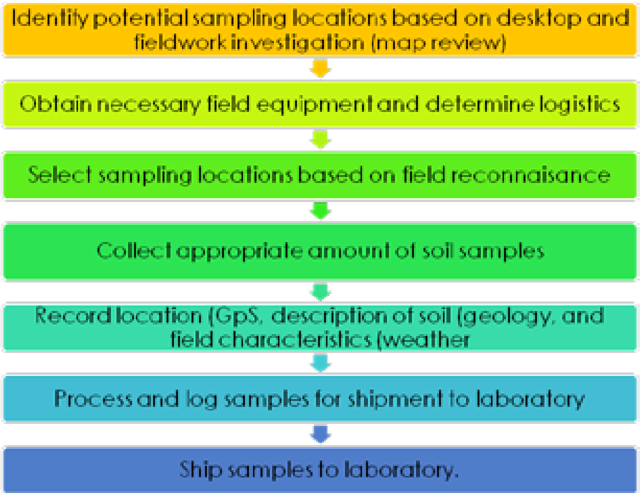
Soil will contain varying levels of naturally-occurring mercury as a product of geological processes from the uplift and weathering of mercury-containing rocks and atmospheric fall-out and deposition. While sampling soil will provide an understanding of differences in deposition of mercury between areas and allow for an assessment of ambient mercury levels in the soil, soil characterization is typically not a primary source of mercury contamination in water bodies and fish. Depending on the objectives, monitoring in this medium will make the conceptual model of mercury contamination in an area more holistic.



Soil sampling is typically mistaken for sediment sampling, as both involves the collection of land materials. However, their difference lies in the process by which they were developed. Soils are vertically weathering profiles that develop in place. They require time and a stable ground surface to develop. Sediments, on the other hand, are a collection of mineral or rock particles transported by water or wind or, most often on the mountaintop, by people. We call these transported sediments deposits. Thus, deposits of sediment are the result of movement, while soil profiles develop in the absence of movement [28]. Sediment sampling will be discussed in the next section.

A well-developed soil profile will have a sequence of zones, called horizons [29]. The O horizon is made up of loose and partly-decayed organic matter, while the A horizon is made up of mineral matter mixed with humus. These are important layers for analyses since mercury is strongly sorbed to humic materials. These two horizons are followed by the E, B and C horizons, until the unweathered bedrock or parent material is reached. Because of the presence of these distinct zones, soil sampling requires stratification of analyses using the soil horizons as categories—that is, analysis of mercury levels in the soil will be different for each horizon.

3.2.1 FLOW CHART FOR SAMPLING



3.2.2 SAMPLING POINTS

The importance of ascertaining relative soil concentrations is to identify whether there are significantly higher concentrations of mercury in soil that could represent a source of contamination for downgradient water bodies. Thus, measurements of total mercury in soil will be considered representative of the mass of total mercury that is transportable to surface water by means of physical erosion (i.e., mass wasting, runoff, and wind).

ILLUSTRATIVE EXAMPLE

Municipality E was found by the Mines and Geosciences Bureau (MGB) of the DENR as having high deposits of mercury-containing ores or cinnabar. This discovery was a result of the baseline data gathered by the bureau after a magnitude 6.3 earthquake hit the community. The residents were alarmed by this discovery since their community is near water bodies. They requested the MGB to determine the approximate size of the area by which the ore is deposited. The results of the sampling activity will serve as the basis of the land use plan of the municipality.

Three replicates of soil samples from 16 sampling points located 500 m- and 1 km- away from the site was collected. A 5-cm diameter corer is used and drilled to a depth of 10 centimeters in the ground. This depth is based on the observable length of the horizons. Formation and soil characteristics of the sample were noted, such as the length of distinct horizons/ layers, texture, color and particle size. Analyses of the soil sample included stratification between the O/A and E/B horizons, together with other soil parameters such as:

- Soil pH;
- Soil moisture;
- Humic content; and
- Mineral/ nutrient content (phosphorus, magnesium, potassium, calcium, total nitrogen, ammonium nitrogen and soluble salts).

Additionally, parameters for climatic conditions (week-long and month-long) precipitation data, temperature and humidity. The results of the study were plotted in a map which also presents the location of water bodies and residential areas in the project site. The land area of the deposit is estimated by comparing the sample results with the known natural or background concentrations of mercury in the country.

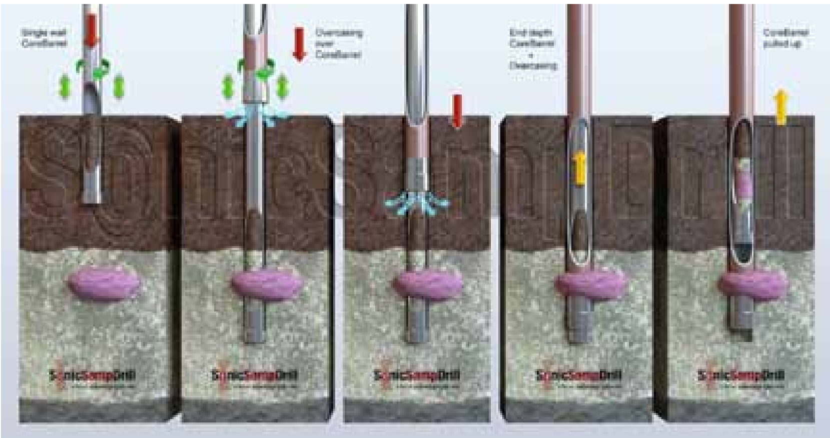
PARCCS ASSESSMENT:

The number and location of sampling points can be determined by answering the following guide questions:

- Do sampling results characterize contamination in soils of areas with different land uses (e.g., restricted access areas, roadsides, gardens, farms, residential yards, parks, playgrounds)?
- At what depths were the soils sampled? Soil less than 3 inches deep is considered surface soil, and soil deeper than 3 inches is considered subsurface soil. Soil samples representing other depths (e.g., EPA defines surface soil as 0-12 inches deep) are usable, but the depth should be noted.
- Is the type of soil described in the data? If not, you should assume soil includes any unconsolidated natural material or fill above bedrock and excludes human-generated materials such as slabs, pavements, asphalt, concrete, brick, rock, ash, or gravel.
- Were samples collected upwind and downwind of sources of air pollution—both on site and off site—and at “hot spots?” Were samples collected appropriately for identifying “hot spots”?
- Have any soil removal activities (e.g., excavation) occurred that may have changed contamination levels?
- Are the soil samples grab or composite samples?

