



DHV BV in joint venture  
with COWI A/S, ECORYS,  
and WL | Delft Hydraulics

# Caspian Water Quality Monitoring and Action Plan for Areas of Pollution Concern

## Proficiency Testing

Stephen de Mora

February 2008



# Caspian MAP

Tacis/2005/109244



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## Outline

- Introduction
- First Proficiency Test (PT 2005)
- Proposed Proficiency Test (PT 2008)

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## Introduction



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## Data Quality

### *Accuracy:*

A fundamental requirement for the monitoring and assessment of marine contamination is *accurate* analytical data for pollutant concentrations in the various environmental compartments.

### *Precision:*

While trueness (accuracy) cannot be compromised, an acceptable level of *precision* may vary depending on the use to be made of the data.

## Definitions

**Accuracy** – the closeness of agreement between a test result and the accepted reference value.

**Trueness** – the closeness of agreement between the average value obtained from a series of test results and the accepted reference value.

**Precision** - the closeness of agreement between independent test results obtained under stipulated conditions.

*From International Standards Organisation (ISO, 1994)*

## QA/QC

### ***Quality Control (QC): (internal)***

QC procedures commonly comprise the analysis of reference materials (RMs) and certified reference materials (CRMs) to assess precision and trueness

### ***Quality Assurance (QA): (external)***

QA procedures are usually realized through participation in proficiency tests that compare and evaluate analytical performance

## Proficiency Testing

### ***Synonyms:***

- Proficiency Test
- Round Robin
- Inter-comparison Exercise
- Inter-calibration Exercise
- Inter-laboratory Study
- Laboratory Performance Study (LPS)

## What is a Proficiency Test? 1

Under the supervision of a qualified reference laboratory:

- A test sample is carefully prepared and bottled in a manner to ensure the material is homogeneous and stable.
- The test sample is distributed to laboratories for analysis of a specified set of parameters.
- Participating laboratories return data to the reference laboratory.

## What is a Proficiency Test? 2

- The reference laboratory interprets data, both individually and collectively.
- Individual laboratory performance for each determination is assessed.
- Advice on remedial action is given to laboratories.
- Laboratory participation is generally anonymous, but laboratories can use their results as proof of external QA when submitting monitoring data to a third party database.

## Value of Proficiency Testing 1

- One-off participation in a blind, external QA programme permits an **independent assessment** of data quality from an individual laboratory or a laboratory network.
- Helps ensure **comparability** between results, either due to multiple laboratories generating data or due to the same laboratory performing measurements over time.



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## Value of Proficiency Testing 2

- Ongoing involvement can **identify trends**, normally towards improving data quality.
- Can **stimulate improved analytical performance** at the individual laboratory level.

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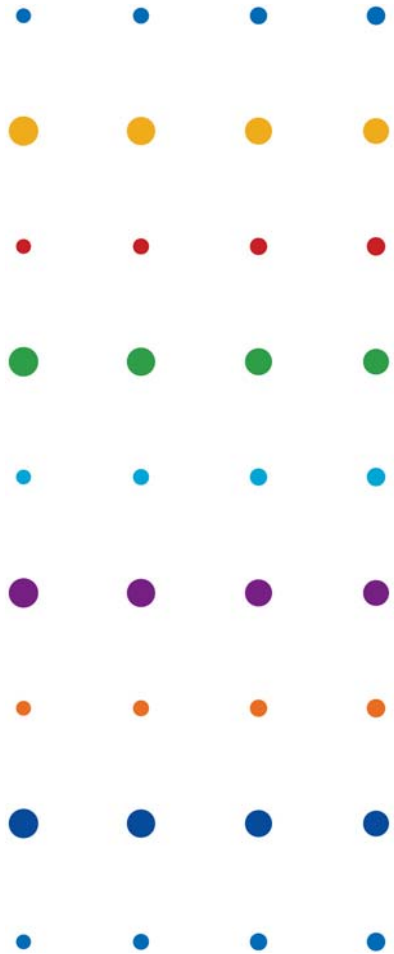
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## PT 2005



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## PT 2005 - Sample Dispatch

