South African highlights & expectations

Dr Jayne de Vos

UNEP/GEF Workshop
Accra, Ghana – 06-08 July 2016
NMISA’s mandate

Described broadly, NMISA’s functions include:

• Providing a measurement framework that is internationally acceptable;
• Ensuring that South Africa (and the region’s) interests are protected in drafting international rules and regulations;
• Assistance with drafting South African National Standards (SANS) and compulsory specifications by guiding attainable measurement limits and ranges;
• Providing accurate and traceable measurements acceptable in a court of law;
• Conducting benchmarking exercises in support of accredited laboratories;
• Coordinating PT comparisons/ inter-laboratory comparisons for industry
• Provide training with regard to measurement science

Source: Act No. 18 of 2006: Measurement Units and Measurement Standards Act, 2006
NMISA’s role

- The primary functions are to:
  - Provide traceability to the international system of units
  - Provide reference measurements
  - Provide calibration services where there is a gap nationally
  - Provide consultation
  - Provide training in the calculation of uncertainty
  - Remain abreast of international developments relating to improved measurement accuracy through dissemination of measurement traceability

- NMISA will establish a capability and then look to partner with industry/ or a laboratory to do the actual measurements; not routine analytical measurements where there is industry capability

- NMISA will also train scientists (industry and research) in the methodology and traceability required to obtain good results

- Serve its stakeholders and industry in support of competitive trade including, but not limited to, the food and feed sectors, as well as supporting environmental and health legislation
Technical Infrastructure

Metrology:
underpins testing and calibration through measurement accuracy and traceability

Accreditation:
provides formal recognition to perform calibration and measurement tasks

Standardisation:
documentary standards for validated methods used in industry

Regulation:
administrates regulation to ensure compliance and protect human health and safety

SABS

SANAS

NRCS

NMISA
Regional activities

- 42 principal members (end 2015)
- In support of the CFTA and accredited testing facilities;
  - Produce calibration solutions
  - Introduce a PT scheme category within the comparison framework
  - Services database for metrology institutes (peer reviewed acceptance of capabilities for intra-Africa trade)
- With AFRAC, facilitate technique accreditation for NMIs in Africa
Why do we have to measure POPs?

Countries and trade regions impose regulations and directives to trade goods, protect the health of their people and the environment.

Stricter legislation and the initiation of environmental programs are being applied globally to limit these emissions.

The Stockholm Convention (SC) is a global treaty to protect human health and the environment from persistent organic pollutants (POPs).

In implementing the SC, Governments must take measures to eliminate or reduce the release of POPs into the environment, making the analysis of environmental pollutants a legal obligation.

South Africa has signed this Convention and therefore has an obligation to undertake appropriate research, monitoring, and co-operation pertaining to POPs, and more particularly, PCDD/Fs.
Why do we need this in SA?

The list of potentially hazardous chemicals is ever increasing; the lack of analytical services to monitor these toxins; it’s a compliance issue.

South Africa, as with most developing countries, has no established GC-HRMS facility for dioxin analysis.

Necessitates the development of an alternative solution to measure PCDD/Fs at ultra-trace levels amidst challenging high levels of contaminants.

Investigate selectivity, understand LOD/LOQ to reliably quantify PCDD/Fs in the presence of interferences and assess the accuracy of the GCxGC-TOFMS method.

Dioxins

Furans

PCBs
Research outcomes & collaboration

• Metrologically traceable reference measurement for the accurate quantification of dioxins and brominated flame retardants in the South African environment
• Developed methods for the extraction, analysis and quantification of PFCs in various environmental matrices
• Pesticide analysis in environmental matrices, as well as human biomonitoring for new generation pesticides and their metabolites
• Analysis of PAHs in abiotic and biotic matrices
• Close collaboration with UP, NWU and ULg
• IVM, MOE, Restek, LECO Africa and EPA Taiwan
Research highlights

- **Data generation** of persistent organic pollutants (POPs) and toxicants in abiotic and biotic matrices
  - Perfluorinated compounds (PFCs)
  - Polychlorinated biphenyls (PCBs)
  - Organochlorine pesticides (OCPs)
  - Polycyclic aromatic hydrocarbons

- **Training Programmes**
  - Introduction to the analysis of POPs
  - Use of the QuEChERS extraction technique for the analysis of PAHs
  - Analytical Proficiency
  - Analytical quality assessment and quality control
Publications & posters

Experience in South Africa of combining bioanalysis and instrumental analysis of PCDD/Fs

Jayne de Vos, Laura Quinn, Claudine Roos, Rialet Pieters, Peter Gorst-Allman, Egmont Rohwer, John P. Giesy, Henk Bouwman