3.2.3 SAMPLING PROCEDURE

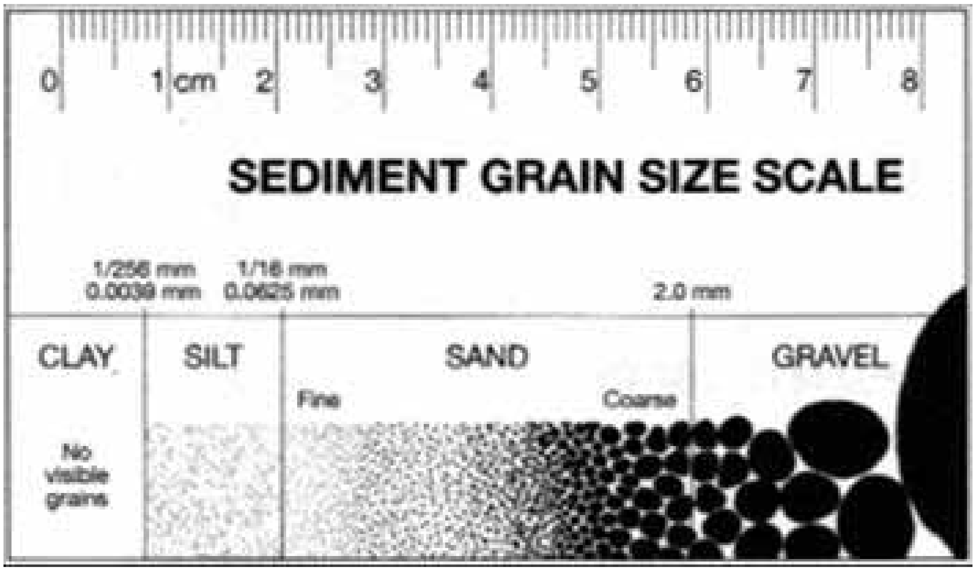
Since soil sampling is characterized by stratification, soil coring devices are typically used to ensure the differentiation of sample strata. A corer is a device which is pushed into the soil and held in place by suction pressure whilst being brought to the surface. Procedures on the use of this device can be found in the user’s manual provided by the manufacturer.



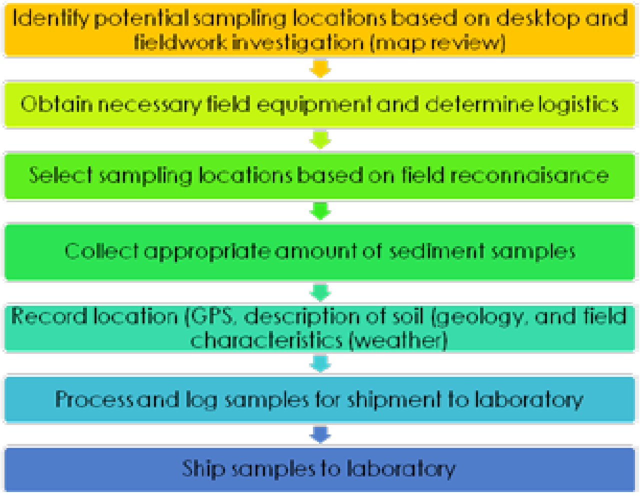
3.3 SEDIMENTS [30]

Since sediments are products of the physical movements of mineral or rock particles, sampling of sediments provide an understanding of the diffusion of mercury across a wide area encompassing several mediums. For example, windborne tailings dust can be deposited to adjacent forest soils, or downwind along riparian areas of water bodies. For the latter, the methylization process and subsequent bioavailability of mercury can be inferred.

According to a study by Grabowski, et al. (2011), the chemical and physical nature of sediments is strongly influenced by the size of the individual particles of sediment [31]. Sediments composed of sands (0.06-2.0 mm) and larger sized particles are often stable inorganic silicate minerals. They form non-consolidated deposits which have a relatively lower specific capacity (amount of interstitial water) and a more neutral surface electrical charge. Thus, they are often not associated with contaminants and are not recommended for analysis. Fine grained silts and clays (<0.06 mm), however, have a much larger specific capacity, have unbalanced electrical charges and much larger surface area to volume ratio. Therefore, are more chemically, physically and biologically interactive. Sediment sampling must be biased towards collecting these types of sediments.



3.3.1 FLOW CHART FOR SAMPLING



3.3.2 SAMPLING POINTS

Sediment sampling is effective only when over 30 percent of the collected sample contains silt and clay. Finer grained sediments are often located in still waters of the sample area in deep water, at stream margins, behind bounders and other obstructions, or at inside bends or river meanders. Particularly for sediment collection near lotic systems (such as rivers or streams), slow flow rates along stream bends provide for higher sediment accumulation. It is therefore important to conduct an initial reconnaissance of the sample area so that field limitations in the study design can be addressed prior to sample collection. If available, an initial reconnaissance should include a cursory bathymetric survey using a wading staff in shallow streams and rivers or an echosounding (sonar) depth finder for deeper waters. However, local knowledge or recent navigation charts can often provide similar information to an echo-sounding survey.

