# Sample Handling Requirements of Environmental Samples

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**ERLSD – Environmental Laboratory Services Section**

# OUTLINE

- Sample Handling Requirements
- Sample Receipt and Login
- Overview of Analytical Methods
- Regional Distribution of DENR-Recognized Environmental Laboratories (as of September 2021)

# SAMPLE HANDLING

Procedures for collecting, preserving, and transporting of specimens sufficiently stable to provide accurate and precise results suitable for interpretation.

When sample handling is imprecise, inconsistent or both, the validity of results can be called into question[1]

[1] *retrieved from https://www.labcompare.com/10-Featured-Articles/188628-Sample-Handling/*

# SAMPLE HANDLING

**Procedures for sampling and analysis influence each other, and so plans for sampling and analysis are codependent.**

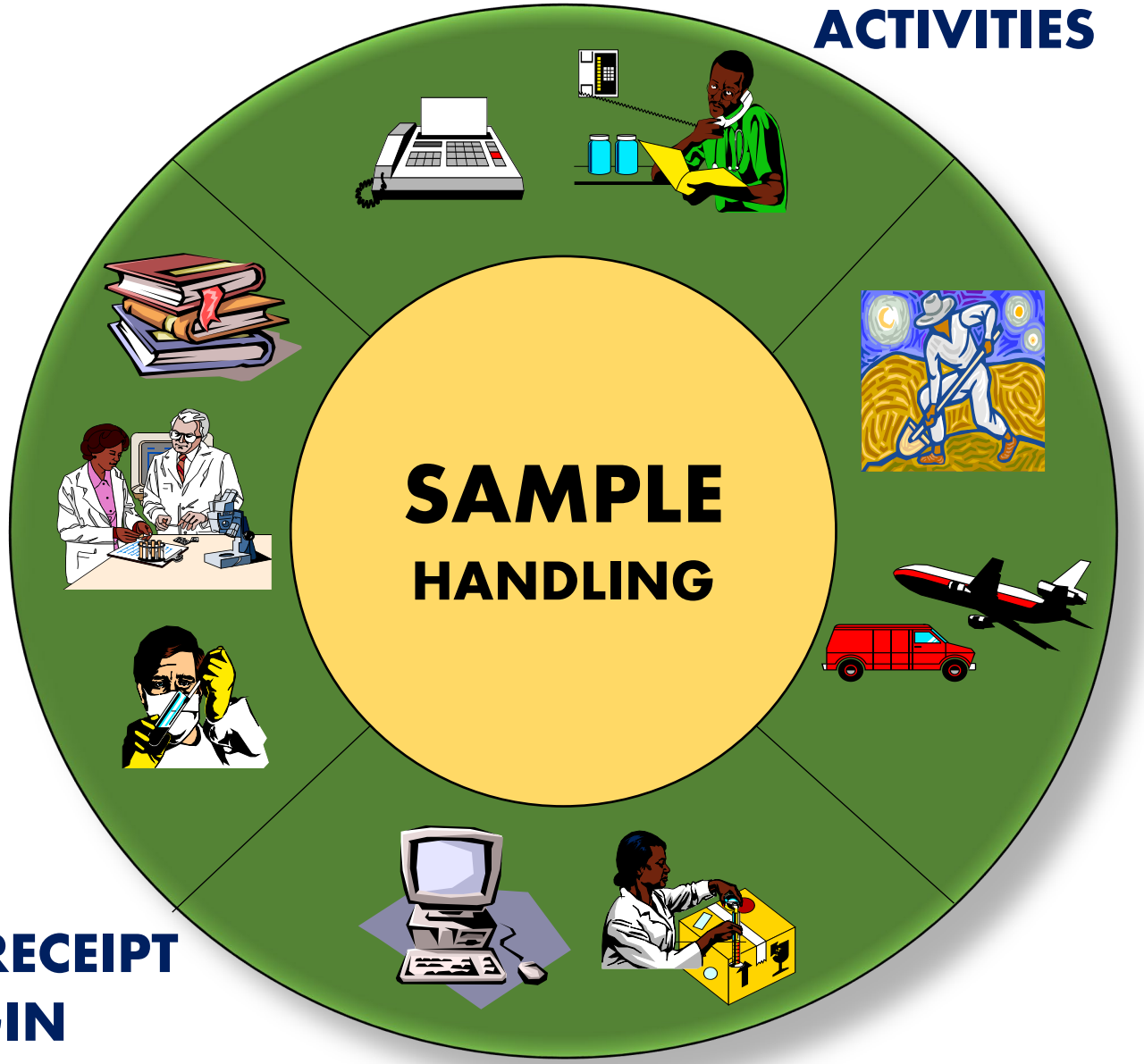
***All sampling activities must be coordinated with the laboratory…***

PRE-SAMPLING ACTIVITIES

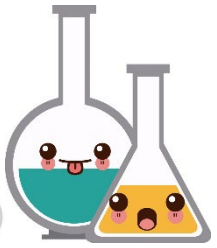
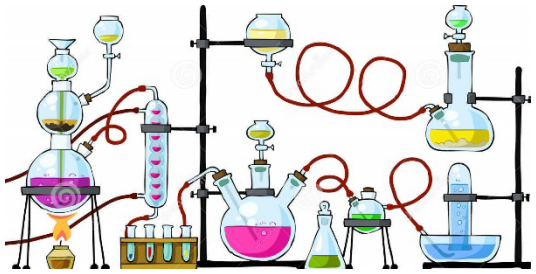
SAMPLE COLLECTION AND TRANSPORT

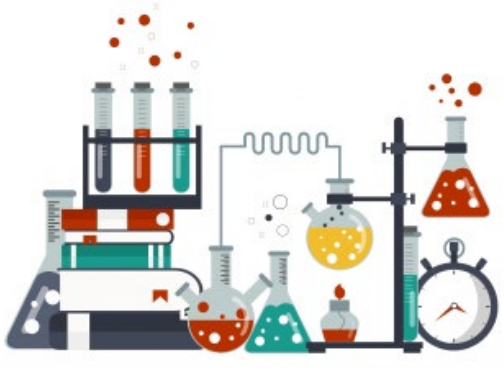
SAMPLE RECEIPT AND LOGIN

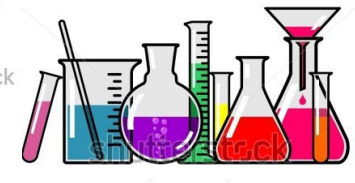
LABORATORY ANALYSIS AND DATA MANAGEMENT



# SAMPLE REQUIREMENTS



# HOLDING TIME

**The maximum amount of time that can pass from collection until analysis and still obtain a valid result.**

**In addition to meeting the published holding times, sample collectors must keep in mind the courier routes and scheduling and the hours of operation of the assigned laboratory.**

# SAMPLE VOLUME

**Sufficient to perform all the required analyses with an additional amount collected to provide for any QC needs such as:**

- ✓ **duplicates**
- ✓ **matrix spikes**
- ✓ **split samples**
- ✓ **confirmations or repeat examinations**

# SAMPLE CONTAINER

**Selection of a sample container should be:**

- ❑ **Based on the parameter to be measured**
- ❑ **Made of chemically resistant material, and do not affect the concentrations of the pollutants to be measured**
- ❑ **Have a closure (i.e., leak proof/resistant, Teflon lined) that protects the sample from contamination**

# PRESERVATION

- Prevent or minimize:

✓ Biological activity (e.g. microbial respiration);

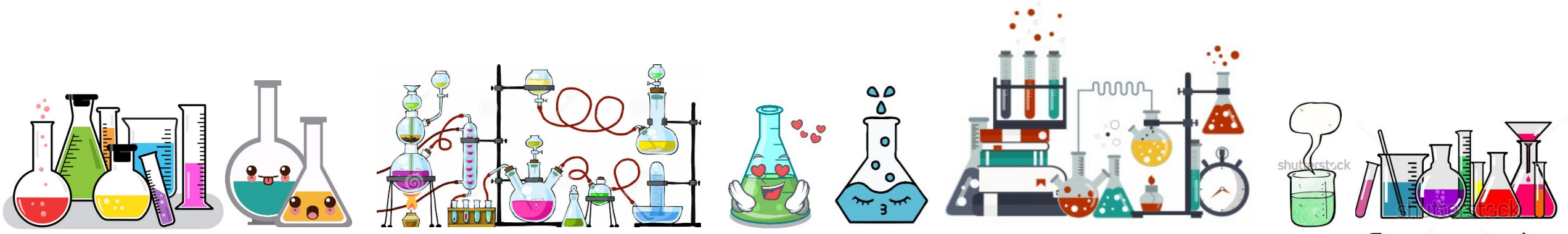
✓ Chemical activity (e.g. precipitation or pH change);