Levels of PCBs in wild bird eggs: Considering toxicity through enzyme induction potential and molecular structure

L.P. Quinn a,b,*, C. Roos a, R. Pieters a, K. Laken c, A. Polder a, J.U. Skaare b, H. Bouwman a

PERFLUORINATED COMPOUNDS IN WATER, SEDIMENT AND WILD BIRD EGGS FROM THE ORANGE-SENQU RIVER, SOUTH AFRICA

Swiegelaar CR 1,2, Quinn LP 1,2, Prevoor-Franzsen D 1, Bouwman H 2

METHOD VALIDATION FOR THE QUANTIFICATION OF PFOS AND PFOA IN FISH

Swiegelaar CR 1,2,*, Prevoor-Franzsen D 1, Bouwman H 2, Quinn LP 1,2

ANALYTICAL ADVANTAGES OF SELECTIVE PRESSURISED LIQUID EXTRACTION COMBINED WITH TIME OF FLIGHT MASS SPECTROMETRY FOR THE QUANTIFICATION OF POLYBROMINATED DIPHENYL ETHERS IN SEDIMENT

Brits M 3,4,5, Quinn LP 1, De Vos J 1, Weerts J 1, Rohwer E 1, De Boer J 1, 4.
1. NMISA, Organic Analytical Section, Meteor Neutelpoel Road, Bruma, Pretoria, South Africa, 2. University for Environmental Studies (UVM), De Boelelaan 1087, 1081 HV Amsterdam, The Netherlands, 3. University of Pretoria, Department of Chemistry, Pretoria, South Africa, 4. North-West University, Unit for Environmental Sciences and Management, Potchefstroom, South Africa

NMISA © Copyright 2016
Green economies
- Primary reference gas mixtures (PRGMs)
- Traceability to GAW Cape Point
- Particle size for suspended particulate matter
- Silicon nano-wires and organic solar cells
- Surface analysis (elemental and chemical composition)
- Environmental monitoring (PAHs, PFCs, PCBs, Dioxins, BFRs, PFOS and pesticides)

African Food and Feed Certified Reference Materials program
- Certification of toxic/nutritional elements in wheat flour
- Multi-mycotoxins in maize RMs, CRMs and reference measurements
- Amino acid content in infant formula (nutritional labelling)
- Phthalates in PVC food packaging
- Hazardous organic chemicals in South-African fish
- Dioxins and dioxin-like PCBs in food and feed, etc

Integrated Human Capital Development Program
- Improve staff qualifications
- Appoint qualified and experienced research staff
- Interns and Bursars
- Contract: retired, experienced individuals to partner with students and assist with training
- External training provided by NMISA
## Analytical capability