Bathymetry is the measurement of the depths of water bodies from the water surface. It's the marine equivalent to topography [32].

The most upstream or reference sediment site is collected first to reduce the possibility of contamination between sampling points. However, if the sediment sampling locations are near each other, the most downstream sample should be collected first to avoid contamination from disturbance and re-suspension of sediment due to sampling activities.

An example of a sediment sampling design is described in section 2.2.1. Additional guidelines for designing sediment sampling activity can also be derived from the PARCCS assessment tool presented in the previous section on soil sampling.

3.3.3 SAMPLING PROCEDURES

Several sampling methods can be conducted to collect sediment samples. These are summarized in the tables below:

SURFACE GRAB COLLECTION METHODS	ADVANTAGES	DISADVANTAGES
Scoops and spoons	- Inexpensive - Widely available - Non-mechanical - Very portable - Able to sample nearly every sediment type - Easy to use	- Limited sample volume - Possible loss of very fine material during retrieval - Not useable in waters greater than 4 to 5 feet
Dredges	- Relatively inexpensive - widely used and available - Standard for some sampling purposes; - Often don't need expensive equipment to operate - Come in a wide variety of sizes	- Shallow depth of penetration - Possible shock wave and loss of very fine grained surface deposits - Potential for water column contamination and nearby downcurrent sediment re-deposition - Loss of depth profile - Not appropriate for waters with current - Large materials such as twigs and stones prevent jaw closure - Possibility of diluting the toxic pore water with relatively clean surface water

STANDARD CORE COLLECTION METHODS	ADVANTAGES	DISADVANTAGES
	- Simple and inexpensive - Manufactured in a variety of materials - Can collect samples at depth - Can maintain a more representative vertical profile of the sediment stratigraphy - Create less disturbance by shock waves - Can collect more highly consolidated deposits.	- Do not work well with sandy sediments - Collect limited sample volume and very small surface area - Sometimes require expensive and bulky equipment to work in deeper waters and sediments

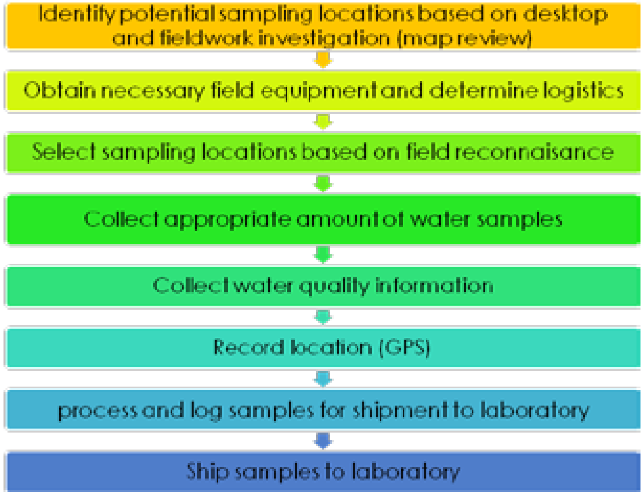
Procedures on the actual use and handling of these equipment can be found in the user's manual provided by the manufacturers. Additional parameters to be measured during sampling are:

CATEGORIES	PARAMETERS
Physical	- Particle size - Appearance, texture, odor, color
Biological/ biochemical/ chemical	- Sediment oxygen demand - Macroinvertebrate survey - Mineral content
Others	- Overlying water quality including: water temperature, water depth, dissolved oxygen, conductivity, pH, turbidity, water velocity

3.4 SURFACE WATER

The objective of sampling surface water is to quantify the mass of mercury contained in the suspended and dissolved loads of surface waters.

3.4.1 FLOW CHART FOR SAMPLING



3.4.2 SAMPLING POINTS

The guiding principle on selecting the appropriate site for sampling is to determine the location that accurately represents the intended conditions (such as time of year and flow rate or stage) of the aqueous system being studied with respect to the study objectives. In most bodies of water, a single sampling point is not adequate to represent the physical properties and distribution and abundance of chemical constituents such as mercury. Location, distribution, and number of sampling sites can affect the quality and applicability of the resulting data.

Wilde (2005) of the USGS provided the sampling sites for both lotic (flowing) and lentic (stationary) water systems described in the table below [33]:

SAMPLING IN LOTIC SYSTEMS

Refer to streams (fast or slow, intermittent, ephemeral or perennial), canals, ditches, and flumes of all sizes and shapes, or to any other surface feature in which water moves unidirectionally. All or parts of reservoirs and estuaries that flow unidirectionally are considered to be flowing water.

- Points immediately before the inflow of river or stream into a marine water body;
- Points along the main river; (a) downstream of confluence and (b) upstream of the confluence with tributaries or drainage channels that may greatly affect the water quality;
- Points in the tributaries or drainage channel immediately before the confluence with the main or a major river;
- At areas of public use for water contact recreation;
- Points along the river where there is a marked transition in topography such as where a waterfall occurs; (a) upstream of the waterfall, and (b) downstream at a point where mixing has already occurred;
- Points immediately before the inflow of the river or stream into a lake, marshes or reservoir;
- At habitat areas of sensitive species (e.g. spawning areas of important freshwater fishes);
- Variability of flow patterns caused by artificial physical structures such as dams, weirs, and wing walls must be considered in sampling site selection. These structures may influence the representative quality of the water. Samples should be taken (a) upstream of the structure and (b) downstream of the structure;
- Tributaries should be sampled as near the mouth of the tributary as possible;
- Where there are suspected point (e.g., wastewater treatment plants) and non-point pollution sources; (a) upstream of the discharge point and (b) downstream of the discharge point;
- Generally for small streams less than 20 feet wide, a sampling site should be selected where the water is well-mixed. In such cases, a single grab sample taken at mid-depth at the center of the channel is adequate to represent the entire cross-section;
- When several locations along a stream reach are to be sampled, they should be strategically located:
  - At intervals based on time-of-water-travel, not distance;
  - At the same locations if possible, when the data to be collected will be compared to a previous study;
  - Whenever a marked physical change occurs in the stream channel;
  - To isolate major discharges, as well as major tributaries.