✓ Physical activity (e.g. aeration or high temperature)

within the period after the sample has been collected

- Responsibility of the sampling personnel, NOT the laboratory personnel

# SAMPLE REQUIREMENTS
# (Summary)



# *Aggregate Organics in Water*

| PARAMETERS | MINIMUM SAMPLE SIZE | SAMPLE CONTAINERS | PRESERVATION |
|---|---|---|---|
| BOD | 1000 mL | Polyethylene/ Teflon/ Glass bottle | Cool, ≤ 6°C |
| COD | 100 mL | Polyethylene/ Teflon/ Glass bottle | Add Sulfuric Acid to pH < 2; Cool, ≤ 6°C |
| Oil and Grease | 1000 mL | Glass, wide-mouth, with Teflon-lined cap | Add hydrochloric acid/ sulfuric acid pH < 2; Cool, ≤ 6°C |

# *Aggregate Organics in Water*

**BOD TEST**

**- measures the change in DO concentration caused by microorganisms as they degrade organic matter in a sample held in a stoppered bottle incubated for 5 d in the dark at 20°C[1]**

**COD**

**- defined as the amount of a specified oxidant that reacts with the sample under controlled conditions[1]**

[1] *Standard Methods for Examination of Water and Wastewater (APHA-AWWA), 23rd ed. 2017*

# *Aggregate Organics in Water*

## OIL and GREASE

- ✓ **Glass**
- ✓ **Wide-mouth**
- ✓ **PTFE-lined cap**
  ***(alternatively, aluminum-lined cap)***

# *Aggregate Organics in Water*

## OIL and GREASE

- **Wash with soap, rinsed with water, then with solvent**
- **Alternatively bake at 200 – 250$^0$C for at least 1 hr**
- **Cap is treated in the same manner**

# *Individual Organics in Water*

| PARAMETERS | MINIMUM SAMPLE SIZE | SAMPLE CONTAINERS | PRESERVATION |
|---|---|---|---|
| Pesticides and PCBs | 1000 mL | Amber Glass, PTFE-lined cap | Cool, ≤ 6°C; add 3 mL of 10% Thiosulfate per gallon (if residual chlorine is present) |
| Benzo(a)pyrene | 1000 mL | Amber Glass, PTFE-lined cap | Cool, ≤ 6°C; add 3 mL of 10% Thiosulfate per gallon (if residual chlorine is present) |

# *Individual Organics in Water*

| PARAMETERS | MINIMUM SAMPLE SIZE | SAMPLE CONTAINERS | PRESERVATION |
|---|---|---|---|
| BTEX and TCE | 2 x 40 mL | Glass, PTFE-lined cap VOA vial | Cool, ≤ 6°C and adjust pH to < 2 using sulfuric acid; add 3 mL of 10% Thiosulfate per gallon (if residual chlorine is present) |
| Phenols and Phenolic substances | 500 mL | Glass, PTFE-lined cap | Cool, ≤ 6°C; and adjust pH to < 2 using sulfuric acid |

# *Individual Organics in Water*

## Example of Sampling Containers

- ✓ **Pesticides**
- ✓ **PCBs**
- ✓ **Benzo(a)pyrene**

**Glass Amber Bottle w/ PTFE-lined cap**

- ✓ **BTEX and TCE**

**VOA Vial**

# *Individual Organics in Water*

## Example of Sampling Containers

UNDERGOES SOLVENT RINSING

**Glass Amber Bottle w/ PTFE-lined cap**

**VOA Vial**

# NUTRIENTS IN WATER

| PARAMETERS | MINIMUM SAMPLE SIZE | SAMPLE CONTAINERS | PRESERVATION |
|---|---|---|---|
| Ammonia as $NH_3$-N | 500 mL | Glass/ Polyethylene or Teflon bottle | Add Sulfuric Acid to pH <2; Cool ≤ 6°C |
| Nitrate as $NO_3$-N | 100 mL | Glass/ Polyethylene or Teflon bottle | Cool ≤ 6°C |
| Phosphate | 100 mL | Glass/ acid-washed | Cool ≤ 6°C |

# OTHER ANIONS IN WATER

| PARAMETERS | MINIMUM SAMPLE SIZE | SAMPLE CONTAINERS | PRESERVATION |
|---|---|---|---|
| Chloride and Fluoride | 100 mL | Glass/ Polyethylene or Teflon bottle | None Required |
| Sulfate | 100 mL | Glass/ Polyethylene or Teflon bottle | Cool $\leq$ 6°C |
| Cyanide as Free Cyanide | 1000 mL | Glass/ Polyethylene or Teflon bottle | Analyze within 15 min. Add NaOH to pH >12 if sample is to be stored, Cool, 6°C, in dark |

# *PHYSICAL AGGREGATES IN WATER*

| PARAMETERS | MINIMUM SAMPLE SIZE | SAMPLE CONTAINERS | PRESERVATION |
|---|---|---|---|
| Color | 500 mL | Glass/ Polyethylene or Teflon bottle | Cool $\leq$ 6°C |
| Total Suspended Solids | 200 mL | Glass, Polyethylene | Cool $\leq$ 6°C |

# METALS IN WATER

| PARAMETERS | MINIMUM SAMPLE SIZE | SAMPLE CONTAINERS | PRESERVATION |
|---|---|---|---|
| Arsenic, Barium, Cadmium, Iron, Lead, Manganese, Nickel, Zinc, Mercury, Selenium | 1000 mL | Glass/ Polyethylene or Teflon bottle; acid washed | Add Nitric Acid to pH < 2 |

# METALS IN WATER

| PARAMETERS | MINIMUM SAMPLE SIZE | SAMPLE CONTAINERS | PRESERVATION |
|---|---|---|---|
| Copper as Dissolve Copper | 500 mL | Glass/ Polyethylene or Teflon bottle; acid washed | Filter with 0.4 to 0.45 um membrane filter then acidify to pH < 2 using Nitric Acid |
| Boron | 1000 mL | Teflon or quartz bottle | Acidify to pH < 2 using Nitric Acid |
| Chromium Hexavalent | 250 mL | Glass/ Polyethylene or Teflon bottle; acid washed | Cool, ≤6°C, pH 9.3–9.7, ammonium sulfate buffer |