### *Organics:*

- Test material was IAEA-417
- 12 sets were sent by DHL in March 2005
- Only 3 returns by end of July, 2005

### *Metals:*

- Test material was IAEA-356
- 10 sets were sent by DHL in March 2005
- 7 returns by end of July, 2005

## PT 2005 - Z-scores for OCPs

Lab	HCB	<i>pp'</i> -DDE	<i>pp'</i> -DDD	<i>pp'</i> - DDT	<i>op'</i> -DDD
1	-	-5.5	-	-7.7	-
2	-6.8	-7.8	-7.9	-6.6	-7.6
Lab	<i>op'</i> -DDT	Heptachlor	Aldrin	Dieldrin	Endrin
1	-	-	-	-	-7.2
2	-7.6	-7.4	-7.5	-7.6	-7.9
Lab	$\alpha$ -Chlordane	$\gamma$ -Chlordane	PCB-138	PCB-153	PCB-180
1	-	-	-7	42	-3.8
2	-7.6	-7.2	-	-	-

## PT 2005 - Z-scores for PAHs

Lab	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz (a) anthracene	Chrysene
1	2.2	-1	0.3	5.4	3.4	4.6
2	0.3	-2	-0.4	1.1	-	0.3
3	-2.1	-5.9	6.5	1.5	3.1	-4.5
Lab	Benzo (b) fluoranthene	Benzo (k) fluoranthene	Benzo (a) pyrene	Indeno (123cd) pyrene	Dibenz (ah) anthracene	Benzo (ghi) perylene
1	-0.2	0.7	4.8	-	-	11
2	-2	-	0.7	0.1	-0.4	4
3	-	-	9.9	-	-	-

## PT 2005 - Z-scores for Metals

Lab	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
1		-2.8	-0.5	-0.4	-2.5	0.2		-1.1	-0.4	-1.3	0.7	-1.2
2	3.2	1.1	-4.8	-0.8	-0.5	-1.2	0.0	-7.2	-0.1	-1.4	0.2	-0.2
3		-0.4	-1.0	0.1	1.3	0.1	0.0	-1.1	0.9	0.1	0.0	1.1
4			-5.3	-0.1		-0.3	11.1		0.7		0.5	-3.5
5			-3.7			-7.3		-7.9			-5.0	-6.8
6			6.8			4.8				10.8	5.5	-3.4
7	-5.7		-6.8	-4.0		-5.9	-2.8		-5.2	-5.0	-4.0	-3.3

## PT 2005 - Conclusions

### Poor participation in proficiency tests

- 7 out of 10 for metals
- 3 out of 12 for organics

### Poor performance on the part of laboratories

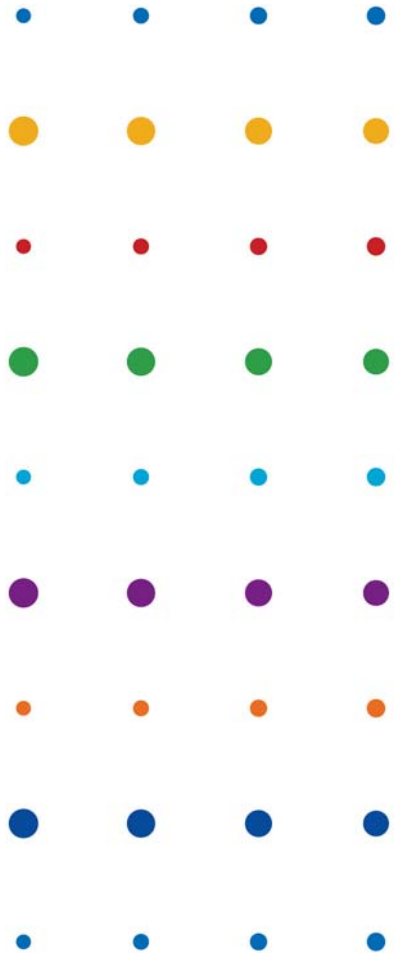
#### **Metals:**

- 2 very good labs, 3 very poor labs

#### **Organics:**

- No labs able to analyse chlorinated pesticides
- 1 lab can measure PAHs

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## PT 2008 - Improvements

1. Use sediment from the Caspian Sea
2. Parameters to include radionuclides
3. Involve only national laboratories (max 2 per country) that are **willing and able** to participate, and **guarantee to submit results**