SAMPLING IN LENTIC SYSTEMS

Refer to all sizes and shapes of lakes, reservoirs, ponds, swamps, marshes, riverine backwaters, or any other body of surface water where water generally does not move unidirectionally. All or parts of the reservoirs that do not flow unidirectionally could be considered as still water.

- Use in situ field measurements to help determine vertical and spatial distribution of sampling locations;
- Avoid areas near structures such as harbors, boat ramps, piers, fuel docks, and moored houseboats to avoid point sources of contamination, unless these structures are part of the study;
- Select sites with a record of historical data, if possible; and
- As a general rule, samples should be taken from each section of a lake which can be regarded as a homogenous water mass.

Water quality information should also be collected at each sampling point to include the following:

- Water temperature;
- Dissolved oxygen;
- Specific conductance;
- pH;
- Salinity;
- Depth of water body; and
- Flow rate (streams and rivers).

ILLUSTRATIVE EXAMPLE

The majority of the population of municipality M is composed of small-scale gold miners and their families. Each family will normally have their own ball/rod mill facilities, where they process gold ores using whole-ore amalgamation. Mine wastes from these mill facilities, suspected to contain high concentrations of mercury, are dumped in the interlinked streams that ultimately flow towards the bay. This bay also serves as a source of livelihood of the fisher folks of the community, as well as a recreational bathing ground for some of the children.

The Municipal Environment and Natural Resources Office (MENRO) wanted to know how much mercury is present in the surface water of their streams. To maximize their resources, they plotted the contributory milling stations vis-à-vis the streams. They prioritized areas that are: (1) upstream the suspected pollution source; (2) downstream the pollution source; (3) convergence of 2 or more streams; and (4) areas near the mouth of the bay. They came up with the following points for monitoring stations.

For each sampling point, the MENRO staff took 3 samples, as illustrated below:
Insert 3 sampling sub-points.

Other water quality parameters were also measured, as well as the time and location of sampling.

PARCCS ASSESSMENT

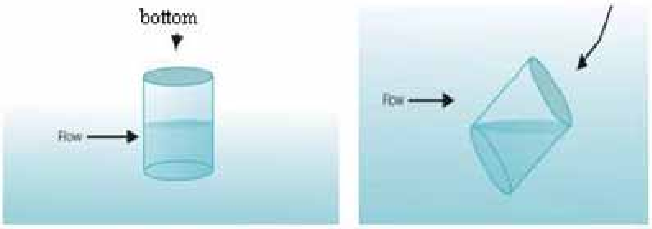
The number and location of sampling points can be determined by answering the following guide questions:

- Do surface water data include results for samples both upstream and downstream of the primary source of contamination?
- Is there information about the number of surface water samples taken at each sampling station, as well as the frequency, duration, and dates of sampling?
- How does the timing of surface water sampling compare to the timing of site releases?
- Were the samples filtered?
- Were the samples collected at locations where people have access (e.g., beaches)?

3.4.3 SAMPLING PROCEDURE

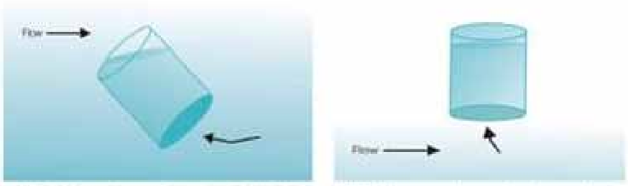
Collecting water samples can be done through both manual and automatic methods. This manual will focus on the manual method, particularly dividing the procedure based on the depth of the water body. For instance, for wadable waters, direct sampling with the sample container can be done. For mercury, a 100 ml glass is used, which have been initially prepared by rinsing it three times with tap water, once with chromic acid, three times with tap water, once with 1:1 nitric acid and then three times with distilled water (in that order). Note however that there are restrictions on the use of nitric acid, as such, the glass containers must be prepared in advance in a laboratory [34].

Aside from wadability, it is important to note that the condition of the water body should be checked first before choosing this method, such as the presence of significant pollution from sewage and/or industrial discharges.



(a) Dip the beaker into the river face down about 4 inches below the surface or halfway to the bottom of the stream

(b) Slowly lift the beaker towards the flow



(c) Fill the beaker up to about 4/5 full

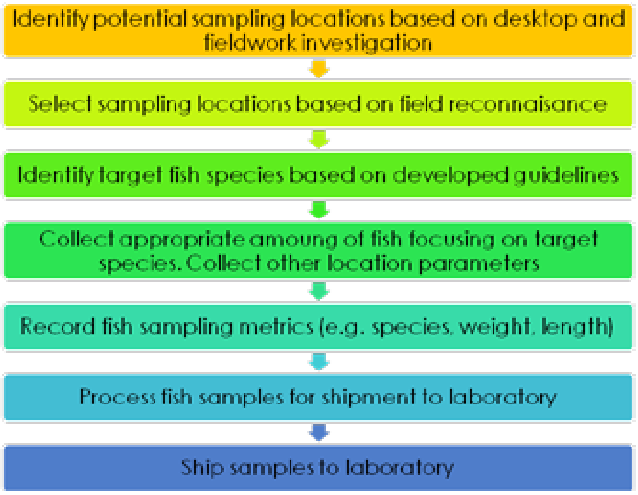
(d) Water sample ready for analysis

Secondly, intermediate containers can be used if the water is too deep for wading, is significantly polluted and direct contact is not advisable, and if the laboratory provides pre-preserved sample containers. For a list of intermediate containers, see Annex 3.