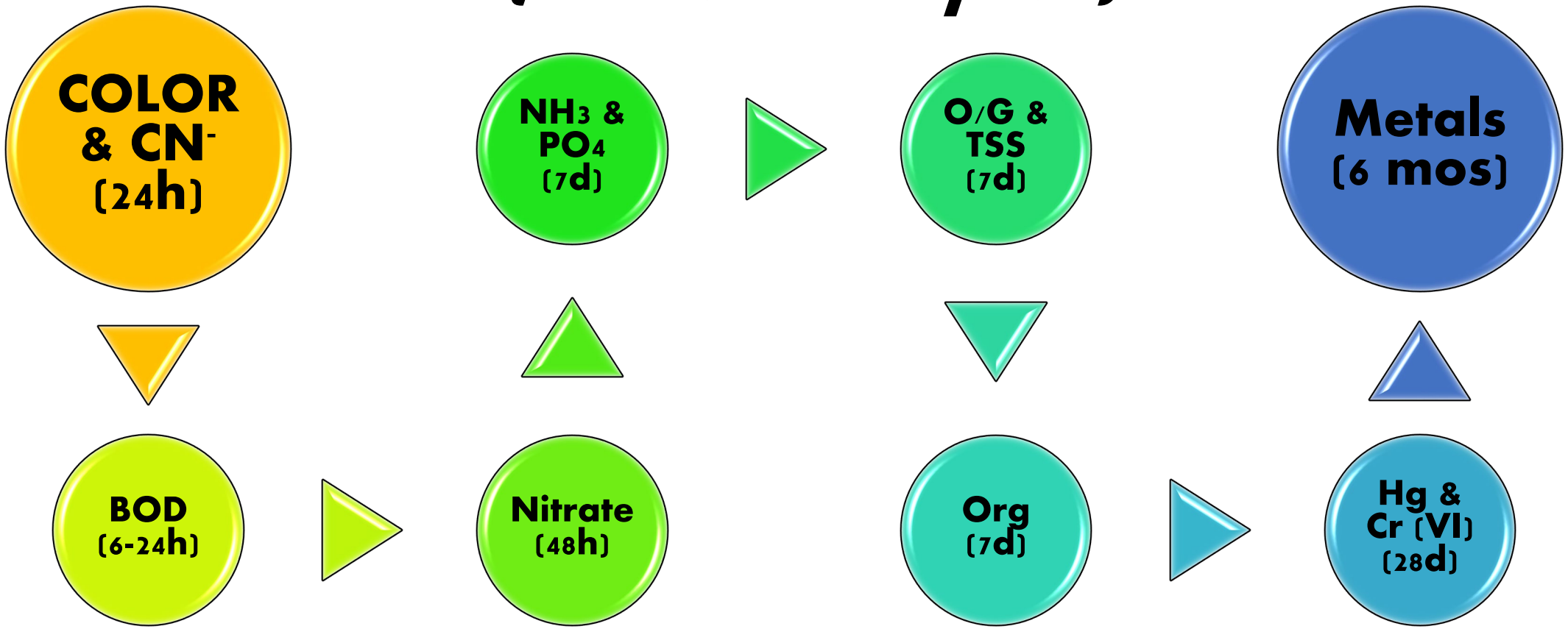
# MICROBIOLOGICAL CONSTITUENTS IN WATER

| PARAMETER | MINIMUM SAMPLE SIZE | SAMPLE CONTAINERS | PRESERVATION |
|---|---|---|---|
| Total and Fecal Coliforms | 100 mL | Sterile and non-reactive borosilicate glass or plastic bottles, pre-sterilized plastic bags | Maintain samples in the dark at temperatures < 10°C (but not frozen) |

- Samples, especially those for regulatory compliance should be brought to the lab within 6 hours from collection and be analyzed within 2 hours from receipt in the laboratory.

- Dechlorinating agents, such as Sodium Thiosulfate, should be added to sampling bottles whenever samples are expected to contain residual chlorine.

# SUMMARY OF HOLDING TIMES
## (Water Samples)




***For BOD, 6-hr holding time is observed for samples for compliance purposes.***

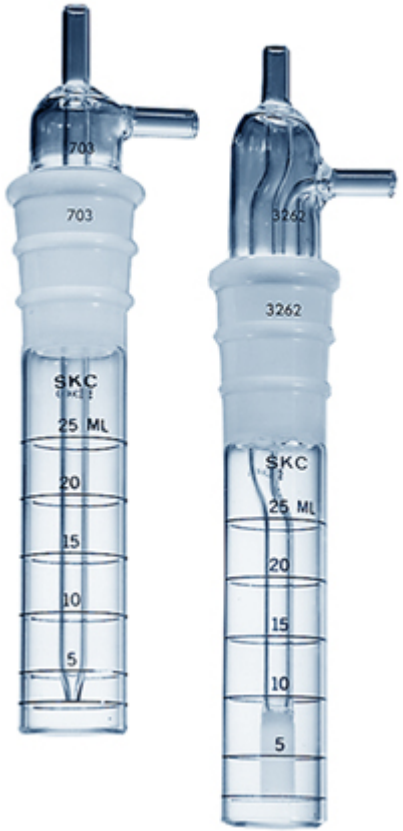
# SEDIMENTS AND SOIL

Solvent-rinsed, wide-mouth amber glass containers – Organics

Resealable PET plastic bags – Metals

Plastic bottles for water samples for Inorganics and some aggregate organics testing

Amber glass bottles for water samples for organics testing




Glass midget impingers for air sampling

Amber glass jars for sediments/ soils/ biota for organics testing

Wide-mouth glass bottles for water samples for O&G testing

Sterile Bottles for samples for microbiological analysis

# *WASTES for TCLP*

| PARAMETERS | MINIMUM SAMPLE SIZE | SAMPLE CONTAINERS | PRESERVATION |
|---|---|---|---|
| Non Volatile Inorganic Analytes | 100 g | Glass bottle/ resealable plastic bag | Cool to ≤6°C |

# TRANSFORMER OIL

| PARAMETERS | MINIMUM SAMPLE SIZE | SAMPLE CONTAINERS | PRESERVATION | HOLDING TIME |
|---|---|---|---|---|
| PCBs | 20 mL | Glass amber bottle, previously rinsed with solvent or bake | Cool, dry and dark place | Four weeks |

*Determination of PCB by GC-ECD, EPA Victoria 6013, October 2003*

# *DIOXINS and FURANS*

| MATRIX | SAMPLE CONTAINERS | PRESERVATION | HOLDING TIME |
|---|---|---|---|
| **STATIONARY SOURCE** | | | |
| - XAD resins | XAD Tube sealed with Teflon tape | | 30 days |
| - Glass Fiber Filter | Petri dish sealed with Teflon tape | Less than $4^0$C but not frozen | |
| - Solvent Rinses | Amber Glass Jar | | |

# *DIOXINS and FURANS*

**XAD Tubes**

**XAD resins**

# *DIOXINS and FURANS*

- ❑ Soaking in ultrapure water
- ❑ Extraction with water for 8 hrs
- ❑ Extraction with methanol for 22 hrs
- ❑ Extraction with DCM for 22 hrs
- ❑ Extraction with Toluene for 22 hrs

Drying using vacuum oven

# *DIOXINS and FURANS*

| MATRIX | SAMPLE CONTAINERS | PRESERVATION | HOLDING TIME |
|---|---|---|---|
| **Ambient Air** | | | |
| - PUF cartridge | Glass bottle sealed with Teflon cap | Less than $4^0$C but not frozen | 7 days |
| - Quartz Fiber Filter | Petri dish/ aluminum foil | | |

# *DIOXINS and FURANS*

## PUF with XAD Resin

# *DIOXINS and FURANS*

| MATRIX | SAMPLE CONTAINERS | MINIMUM SAMPLE SIZE | PRESERVATION | HOLDING TIME |
|---|---|---|---|---|
| Aqueous | Amber glass bottle | 1000 mL | 0 – 4$^0$C | 7 days |
| Soil / Sediments | Amber glass jar | 100 g | | |
| Fish tissue samples | Amber glass jar | 500 g | | |

# AMBIENT AIR AND STATIONARY SOURCE EMISSIONS

General Considerations:

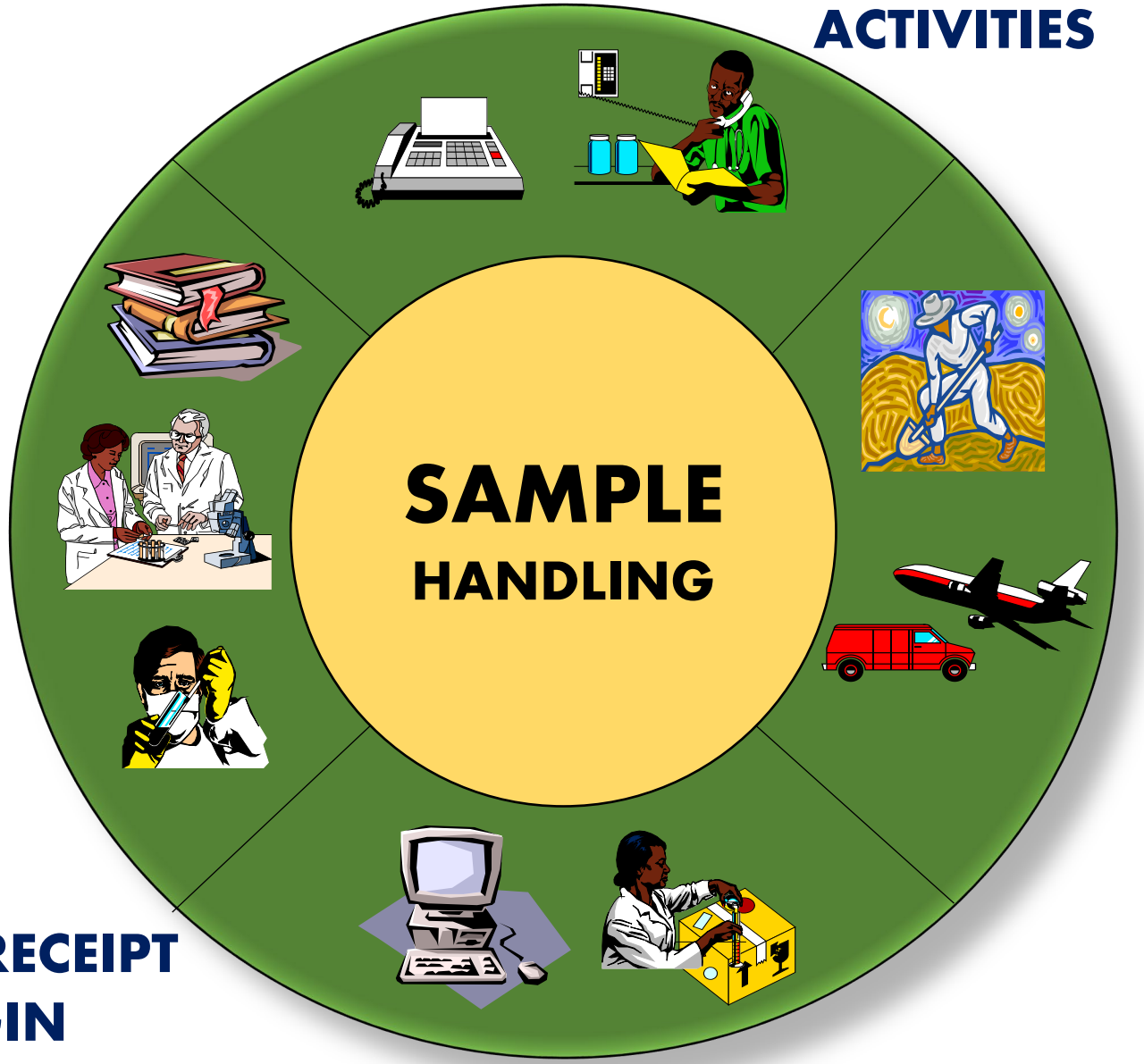
- Pre-conditioning and pre-weighing of filters (for particulates)
- Preparation of Absorbing Solutions (where applicable)
- Preparation of collection bottles and rinsing solvents/ solutions (for rinses)