<table>
<thead>
<tr>
<th>Chemical class</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pesticide and pesticide metabolite residues</strong></td>
<td></td>
</tr>
<tr>
<td>Pyrethroid, triazines, carbamates, organophosphates, organophosphates and aniline pesticides</td>
<td>Plant material</td>
</tr>
<tr>
<td>Pyrethroid, organophosphates, carbamates and associated metabolites</td>
<td>Urine and breast milk</td>
</tr>
<tr>
<td>Organochlorine and organophosphates pesticides</td>
<td>Water</td>
</tr>
<tr>
<td>Organochlorine pesticides</td>
<td>Soil, sediment and mussel</td>
</tr>
<tr>
<td><strong>Priority pollutants</strong></td>
<td></td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons</td>
<td>Soil, sediment, mussel, fish and bird eggs</td>
</tr>
<tr>
<td>Phthalates</td>
<td>PVC</td>
</tr>
<tr>
<td><strong>Persistent organic pollutants</strong></td>
<td></td>
</tr>
<tr>
<td>Polychlorinated dibenzo-p-dioxins</td>
<td>Soil and sediment</td>
</tr>
<tr>
<td>Polychlorinated dibenzofurans</td>
<td>Soil and sediment</td>
</tr>
<tr>
<td>Polynbrominated diphenyl ethers</td>
<td>Soil, sediment</td>
</tr>
<tr>
<td>Polychlorinated biphenyls</td>
<td>Soil, sediment and mussel</td>
</tr>
<tr>
<td>Perfluorinated compounds</td>
<td>Soil, sediment, water, bird eggs and fish</td>
</tr>
<tr>
<td><strong>Food contaminants</strong></td>
<td></td>
</tr>
<tr>
<td>Melamine</td>
<td>Infant formula</td>
</tr>
<tr>
<td>Mycotoxins</td>
<td>Maize and wine</td>
</tr>
<tr>
<td><strong>Pharmaceutical residue</strong></td>
<td></td>
</tr>
<tr>
<td>Benzodiazepine</td>
<td>Wine</td>
</tr>
<tr>
<td>Antibiotic residue</td>
<td>Milk and pork meat</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical class</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas Analysis</strong></td>
<td></td>
</tr>
<tr>
<td>Volatile Organic compounds</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Green-house gasses</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Stack emission gases (CO(_x), SO(_x), NO(_x))</td>
<td>Nitrogen/Air</td>
</tr>
<tr>
<td>Indoor and outdoor Air Quality Standards (medical gases)</td>
<td>Nitrogen/Air</td>
</tr>
<tr>
<td>Air Pollution gases</td>
<td>Nitrogen/Air</td>
</tr>
<tr>
<td>Automotive exhaust gas mixtures for emissions</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Ethanol (breath alcohol)</td>
<td>Nitrogen/Air</td>
</tr>
<tr>
<td>BTEX</td>
<td>Nitrogen</td>
</tr>
<tr>
<td><strong>Metal analysis in food matrices</strong></td>
<td></td>
</tr>
<tr>
<td>Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn</td>
<td>Water</td>
</tr>
<tr>
<td>Essential (Fe &amp; Zn) and Toxic Elements (Cd, Pb)</td>
<td>Bovine liver</td>
</tr>
<tr>
<td>Trace metals (Ni, Pt, Cd, Cr, Hg, Pb)</td>
<td>Algae</td>
</tr>
<tr>
<td>Essential element (Se)</td>
<td>Wheat flour</td>
</tr>
<tr>
<td>Toxic elements (Sn, Pb and Cd)</td>
<td>Tomato paste</td>
</tr>
<tr>
<td>Trace elements (Zn)</td>
<td>Soybean</td>
</tr>
<tr>
<td>Trace elements (Pd, Cd, Ca and Fe)</td>
<td>Wine</td>
</tr>
<tr>
<td>Trace elements (Cd)</td>
<td>Rice</td>
</tr>
<tr>
<td>Essential (Ba, Ca, Cu, Fe, Sr, and Zn) and toxic elements (Cd, Ni and Pb)</td>
<td>Tobacco</td>
</tr>
<tr>
<td>Essential elements (K, Cu)</td>
<td>Infant formula</td>
</tr>
</tbody>
</table>
### Inter-laboratory benchmarking

#### NMI comparisons (CCQM)

<table>
<thead>
<tr>
<th>Coordinating laboratory</th>
<th>Description</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>GLHK/NIM China 2011-2012</td>
<td>CCQM P136 - Endosulfan II and endosulfan sulfate in green tea</td>
<td>Completed</td>
</tr>
<tr>
<td>BIPM 2012-2013</td>
<td>Purity assessment L-valine</td>
<td>Completed</td>
</tr>
<tr>
<td>NIM China 2012-2013</td>
<td>CCQM K103 Melamine in milk powder</td>
<td>Completed</td>
</tr>
<tr>
<td>BIPM/NIM 2014-2015</td>
<td>CCQM K115 - Peptide purity</td>
<td>Completed</td>
</tr>
<tr>
<td>GLHK 2015-2016</td>
<td>CCQM K126 - Carbamazepine in Surface Water</td>
<td>Completed</td>
</tr>
<tr>
<td>IRMM 2015-2016</td>
<td>CCQM K102 - PBDEs in sediment</td>
<td>Completed</td>
</tr>
<tr>
<td>BIPM 2016-2017</td>
<td>CCQM K55d - Purity assignment Folic acid (mass balance)</td>
<td>Completed</td>
</tr>
<tr>
<td>BIPM 2016-2017</td>
<td>CCQM.P117d - Purity assignment Folic acid (Q-NMR)</td>
<td>Completed</td>
</tr>
<tr>
<td>UME 2016-2017</td>
<td>CCQM K138 - Aflatoxin in figs</td>
<td>In progress</td>
</tr>
<tr>
<td>NIST 2017</td>
<td>CCQM.K95.1 - PAHs in yerba mate tea</td>
<td>In progress</td>
</tr>
<tr>
<td>NIST 2017</td>
<td>CCQM.K131 - PAHs in acetonitrile calibration solution</td>
<td>In progress</td>
</tr>
<tr>
<td>UME 2017</td>
<td>CCQM K138 - Aflatoxin in figs</td>
<td>Registered</td>
</tr>
</tbody>
</table>