3.5 FISH

Fish are considered to be good indicators of the long-term and broad habitat effects of mercury contamination because they are relatively long-lived and mobile. Fish assemblages will generally include different species that represent the tropic levels of the food chain, from omnivores, herbivores and predatory fishes. Thus, fish tend to be reflective of the over-all environmental health through responses displayed in community structure and composition. As one of the main food source of humans, fish sampling is important in attempts to assess contamination.

3.5.1 FLOW CHART FOR SAMPLING



3.5.2 SAMPLING POINTS

Sampling locations will be undertaken via an authoritative or biased manner where aquatic species occur in both background locations (e.g., sites outside the influence of anthropogenic mercury contamination) as well as in areas where mercury contamination is suspected. Reviewing available maps will provide good indicators of where sampling locations should be established through the identification of key characteristics such as systems containing perennial water (more likely to contain fish year round) and natural habitat characteristics. Areas of interest can be further refined by doing field reconnaissance and field interviews with local fishermen, if possible. For example, concentrations of mercury would be expected to occur in greater concentrations within fine-grain bottom substrates with larger surface areas and reducing conditions conducive to methylation of mercury (e.g., pools, ponds).

Similar to surface water sampling, fish sampling approaches for lotic and lentic systems will vary since the types of habitats within them are distinctly different. The protocol developed by TechLaw, Inc for the Utah Division of Solid and Hazardous Waste summarizes the key consideration for each system as follows:

1. Flowing Systems: There are three general types of macrohabitats in flowing systems, including pools, riffles, and runs. Pools often support the most diversity of species, although there are species that may not occur in these macrohabitats. Pools also act as sinks for certain contaminants, as sediment deposits accumulate in these macrohabitats. As such, pools and depositional areas should be targeted when evaluating sampling locations. Sediment-associated mercury is likely to accumulate, methylate, and enter into most food chain components within pool and depositional settings, whereas riffles and runs represent environments with more constant water and sediment turnover. The likelihood of retention of mercury contaminated sediments is then lower in these macro habitats. However, riffles or runs may need to be sampled in order to obtain target fish species especially given the mobile nature of fish.
2. Static Systems: Macrohabitats in static systems vary based on a variety of factors, including water depth, available cover (e.g. woody debris, macrophytes, undercut banks, among others), and substrate composition. These types of environments can be more difficult to sample for aquatic organisms than flowing systems due to water depths. Techniques such as sediment core or grab samplers for collecting

invertebrates, and boat electroshocking, gill nets, or line and pole methods for collecting fish. However, given that static systems are more contained than flowing systems, there is a greater likelihood that all necessary target species will be present.

Site-specific factors, such as the size of the suspected area of contamination, size of water bodies, among others, will determine the specific number of investigative sampling locations necessary for determining potential mercury contamination. If possible, the sampling locations should be selected to establish a gradient of mercury contamination, which will hypothetically demonstrate the extent of contamination based on a suspected contaminant source. This can be done by sampling from upstream and downstream suspected contamination sources.

Fish sampling can be done concurrently with surface water and sediment sampling programs to understand the fate and transport processes for mercury in a specific area. To a degree, temporally and spatially placing biotic and abiotic samples side by side assists in examining contaminants detected between sites with differing environmental contaminant conditions and removing a level of uncertainty.

Selection of the most appropriate sampling period is very important. It is desirable to complete fish sampling in seasons when the lipid content of many species, which represents an important reservoir for bioaccumulative chemicals, are generally highest. It is also important to consider the amount of surface water dilution and the spawning season. Lower water levels can facilitate smoother sampling activities.

3.5.3 SAMPLING PROCEDURE

The first step is to identify the fish species to be sampled. The collection of multiple species from distinct trophic levels can be advantageous especially in characterizing the bioaccumulation of mercury. This is because the trophic level, as well as the length, weight, and age of a fish, can affect mercury tissue concentrations.

To optimize sample selection, the types of fish and shellfish that are commonly caught and consumed by fisher folks and their families can be the focus of sampling. In addition, those species that are more likely to accumulate chemicals of concern (such as bottom dwelling species) may be prioritized from a longer list of potential target species. If resources will allow, sampling and analysis of species that are suspected to contain lower levels of the contaminant can be done to provide a comprehensive guideline for fish consumers.

The following criteria based on guidance from the California EPA should be used [35]:

- For small- and moderate-sized lakes and reservoirs (approximately 800 surface hectares), at least 9 legal and/or edible-sized fish per species should be sampled and analysed as individuals or as 3 composite samples. Additional fish should be sampled and analysed for larger lakes and those with multiple arms. Multiple sampling sites for large water bodies may be obtained on the basis of north/ south designations, collected from different arms of a reservoir, or simply collected from multiple locations where fish are most accessible to fishers. For small- and moderate-sized creeks and river segments (approximately 40 kilometers in length, at least 9 legal and/or edible-sized fish per species should be sampled and analysed as individuals or as 3 composites. Additional fish should be sampled and analysed from fishing areas spread along larger rivers.