PRE-SAMPLING ACTIVITIES

SAMPLE COLLECTION AND TRANSPORT

SAMPLE RECEIPT AND LOGIN

LABORATORY ANALYSIS AND DATA MANAGEMENT



# SAMPLE RECEIPT AND LOGIN

- Laboratory's FIRST contact is the arrival of samples
- to improve the overall quality of the analytical process, the laboratory must do all it can to receive APPROPRIATE, APPLICABLE, DEFENSIBLE samples

# SAMPLE RECEIPT AND LOGIN

**1st**

- COC Verification

**2nd**

- Physical inspection
- Volume
- Holding Time
- Container type
- Preservative
- Label

**3rd**

- Recording of samples
- Assigning unique code

# SAMPLE RECEIPT AND LOGIN

## 4th

- Perform sample pre-handling (e.g. sub-sampling)

## 5th

- Store samples

# SAMPLE RECEIPT AND LOGIN

- **CHAIN OF CUSTODY (COC)**

  **- written documentation of the security of a sample from the time it is collected to the time it is transferred to the representative of the laboratory that is conducting the analysis**

SS/COC Control # _____

# SAMPLE SUBMITTAL / CHAIN OF CUSTODY FORM

Page ____ of ____

Client : ( 1 ) Tel: ( ) Fax: ( )

Contact Address: ( 1 )

Project Name: ( 2 )

Sampled By: ( 3 )

Sampling Source: ( 4 )

Submitted By: ( 5 ) (Signature and Printed Name) | Date: ( 6 ) mm/dd/yy | Time: ( 6 ) ____ am ____ pm

Special Instructions/ Comments: ( 7 )

Department of Environment and Natural Resources
ENVIRONMENTAL MANAGEMENT BUREAU
Research and Development Division
DENR Compound, Visayas Avenue, Diliman, Quezon City
Tel Nos. (0632) 426-4338/ 4339; Fax No. (0632) 426-4335/ 4340

FOR LABORATORY USE ONLY

| Mode of Delivery | Condition Received | Category of Sample | Payment |
|---|---|---|---|
| ❒ Walk-in<br>❒ EMB<br>❒ Courier<br>❒ Other, _____ | ❒ Frozen ❒Y ❒N Sealed<br>❒ Cold ❒Y ❒N Container Intact<br>❒ Ambient ❒Y ❒N # of Spls Match COC<br>❒ Preserved<br>❒ Other, specify _____ | ❒ Private<br>❒ Regional<br>❒ Project<br>❒ EMB<br>❒ Other _____ | OP No.: _____<br>Amount: _____ |

Received By: (Signature and Printed Name) | Date: mm/dd/yy | Time: ___ am ___ pm | Sample Initially Stored at:

Total # of Samples Received _____ | Samples Relinquished To

| Lab Sple Number | Station No./ Pt. | Sample Identification | Sple Type | Date/Time Sampled: mm/dd/yy | am | pm | Analyses Requested | Field Preservation | Container # | Container Type | Quantity Rec'd |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | (8) | (9) | (10) | (11) | | | (12) | (13) | | (14) | |
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Lab Unit Concerned:

Date: mm/dd/yy | Time: ___ am ___ pm

Name/ Initial of Lab Personnel:

Remarks:

**Sample Type:**

A(A) – ambient air A(S) – source emission

Creek – creek Falls – falls F – fishpond L- lake RW – river water SW – seawater S – spring water

C- crustacean Fish – fish SG – sea grass Sed – sediment SF- shellfish

DW – deepwell TW – treated water

IN – influent EF – effluent MW – mining waste OF – outfall WW – wastewater

QC– QC/ PT sple LF – landfill SE – sewage RW – rainwater sludge – sludge Oil-oil Other, _____

**Container Type:**

Al – aluminum foil G – glass P-plastic G(B) – glass, borosilicate Al(S) – aluminum foil, solvent rinsed G(E)-glass, sterile

G(S) – glass, solvent rinsed G(A) or P(A) – glass or plastic, acid washed O – other, specify _____

**Sample Source**

❒ Air
❒ Surface water
❒ Biota/ sediments
❒ Ground/ drinking H2O
❒ Industries
❒ Other

**Sample Disposal**

❒ Laboratory procedure
❒ Other procedure, specify _____
Total Quantity Disposed:
_____ ❒ milliliters _____ ❒ grams

Disposed By: (Signature and Printed Name) | Date: mm/dd/yy

Other Comments:

PRE-SAMPLING ACTIVITIES

SAMPLE COLLECTION AND TRANSPORT

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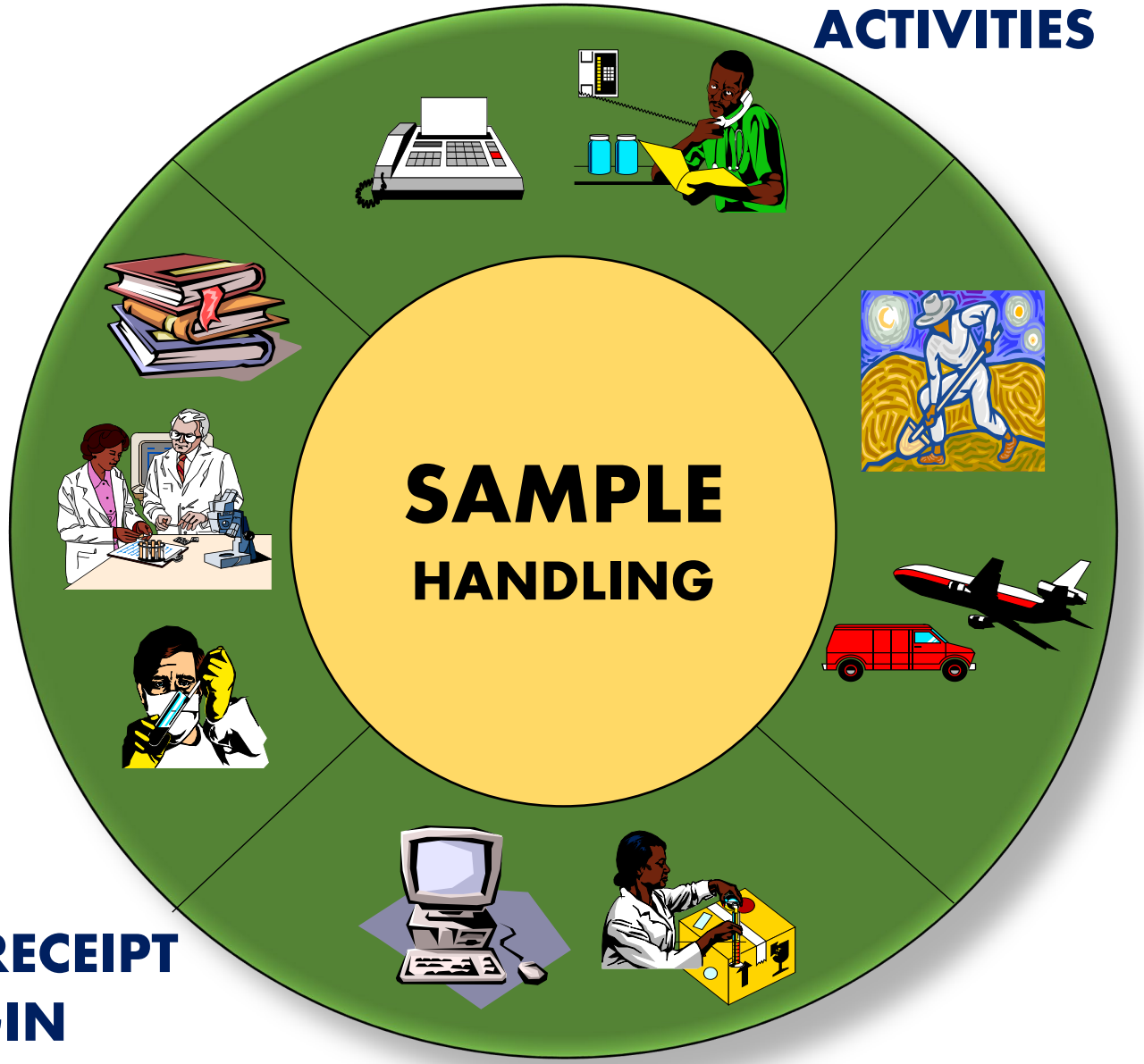