## PT 2008 - 1. Test Sample

- Sediment core collected near the mouth of the Kura River during the IAEA mission in 2006
- Homogeneous mixture - layers from one core combined to give one sample (1.15.kg)
- Sample was dried, milled, & sieved  $<125 \mu\text{m}$

## PT 2008 - 1. Test Sample

- Bottled:
  - Metals: 20 g aliquots in plastic bottles with Teflon-lined plastic caps
  - Organics: 40 g aliquots in amber glass bottles with aluminium caps
- Homogeneity tests to be based on analyses of Cd, Cu, DDT,  $^{137}\text{Cs}$ ,  $^{40}\text{K}$

## PT 2008 - 1. Test Sample

- Material to be characterized by three reference laboratories:
  - Ukrainian Center for Marine Ecology (UCME), Odessa, Ukraine
  - Scientific Industrial Association “Typhoon” (SIA Typhoon), Obninsk, Russian Federation
  - IAEA - Marine Environment Laboratory (IAEA-MEL), Monaco

## PT 2008 - 2. Parameters

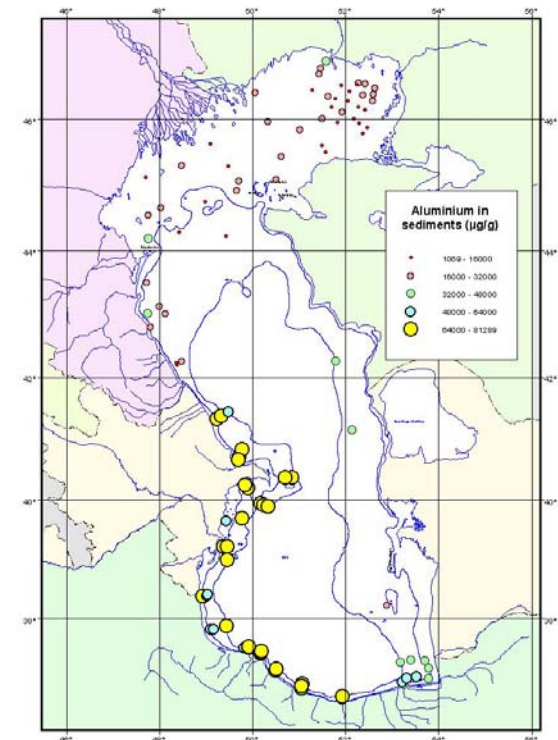
### *2000-2001 CEP Survey*

105 surface sediment  
samples

Pollution observed:

- Petroleum hydrocarbons
- DDT-related compounds
- Lindane
- Hg, Cu & Zn

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## PT 2008 - 2. Parameters

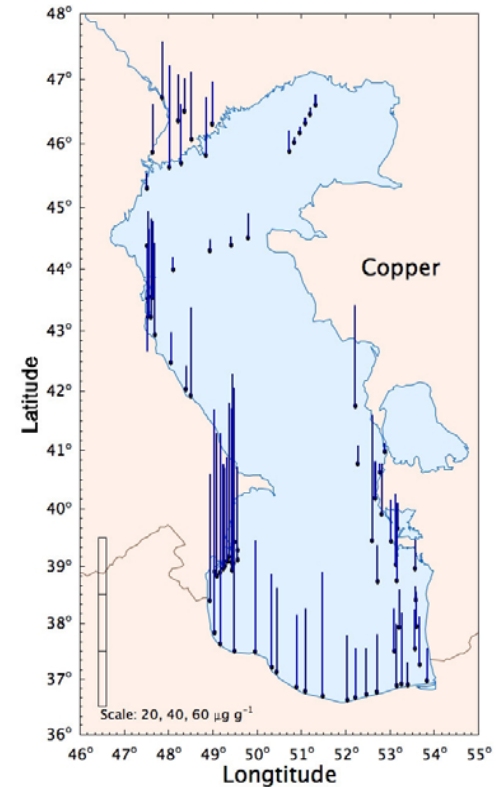
### 2005 CEP Survey

84 surface sediment samples

Pollution observed:

- PCBs
- DDT - related compounds
- Hexachlorocyclohexanes (HCHs), notably Lindane
- Hg & Cu

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## PT 2008 - 2. Parameters

### *Metals:*

- Al, Cr, Cu, Hg, Ni, Zn

### *Organics*

- total petroleum hydrocarbons (TPH)
- PCBs
- DDT - related compounds (DDT, DDD, DDE)
- Hexachlorocyclohexanes (HCHs), notably Lindane

### *Radionuclides:*

- $^{40}\text{K}$ ,  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ ,  $^{238}\text{U}$ ,

## PT 2008 - 3. Participants

### ***National Laboratories:***

- Maximum 2 per country
- Should be capable of performing the required analyses
- Must be willing to participate and provide results

## PT 2008 - Time Table

<b>Jan</b>	Preparation of test sample
<b>Feb</b>	Characterization of test sample
<b>Early March</b>	Distribution to laboratories by DHL (test material, instructions and reporting forms)
<b>April</b>	Chemical analyses in laboratories
<b>Late May</b>	Submission of results to CMSET
<b>June</b>	CMSET interpret data and prepare report



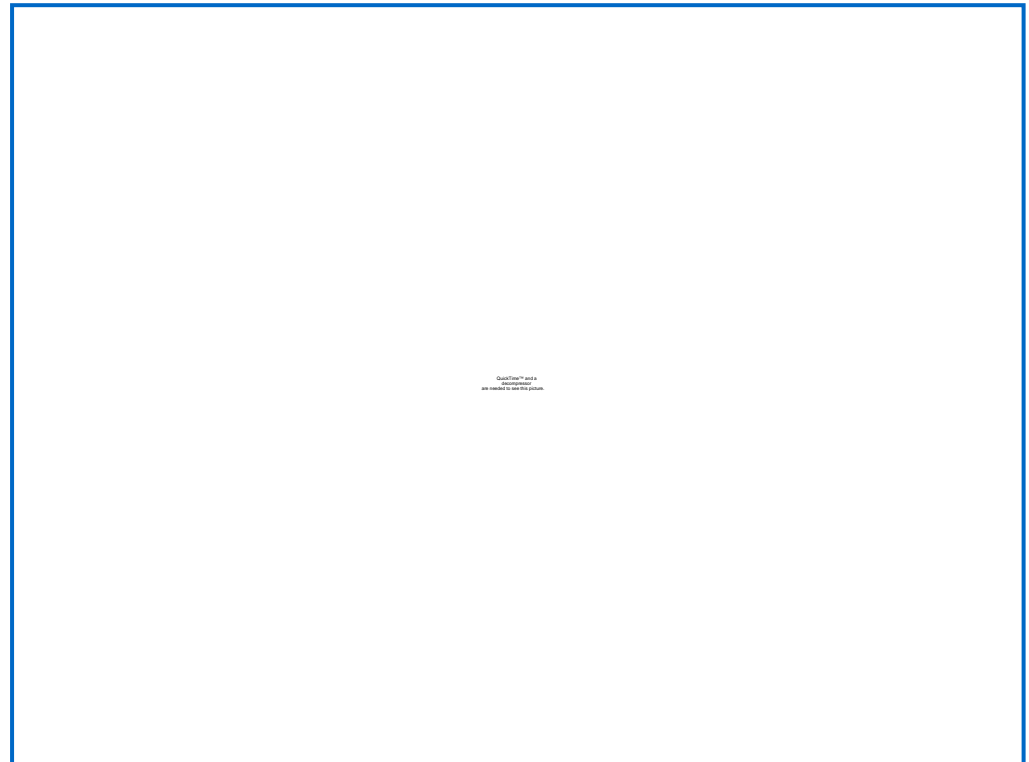
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## Thank You



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