- All composite samples must follow the “75 percent rule”. The length of the smallest fish in a composite should be at least 75 percent of the length of the largest fish in the composite.
- A minimum of three composites per location is necessary to compare sites if one wants to test for site differences. However, evaluating site differences requires examination of the movement patterns and migratory behaviour of the fish species.
- Legal requirements for minimum/ maximum of allowable sizes for harvesting fish samples should be met. However, if these requirements are not present, the fish sample must be of “edible” size, or those that are typically caught and consumed by fishers. This will ensure that the measures of contaminant level are representative of consumer exposures.

PARCCS ASSESSMENT

The number and location of sampling points can be determined by answering the following guide questions:

- Did the fish sampling consider the species that people in the area typically eat?
- Did the sampling project consider the species that are most likely to accumulate contaminants? (Note: Fish at higher trophic levels are known to have greater body burdens of persistent contaminants that bio-magnify than fish at lower trophic levels.)
- What age and size of the selected species were sampled? Do these correspond to the age and size of biota that people would likely capture and eat?
- For the species sampled, were levels of contamination measured in the body parts that people typically eat? (Note: In fish sampling studies, site investigators often measure levels of contamination only in fillets; some individuals consume other parts of fish.)
- Are concentrations reported on a wet weight or dry weight basis? (Note: Wet weight concentrations are more representative of exposure point concentrations for most forms of biota.)

Abiotic parameters similar to surface water and sediment sampling should be collected, such as the measurement of length and width of the pool area, depths, and flow/velocity. In addition, the characteristics of bottom substrate, bank condition, riparian and cover should be recorded.

3.6 HUMANS [36]

Intuitively, the best bioindicators for mercury bio-availability are humans. However, there are ethical issues associated with collecting biological samples from individuals. Thus, it is important to follow the local or national ethical guidelines in obtaining samples from humans and the methodology of the study should be reviewed by the local ethics committee, particularly the DOH.

There are three primary media taken from humans to gauge mercury exposure:

- Mercury in urine, especially from high intensity exposure, such as from mercury vapour exposure during amalgam burning;
- Mercury and methylmercury in hair, which is a useful indicator of long-term exposure to organic mercury contamination, particularly from ingestion of mercury-contaminated fish; and

- Mercury in blood as a further indicator of recent or current exposure, particularly from exposure to mercury vapours or high fish ingestion. While mercury in urine may correlate with long-term exposure, blood analysis gives a combined picture of both metallic and organic mercury contamination.

3.8.1 SAMPLING CONSIDERATIONS

3.8.1.1 URINE

The ideal urine sample would be taken first thing in the morning as it reflects the mercury excreted by the body overnight. The sample donor should be asked not to drink large amounts of water a few hours before sample collection, as this dilutes the urine sample.

3.8.1.2 BLOOD

Assessments of mercury concentrations in human blood and fish muscle suggest that a direct relationship exists between the two. For instance, studies showed that for a 70 kg individual, mercury in blood (ppb) = 0.95 x mercury (mg) daily fish intake.

10 mL of blood can be collected and stored in EDTA-coated vials at 4 °C (NOT frozen) in a refrigerator. Sealed vials with blood samples can be

stored under these conditions for months without a relevant change in mercury concentration. Other procedures include sampling of 7 mL of blood using mercury-free vacutainers containing sodium (or lithium) heparin as anticoagulant. Heparinized vacutainers are available commercially from most laboratory suppliers.

3.8.1.3 HAIR

Hair grows about 1cm per month, excretes methylmercury during its formation and shows a good correlation with blood mercury levels. Though mercury analysis can be affected by several external factors such as use of dyes and mercury vapour exposure, the simplicity of sampling and analysis make it an amenable indicator for toxicological assessments.

Several studies propose different collection procedures for hair samples. Hair strands close to the scalp can be taken from the occipital portion of the head and stored in plastic bags with the root ends stapled. Alternatively, hair from the back part of the head can be collected (from 150 to 250 mg), and afterwards bound together using cotton string and stored at room temperature in paper envelopes. Another collection procedure is to cut only 30 to 50 mg of head hair which are then stored in a paper envelope kept in an airtight plastic bag. The third procedure is particularly suitable when working in hot and humid environments.

The National Institute of Minamata Disease, Japan, recommends to cut at least 20 strands of hair, each one with about 10 cm, close to the root. The "proximal" portion of hair (hair near the root) is better than the "distal" part (hair tip) for analysis as the methylmercury content can decrease during the hair growth under certain conditions, for example treatment with artificial hair waving procedures. Thus, if long hair strands are available (longer than 10 cm), the hair tips can be discarded.

Hair samples do not need to be frozen, but in hot environments it is advisable to keep samples refrigerated until they can be transported to the laboratory.

CHAPTER IV:
INTERPRETING MONITORING RESULTS

Coordination with laboratories must be done even prior to the sampling activity to ensure that specific instructions related to handling, packaging and transport of samples are followed. See Annex 4 for a list of some laboratories that conduct mercury analysis.

4.1 CONCEPTUAL AREA MODELLING

At the end of the day, the main goal of monitoring mercury contamination in any site is to evaluate the exposure pathways of the contaminant of concern. One common approach to do this is to develop a site conceptual model that will help envision how people come into contact with mercury.

The ATSDR, in their Public Health Assessment Guidance Manual, enumerated the five elements of an exposure pathway that should be considered in developing a site conceptual model. These are:

- Element 1: The contaminant source which release contaminants into various media.
- Element 2: Environmental fate and transport. Once released to the environment, contaminants move through and across different media and some degrade altogether.
- Element 3: Exposure point or area. This is the specific location(s) where people might come into contact with a contaminated medium.

- Element 4: Exposure route. The route is the means by which people physically contact environmental contamination at the exposure point (e.g., by inhalation, ingestion, or dermal contact).
- Element 5: Potentially exposed populations.