# WATER SAMPLES

## *Colorimetric Analyses*

**Ammonia**

SAMPLE

**Nitrate**

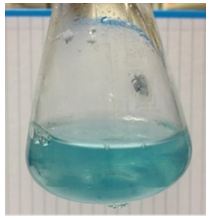
SAMPLE

**Phosphate**

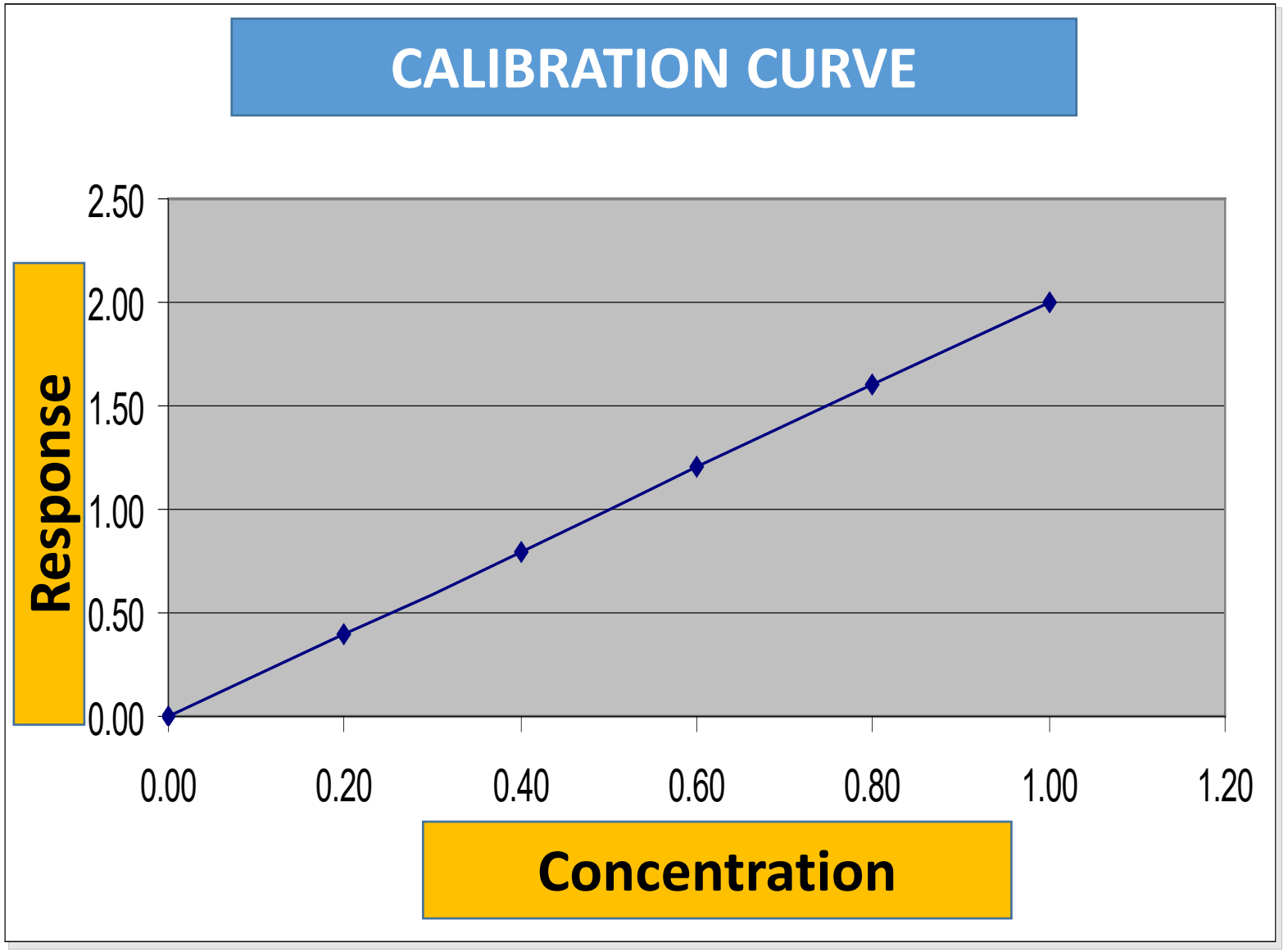
SAMPLE

PRE-TREATMENT

ANALYSIS



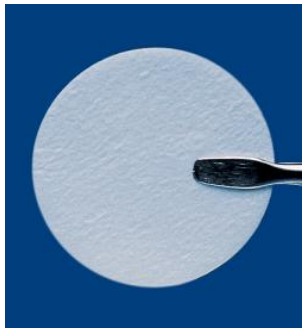

**UV-Vis Spectrophotometer**


CALIBRATION CURVE
Response
2.50
2.00
1.50
1.00
0.50
0.00
0.00
0.20
0.40
0.60
0.80
1.00
1.20
Concentration