#### International comparisons

<table>
<thead>
<tr>
<th>Coordinating laboratory</th>
<th>Description</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>ERA USA 2012-2013</td>
<td>ERA CW 8 - OCPs in drinking water</td>
<td>Completed</td>
</tr>
<tr>
<td>FERA, UK 2013-2014</td>
<td>FAPAS 2998 – Multimycotoxins in maize</td>
<td>Completed</td>
</tr>
<tr>
<td>FERA, UK 2014-2015</td>
<td>FAPAS 04223 – Mycotoxins in maize</td>
<td>Completed</td>
</tr>
<tr>
<td>ERA USA 2015-2016</td>
<td>ERA EF 13 - OPPs in effluent</td>
<td>Completed</td>
</tr>
<tr>
<td>FERA, UK 2015-2016</td>
<td>FAPAS 04280 - Aflatoxins in fig slurry</td>
<td>Completed</td>
</tr>
<tr>
<td>FERA, UK 2016</td>
<td>FAPAS 04276 - Mycotoxins in maize</td>
<td>Completed</td>
</tr>
<tr>
<td>FERA, UK 2016</td>
<td>FAPAS 17156 - Ochratoxin-A in wine</td>
<td>Completed</td>
</tr>
<tr>
<td>FERA, UK 2016-2017</td>
<td>FAPAS 3060 - Melamine in milk</td>
<td>Completed</td>
</tr>
<tr>
<td>Quasimeme 2016-2017</td>
<td>PAH and PFCs</td>
<td>Registered</td>
</tr>
<tr>
<td>UNEP 2016-2017</td>
<td>OCPs, PCBs, PCDD/Fs, PBDEs and PFCs</td>
<td>Registered</td>
</tr>
</tbody>
</table>

- Aqueous ethanol proficiency testing scheme, 3 rounds, 3 levels each
- Aqueous sodium fluoride proficiency testing scheme, 1 round, 2 levels
- Organochlorine pesticides in water proficiency testing scheme, 1 round
- Organophosphorus pesticides in water proficiency testing scheme, 1 round

### NMISA coordinated proficiency testing schemes

- Aqueous ethanol proficiency testing scheme, 3 rounds, 3 levels each
- Aqueous sodium fluoride proficiency testing scheme, 1 round, 2 levels
- Organochlorine pesticides in water proficiency testing scheme, 1 round
- Organophosphorus pesticides in water proficiency testing scheme, 1 round
Strengthening analytical infrastructure

Inlet system:
- Gas chromatography electron impact ionization (GC-EI)
- Gas chromatography electron capture negative ionization (GC-ECNI)

Detector:
- Triple quadrupole mass spectrometer (MS/MS)

Inlet system:
- Comprehensive two-dimensional gas chromatography - electron impact ionization (GC×GC-EI)

Detector:
- Time-of-flight mass spectrometer (TOFMS)
Interchangeable inlet systems:
- High performance liquid chromatography
- Ultra high performance liquid chromatography
- Nano flow ultra-high performance liquid chromatography
- Gas chromatography atmospheric pressure chemical ionization
- Solid sample introduction probe

Detectors:
- Ion mobility accurate-mass quadrupole time-of-flight mass spectrometer (IM-QTOF)
- Triple quadrupole mass spectrometer (MS/MS)
- Photodiode Array (PDA) Detector
Strengthening analytical infrastructure

Accelerated Solvent Extraction (ASE)

TRP Total-Rapid-Prep system performs the pressurised liquid extraction (PLE), multi-column clean-up and concentration
### Trace Laboratory
- PCDDs
- PCDFs
- PBDEs
- PCBs
- PFCs
- PAHs
- Pesticides
- New generation POPs

### Toxicological Testing
- Reporter gene bio-assay
- Acute Toxicity assays
- Mutagenicity assays
- Broad spectrum screening

### CRM Production
- Combined Trace and Toxicological Environmental CRM
- Sediment
- Soil
- Fish
- Mussel
- NONE EXIST
Additional considerations

• The instruments are used for other projects within the section and as routine analysis becomes the primary objective, other activities may be delayed
• Limited/ no research; focus will be routine analysis and product development
• Will need budget to employ more qualified analysts
• Cost benefit to industry – time benefit
• Shift in current operations
• Large capital investment in laboratory space and infrastructure
• Initial investment with little to no return
• Improved collaboration with other institutes involved in monitoring POPs (AISA, DEA, etc)
Expectations

- Support from the expert laboratories in initial setup to establish a routine testing facility for PCDD/Fs
- Further collaboration in terms of the emerging POPs
  - Mr Martin Brits (DST/NRF scholarship under the VU Amsterdam-NRF Desmond Tutu Doctoral Programme and UP)
  - Ms Caitlin Swiegelaar (NWU/ NRF – Orasecom)
- NMISA focus will be geared more toward training and QA/ QC
- NMISA has planned an MSc bursar for 2017/18 (POP extraction techniques)
- NMISA has planned funding for a senior scientist for 2017/18 and 2018/19
QUESTIONS?

Dr Jayne de Vos (bjdevos@nmisa.org)