These five elements largely determine to what extent exposures may have occurred, may be occurring, or may occur in the future at and around a site. All five elements of an exposure pathway must be present to consider that pathway "complete", however, a complete exposure pathway does not necessarily mean that a public health hazard exists, a finding that should be communicated early. Rather, specific exposure conditions must be thoroughly examined to provide a more comprehensive evaluation of the health impacts of the exposure.

ILLUSTRATIVE EXAMPLE

The following site conceptual model was developed for the municipality cited in Section 3.4.1.

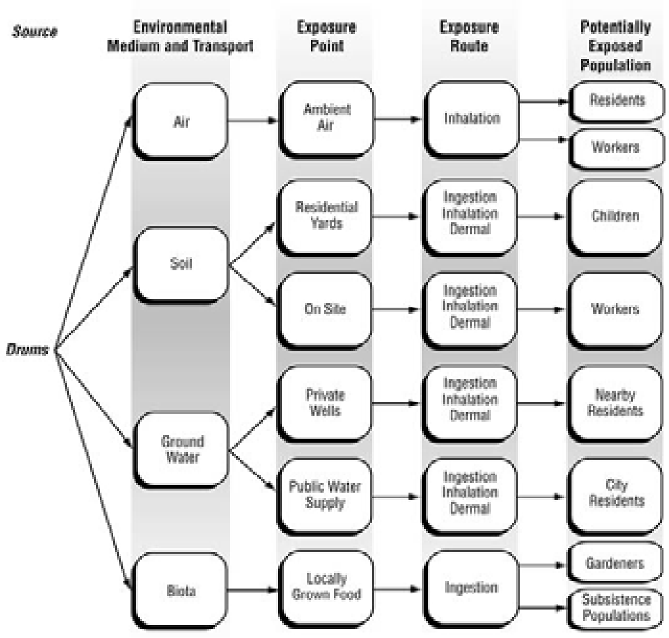


Figure 6-3. Site Conceptual Model—Exposure Pathway Evaluation

4.3 MEASURING IMPACT

4.3.1 STANDARDS/ LIMITS OF EXPOSURE AS REFERENCE FOR INTERVENTION

The reference concentration and reference dose are established by health and safety authorities to control exposure to hazardous substances. They are set forth to represent the maximum amount (concentration) of a chemical that can be present in the environment without presenting a health hazard.

WHAT IS THE DIFFERENCE BETWEEN THE RFC AND RFD? [37]

- The RfC is an estimate of a **continuous inhalation exposure** to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.
- The RfD is an estimate of a **daily oral exposure** to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

The reference values are typically in the range of:

- 10^{-6}, or parts per million (ppm) or microgram (µg)
  - 1 ppm means 1 in 1,000,000 units
  - 1 µg is equivalent to 0.001 milligram
  - 1 µg is equivalent to 0.000001 gram

- 10^{-9}, or parts per billion (ppb) or nanogram (ng)
  - 1 ppb means 1 in 1,000,000,000 units
  - 1 ng is equivalent to 0.001 microgram
  - 1 ng is equivalent to 0.000001 milligram
  - 1 ng is equivalent to 0.000000001 gram

The table below summarizes standards or limits of exposure for different environmental media. Where there are no Philippine values, values provided by the US EPA or other agencies were used.

Medium	Standard	
Air	≤1,000 ng/m^3 0.05 mg/Ncm	ATSDR[38] Philippine Clean Air Act [39]
Soil	16 mg/kg (residential) 250 mg/kg (commercial) 230 mg/kg (industrial)	Ohio EPA [40]
Sediment	None	
Water	0.002 mg/L	Environmental Management Bureau [41]
Fish	0.1 µg/kg	United Nations Environment Programme [42]

However, it must be noted that in spite of these reference levels, the Wold Health Organization (WHO) still concludes that “*there is no safe level of Hg in which there is no adverse effect*”.

CHAPTER V: CONCLUSIONS

Mercury is a very toxic element that easily spreads in the atmosphere, lithosphere and surface water. Concentrated mercury poses serious problems to human health. To control mercury pollution and reduce mercury damage to human health, determination of mercury levels in the environment is important. A wide array of environmental media can be used to do so, however, it is important that the monitoring plan is developed with clear objectives and adhere to scientific principles.

More importantly, the results of the monitoring activity will only be useful if they are communicated to the relevant stakeholders in a clear and concise manner. The results of the monitoring activity are considered to be valuable information that will support and enable the development of public health conclusions. These will help identify public health actions that might be needed to eliminate or prevent exposures of the members of the community.

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ANNEX II:
QUICK FACTS ABOUT MERCURY

GENERAL	
Name, symbol, number	Mercury, Hg, 80
Element category	Transition metal
Group, period, block	12, 6, d
Standard atomic weight	200.592
Electron configuration/ Energy levels/ atomic structure	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$ 1st energy level: 2 2nd energy level: 8 3rd energy level: 18 4th energy level: 32 5th energy level: 18 6th energy level: 2

PHYSICAL PROPERTIES	
Phase	Liquid
Density (near r.t.)	13.534 $g \cdot cm^{-3}$
Melting point	234.3210 K, -38.8290ºC, -37.8922ºF
Boiling point	629.88 K, 356.73ºC, 674.11ºF
Triple point	234.3156 K, $1.65x10^{-7}$ kPa
Critical point	1750 K, 172.00 MPa
Heat of fusion	2.29 kJ·mole
Heat of vaporization	59.11 kJ·mole
Molar heat capacity	27.893 $J \cdot mol^{-1} \cdot mol^{-1}$
ATOMIC PROPERTIES	
Oxidation states	4, 2 (mercuric), 1 (mercurous)
Electronegativity	2.00 (Pauling scale)
Ionization energies	1st: 1007.1 $kJ \cdot mol^{-1}$ 2nd: 1810 $kJ \cdot mol^{-1}$ 3rd: 3300 $kJ \cdot mol^{-1}$
Atomic radius	151 pm
Covalent radius	132±5 pm
Van der Waals radius	155 pm