# WATER SAMPLES

## *Gravimetric Analyses*

**CONSTANT WEIGHING**



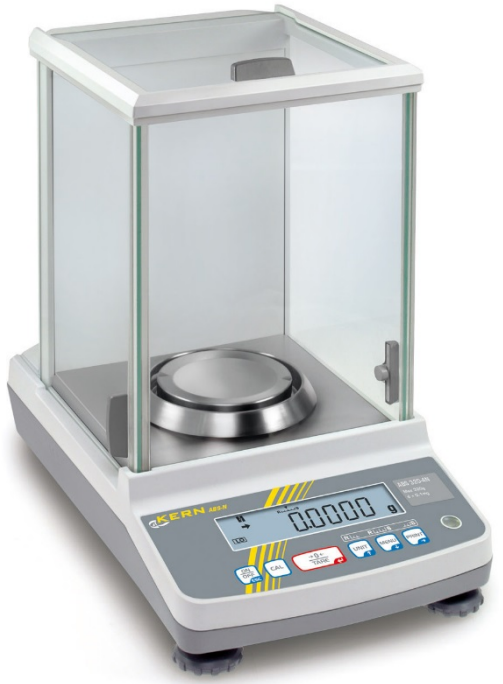
**TSS**

**SAMPLE**

**CONSTANT WEIGHING**

**Oil and Grease**

**SAMPLE**



**Analytical Balance**

# WATER SAMPLES

## *Gravimetric Analyses*

**Filtration set-up for Solids analyses**



**Extraction set-up for Oil and Grease**

# WATER SAMPLES

## *Potentiometric Analyses*

**pH**

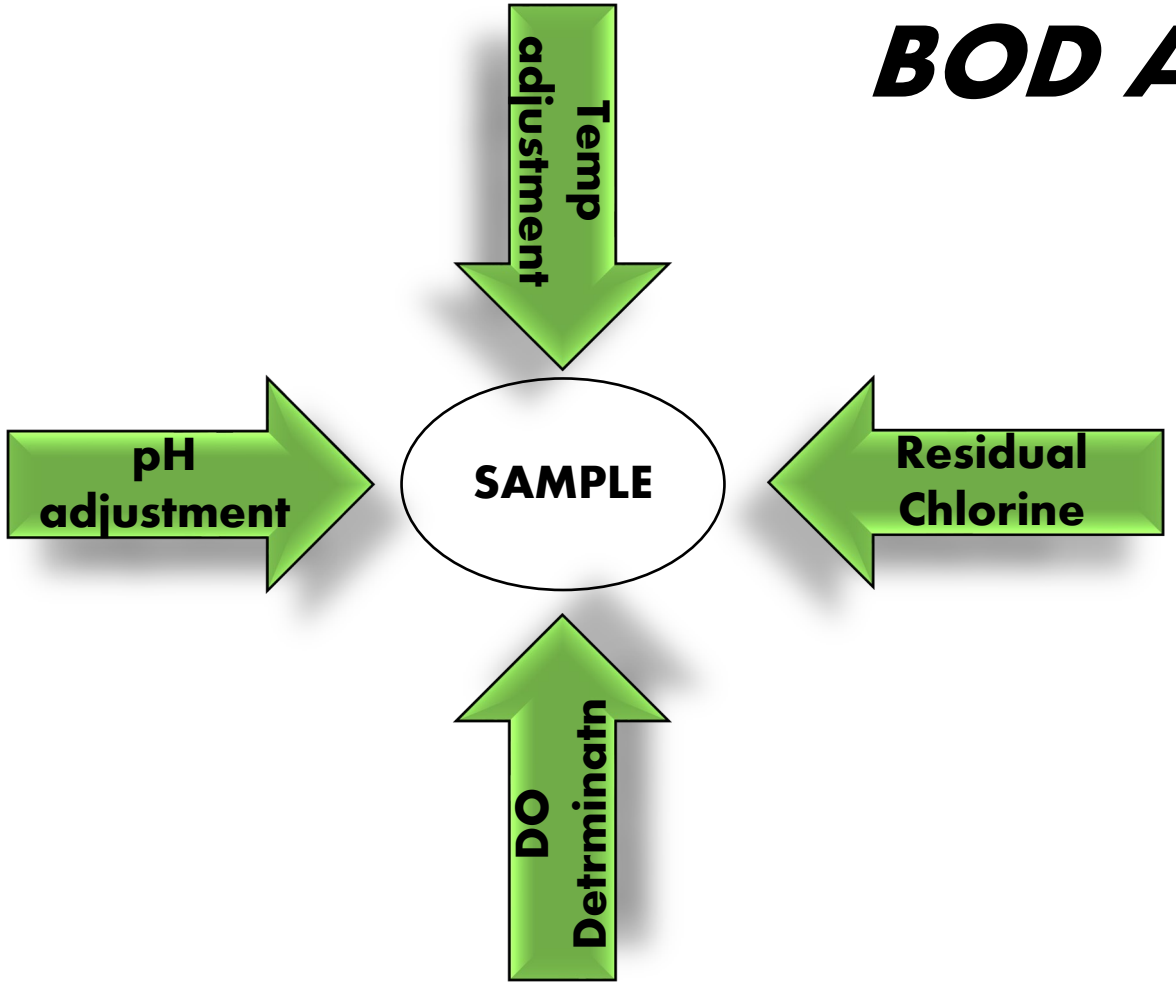
**SAMPLE**

**Cyanide**

**SAMPLE**

# WATER SAMPLES

## *BOD Analysis*




**PREPARATION OF CONTROLS**

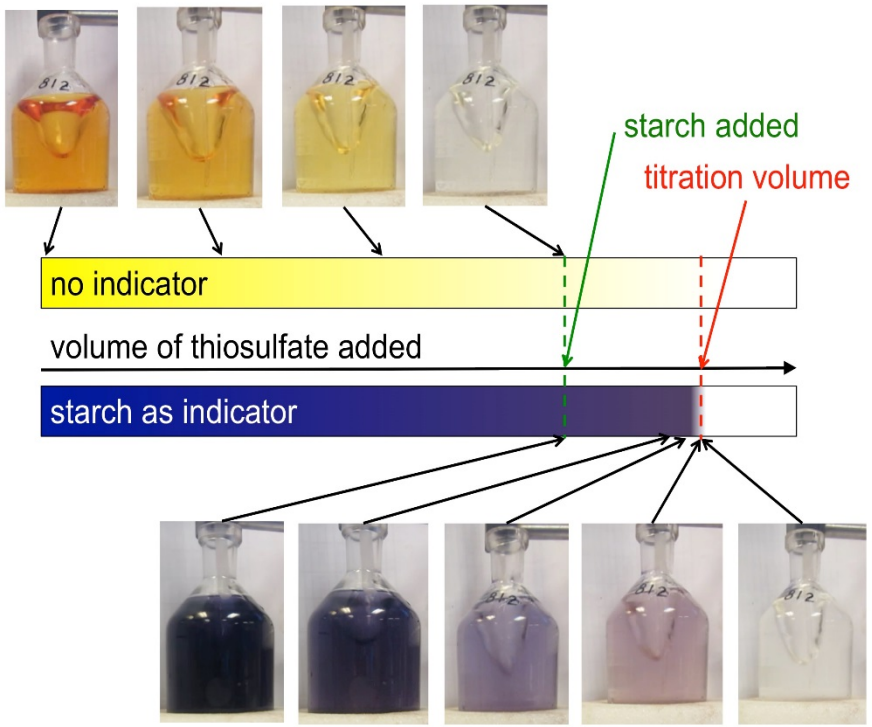
- ❑ **Seed Suspension**
- ❑ **Glucose-Glutamic Acid Check**

# WATER SAMPLES

## *BOD Analysis*

**SAMPLE**

**Initial DO determination**

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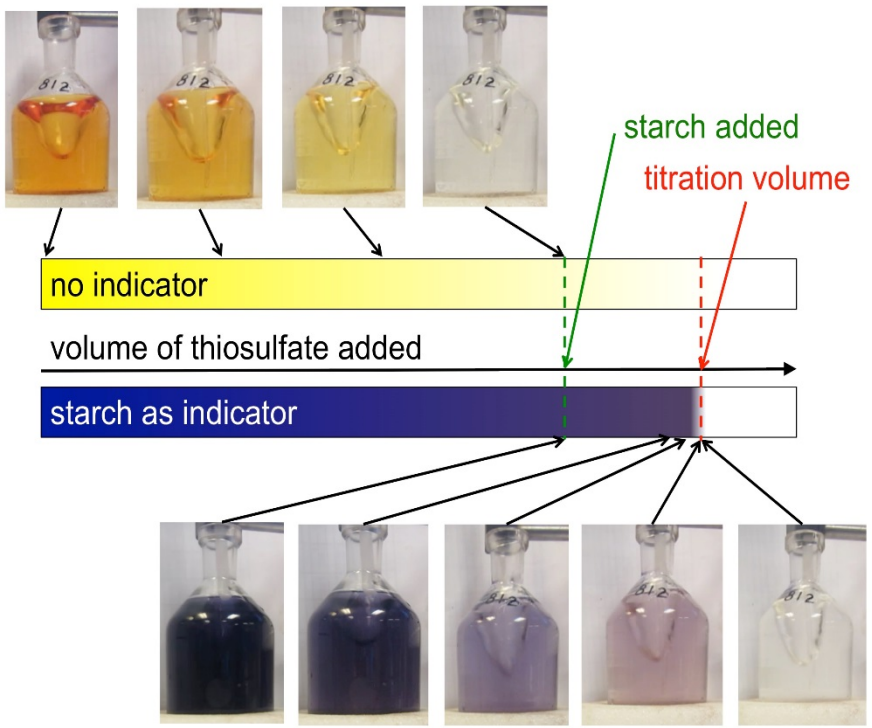
**Incubation for 5 days**

# WATER SAMPLES

## *BOD Analysis*

**Final DO determination**




**Calculation**

# WATER SAMPLES

## *COD Analysis*

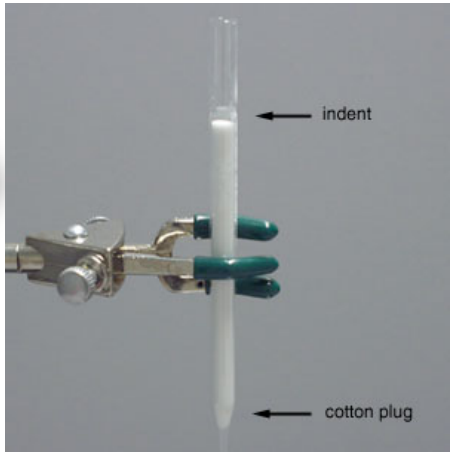
SAMPLE

**COD Digester**

# WATER SAMPLES

## *Individual Organics*

SAMPLE

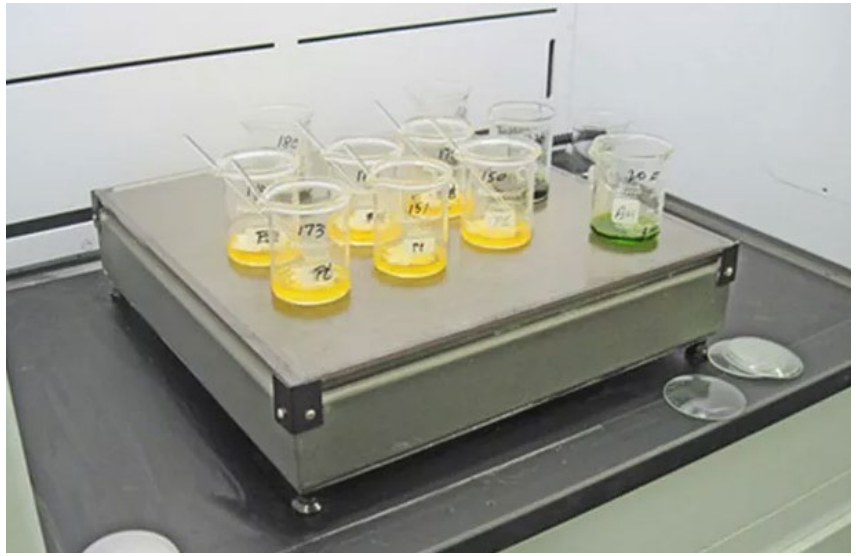



**Extraction** **Purification** **Determinative**

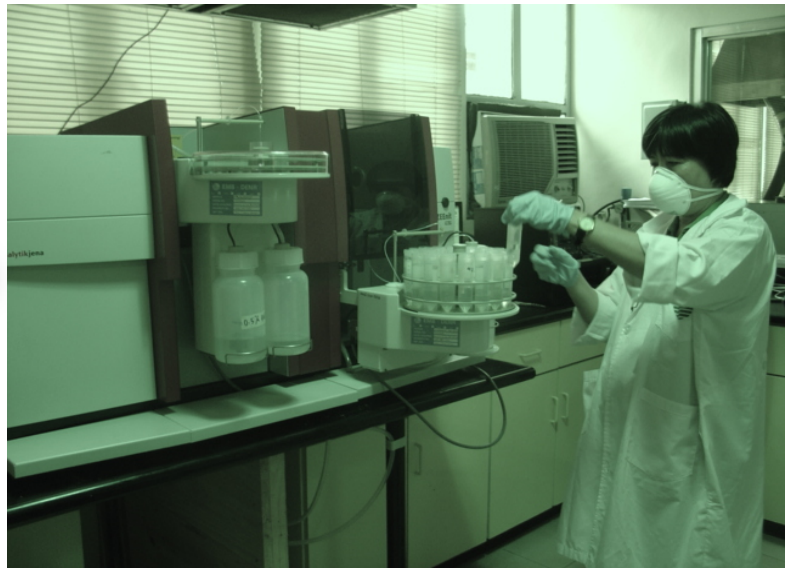
# WATER SAMPLES

## *Metals*

SAMPLE



**Hotplate Digestion**



**Determinative**

# Quality Assurance and Quality Control

## Quality Assurance

*An overall management plan to guarantee the integrity of data (The "system")*

## Quality Control

*A series of analytical measurements used to assess the quality of the analytical data (The "tools")*

# Quality Assurance (QA) elements

-quality system documentation
-staff organization and responsibilities
-sample control and documentation
-test method documentation
-analyst training
-equipment  calibration and maintenance
-corrective and preventive action
-internal quality control
-performance audit
-data assessment
-data reduction, validation and reporting

*(Standard:  PNS ISO/IEC 17025: 2005 Gen. requirements for the competence of testing and calibration labs)*

# Why QA/QC?

- To verify precision and accuracy
- To determine if interferences are present

  Interferences – substances in a sample that cause false positives or false negatives

- To check for contamination

  Results in false positives

  Caused by dirty containers, glassware, improper sampling and handling techniques

  Can happen at any stage of sampling or analysis

ENSURES DATA QUALITY AND GIVES CONFIDENCE!

# QUALITY CONTROLS

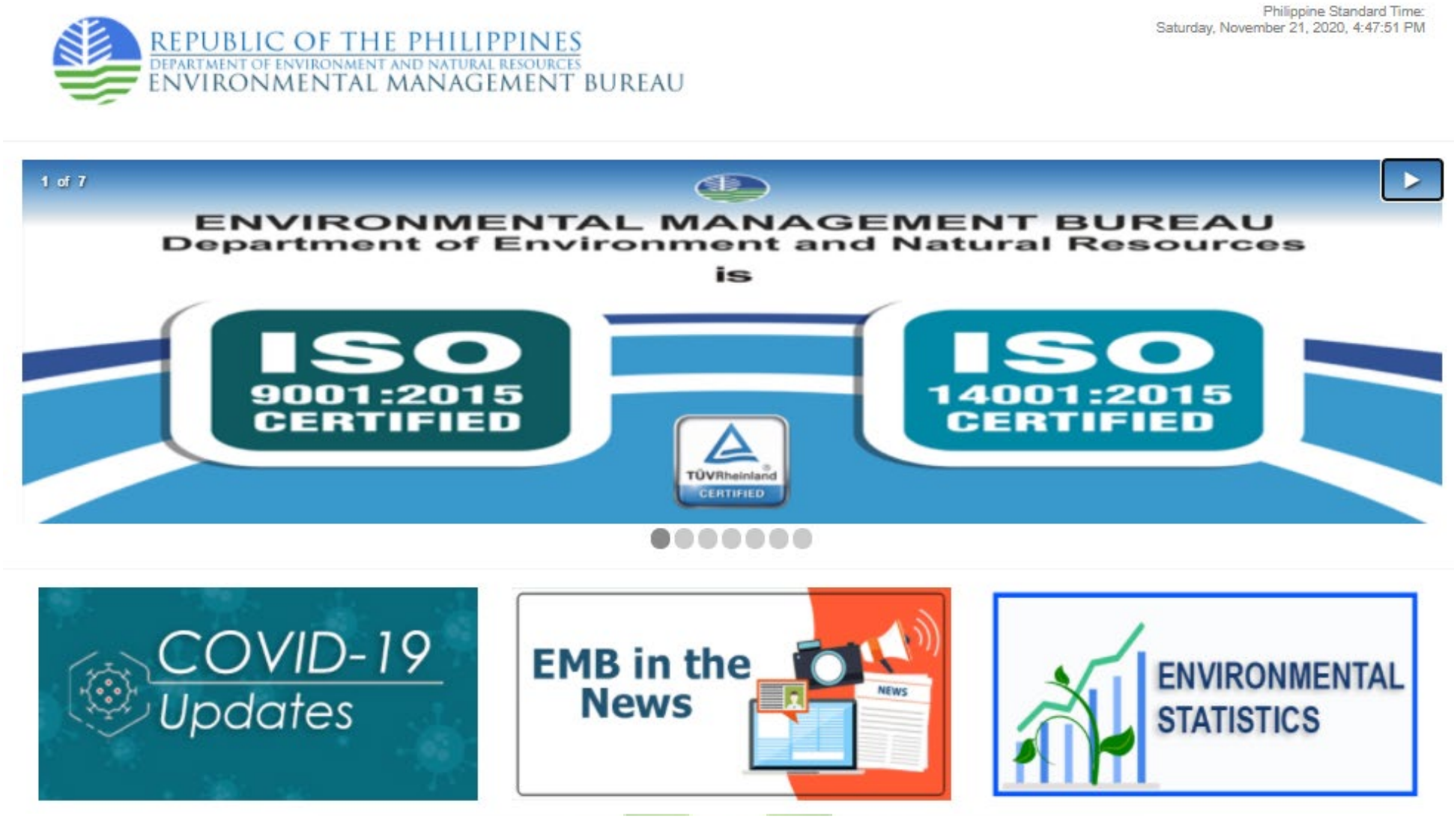
- Laboratory Blank
- Laboratory Fortified Blank
- Laboratory Fortified Matrix
- Calibration Verification Standard
- Calibration/ Standardization
- Duplicate
- Surrogate
- Method Detection Limit
- Proficiency Testing Samples