ANNEX III: INTERMEDIATE CONTAINERS FOR WATER SAMPLING

INTERMEDIATE CONTAINERS	DESCRIPTION
Dip/ Pond Sampler	The pond sampler consists of an adjustable clamp attached to the end of a two- or three-piece telescoping aluminum or fiberglass pole that serves as the handle. The clamp is used to secure the container. Samples can be obtained at distances as far as 3 m from the edge of the source.
Kemmerer Sampler	Many of these samplers are constructed of plastic and rubber. Some newer devices are constructed of stainless steel or are all Teflon or Teflon-coated, making them acceptable for all water quality parameters without restriction. In the open position, water flows easily through the device. Once the device is lowered to the desired depth, a messenger is dropped down the sample line, tripping the release mechanism and closing the container. In the closed position, the bottle is sealed at the top and bottom, isolating the sample during retrieval.
Van Dorn Sampler	The Van Dorn Sampler is suitable if collecting discrete samples at depths 2.0 m or greater. The vertical configuration of the sampler is made of acrylic plastic material so that it can be used for sample removal. A horizontal configuration of the Van Dorn Bottle, should be used when samples are to be taken from the bottom, at the sediment-water interface or when samples are required from a narrow band of the depth profile.

INTERMEDIATE CONTAINERS	DESCRIPTION
Sampling Iron	The sampling iron or multipurpose sampler is suitable for taking samples in flowing streams or rivers. It is a weighted platform attached to a rudder and equipped with clamps for holding sample bottle. The advantage of the sampling iron is that the sample container can be used directly to collect the sample and does not have to be transferred to another container for shipment in the laboratory.
Weighted bottle	The weighted bottle can be used to obtain representative samples from a specific depth. The sampler consists of a glass bottle, a weighted sinker, a bottle stopper, and a line that is used to lower and raise the sampler during sampling. This sampler is more desirable than the Van Dorn in some sampling situations because of its glass construction.

ANNEX IV:
LIST OF DENR-EMB ACCREDITED ANALYTICAL LABORATORIES

CHEMPRO ANALYTICAL SERVICES LABORATORIES, INC.
Address: 2nd Floor MS Building 146 Shaw Boulevard, Extension Corner San Roque St. Barangay Kapitolyo, Pasig City 1602
Telephone no.: 634-8600 or 635-6773
Fax No.: 635-6773
E-mail: chemprophi@yahoo.com
cbmartinez@chemproasli.com
igistaana@chemproasli.com
Contact Person: Crizelle B. Martinez (Quality Assurance Officer)

CRL ENVIRONMENTAL CORPORATION
Address: Unit 02 Berthaphil Industrial Park, Jose Abad Santos Avenue, Mabalacat, Pampanga
Telephone no.: (045) 599 6529; 599 3943
Email: carmela.capule@crllabs.com
crl@crllabs.com

DAVAO ANALYTICAL LABORATORIES, INC.
Address: McArthur Highway corner Union Ave., Matina, Davao City, Davao del Sur
Telephone no.: (082) 297 3278
Email: dalinc_03@yahoo.com

EMD LABORATORY ANALYTICAL SERVICES
Address: Energy Center, Merritt Road, Fort Bonifacio, Taguig, Metro Manila
Telephone no.: (02) 893 6001 to 47 893 1320
Email: santosls@energy.com.ph

F.A.S.T. LABORATORIES
Address: 2/F Allied Concrete Bldg. Km 54, Brgy. Makiling, Calamba, Laguna
Email: fast.laboratories@gmail.com

INTERTEK TESTING SERVICES PHILS., INC.
Address: 2/F ITS Bldg. 2310 Pasong Tamo Ext., Makati City, Metro Manila
Telephone no.: (02) 819 5841 to 47
Email: mines.mercado@intertek.com

MTEC WATER TREATMENT TECHNOLOGIES, INC.
Address: Bldg. #3, LSL CompoundDiode St., LISPPI, Cabuyao, Laguna
Email: mtecchem@info.com.ph

OSTREA MINERAL LABORATORIES, INC.
Address: Brgy. Road, Bo. Mamplasan, Binan, Laguna
Telephone no.: (049) 889 9058
Email: ibe421@yahoo.com

RESEARCH AND ANALYTICAL SERVICES LABORATORY (RASL)
Address: Natural Sciences Research Institute (NSRI), College of Science, University of the Philippines, Diliman, Quezon City
Telephone: 920-7731 or 981-8500 local 3608
Email: ecs@nsri.upd.edu.ph
Contact Person: Dr. Evangeline C. Santiago (Officer-in-charge)

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Marietta Bernardino (Office Manager)

SCIENCE RESOURCE CENTER, UNIV. OF THE IMMACULATE CONCEPTION
Address: Main Campus, Fr. Selga St. Davao City Davao del Sur
Telephone no.: (082) 221 8181
Email: ludyporticos@yahoo.com

SENTROTEK
Address: 208 Pilar St., Mandaluyong City, Metro Manila
Telephone no.: (02) 721 6500
Email: sentro@dakila.com

SGS PHILIPPINES, INC.- MULTI-LABORATORY
Address: 2229 Chino Roces Avenue, Makati City
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meden.peneyra@sgs.com
Contact Person: Ms. Meden Jojemar L. Peneyra (Laboratory Operations Manager)

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Source: http://emb.gov.ph/internal/recognizedlabs.aspx

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