# UPDATE ON DENR-RECOGNIZED ENVIRONMENTAL LABORATORIES (As of September 2021)

| Region | No. of Labs Recognized | Region | No. of Labs Recognized |
|---|---|---|---|
| 1 | 1 | 8 | 2 |
| 2 | 0 | 9 | 1 |
| 3 | 4 | 10 | 6 |
| 4A | 16 | 11 | 3 |
| 4B | 1 | 12 | 1 |
| 5 | 1 | 13 | 1 |
| 6 | 2 | CAR | 1 |
| 7 | 5 | NCR | 17 |

**Total = 60 Environmental Laboratories**

# EMB Website…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1 of 7
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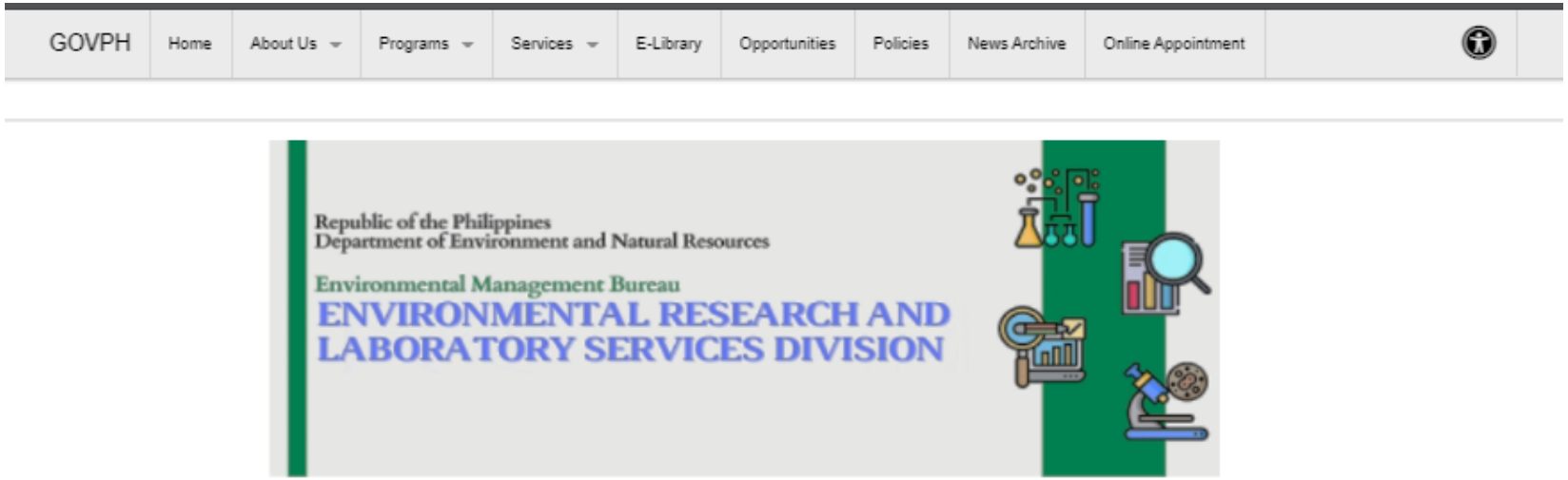
## Environmental Statistics

- DENR Recognized Environmental Laboratories
- Hazardous Waste Management Data
- Chemical Management Data
- Air Quality Management Data
- Water Quality Management Data
- Environmental Impact Assessment Data
- Solid Waste Management Data

# EMB Website…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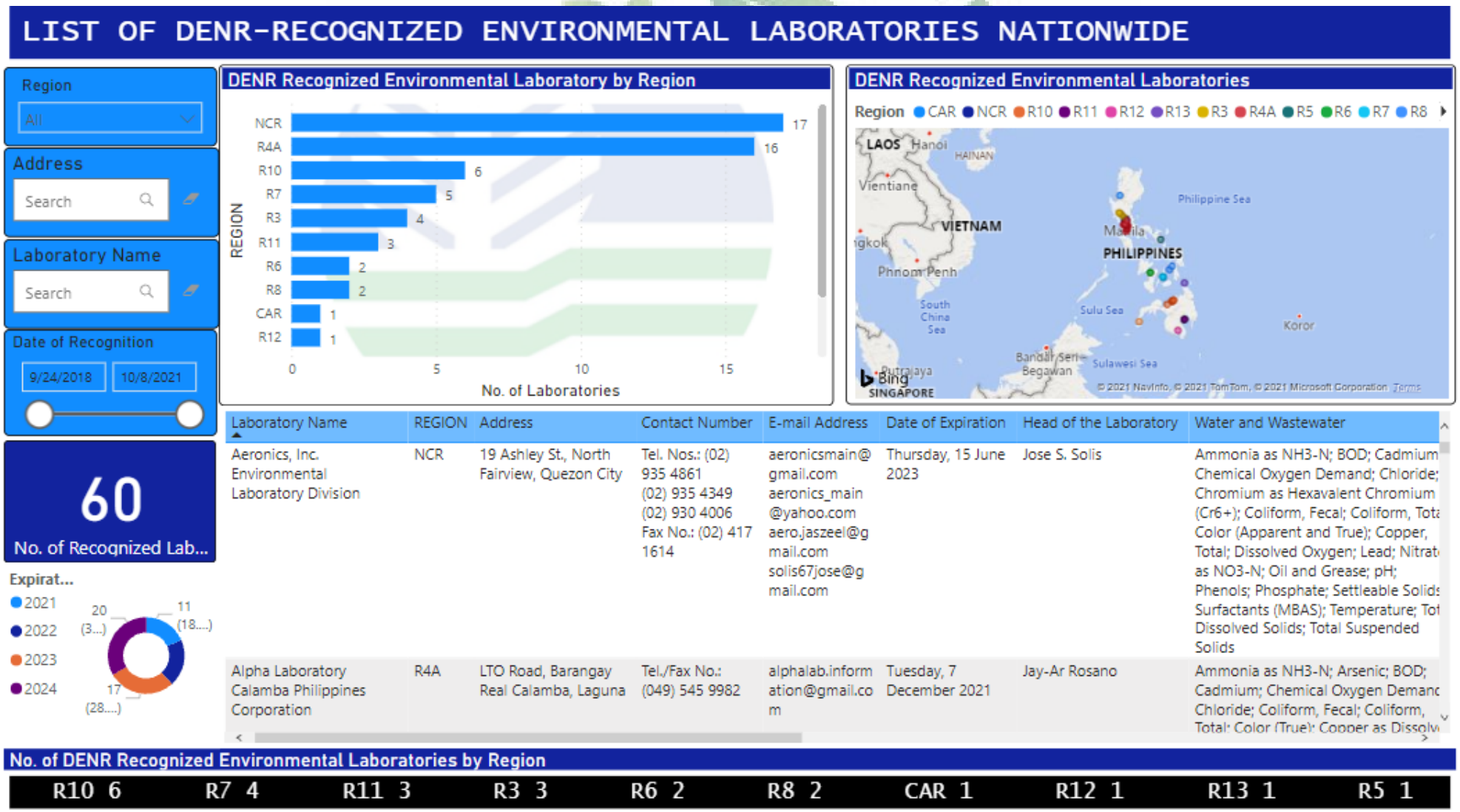
The Environmental Research and Laboratory Services Division (ERLSD), formerly known as the Research and Development Division (RDD), is one of the nine (9) divisions of EMB that support its functions and responsibilities embodied in legal instruments, e.g., Executive Order No. 192, signed in June 1987. It supports the implementation of the different environmental laws that the EMB is mandated to implement, particularly those requiring laboratory support services and research.
ERLSD Data
Capabilities and Directory of EMB Laboratories
DENR Recognized Environmental Laboratories

# List of DENR-Recognized Labs...



# THANK YOU FOR LISTENING! ☺