First mercury reference laboratory is established in Southern Africa

With its reliance on coal as an energy source, South Africa has established a dedicated resource to monitor for mercury released by combustion, and other routes, into the environment, as Project Leader **Vernon Somerset** explains.

Monitoring trace metals in the environment

Heavy metals are some of the most widespread of environmental pollutants. They originate predominantly from anthropogenic activities, such as mining, agriculture, industrial wastewater and effluent, urban runoff, irrigation with treated wastewater, and atmospheric deposition. Through these activities, large amounts of heavy metals are released into fluvial systems and can be transported along hydrogeological gradients for hundreds of kilometres in relatively short times. The release of heavy metals from these sources can occur both in dissolved and in particulate form. The continuous assessment and monitoring of trace metals in the environment is essential to gain a better understanding of the individual and interactive effects of the trace metals in water resources (*i.e.* rivers, lakes, dams, etc.) worldwide. National and international legislation have set limits for the maximum allowable concentrations of various trace metals in the air, water and aquatic ecosystems. In order to regulate and to comply with legislation, routine estimations of the amounts of metals in the environment are needed. Monitoring and measurements of heavy metals in the environment also require accredited sample collection procedures and analytical techniques (Somerset, 2009a).

Exposure sources and toxicity of mercury

Mercury in the environment has been a concern worldwide for many decades. Exposure of the human population to mercury can occur directly through the application of mercury and mercury compounds, and indirectly by eating fish and other aquatic food which have bioaccumulated methylmercury (Clevenger *et al.*, 1997; Dolci *et al.*, 2006; Peng *et al.*, 2005; Moreda-Piñeiro *et al.*, 2002). Mercuric sulphide has been used as a remedy for skin and eye complaints, and metallic mercury and mercuric chloride have also had medicinal applications in the past. Other applications of mercury and its compounds include diuretics, dental amalgam fillings, and antiseptics (Bontidean *et al.*, 2004; Hobman and Brown, 1997; Hobman *et al.*, 2000; Maggi *et al.*, 2009).

Mercury pollution from anthropogenic sources is common in industrialised countries, leading to direct pollution of soil and indirect contamination of groundwater and food sources (Bontidean *et al.*, 2004; Pan-Hou *et al.*, 2001; Di Natale *et al.*, 2006). Sources of mercury pollution include fossil fuel combustion, calcination of pyrites, or the releases from former industries (e.g. chlor-alkali plants), all of which result in the liberation of large amounts of mercury and its compounds into the biosphere (Peng *et al.*, 2005; von Canstein *et al.*, 1999; Krishnan and Anirudhan, 2002).

Elemental and mercuric mercury [Hg(0) and Hg^{2+}] are poorly absorbed from the gastrointestinal tract, but Hg(0) is readily absorbed by inhalation. Methylmercury compounds are absorbed through the skin, by ingestion and by inhalation, and have long retention times in the body. Mercurous salts are probably oxidised to Hg^{2+} in the gastrointestinal tract before absorption. The speciation of mercury compounds [Hg(0), Hg^{2+}, RHg^{+}, RHgR'] influences their distribution and hence their toxicity. The main target organ for inhaled mercury vapour and methylmercury in primates is the central nervous system, while the kidney is the target organ for mercuric mercury in all species. Methylmercury is mainly eliminated in faeces with partial demethylation; the predominant route of excretion of Hg^{2+} is urinary (Clarkson, 1997).

Determination of mercury

Classical methods and techniques for determining mercury in the environment include atomic adsorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS), atomic emission spectroscopy (AES), inductively-coupled plasma mass spectroscopy (ICP-MS), and capillary electrophoresis (CE). These are well-established methods and are characterised by low detection limits (i.e. 0.02 ppb for AAS; 0.001 ppt for AFS; 0.01 ppt for AES and 0.08 ppt for ICP-MS) (Bontidean *et al.*, 2004; Emteborg *et al.*, 1996; Cossa *et al.*, 1995; Jamoussi *et al.*, 1995; Hintelmann *et al.*, 1995; Peng *et al.*, 2005; Liu and Lee, 1998; Buffle and Tercier-Waeber, 2005).

Alternatives to the classical methods and techniques include electrochemical methods of mercury determination (e.g. ion-selective electrodes (ISE); anodic stripping voltammetry (ASV); potentiometric stripping analysis (PSA); current stripping chronopotentiometry (CSP); and differential pulse voltammetry (DPV). These methods are characterised by higher detection limits (i.e. 0.2 ppt for ASV; 0.5 ppb for PSA; 0.1 ppb for CSP and 2 ppt for DPV. However, they provide the opportunity for on-site screening for mercury in the environment (Bontidean *et al.*, 2004; Shatkin *et al.*, 1995; Wang and Tian, 1993; Beinrohr *et al.*, 1996; Ugo *et al.*, 1995; Dolci *et al.*, 2006).

Mercury in the South African environment

In order to investigate and understand the behaviour of mercury in the South African environment, the Council for Scientific and Industrial Research (CSIR) has established the first Mercury Reference Laboratory at the CSIR in Stellenbosch, Western Cape, South Africa. The laboratory forms part of the Water Ecosystems and Human Health research group, within the Natural Resources and the Environment (NRE) research sector in the CSIR. With this laboratory in operation, a team of CSIR researchers were able to conduct a national survey of mercury in the country's surface water resources. This investigation was conducted at over sixty sampling sites in all nineteen of South Africa's water management areas.

***Figure 1:** Water, sediment and biota samples from specific rivers were taken to the CSIR Mercury Reference Laboratory in Stellenbosch for sample preparation, digestion and analysis for total mercury and methylmercury concentrations, respectively*

Through this investigation we have gained a better understanding of the condition of our country's water and atmosphere in terms of the mercury released into the environment. The collected data also allowed us to assess how bioaccumulation occurs in the national freshwater aquatic food chains, and thereby determine the impact on the associated water resources and human health. Mercury in South Africa is typically released into the environment through coal combustion, waste incineration, base-metal smelting, artisanal gold production, and cement production. South Africa relies primarily on coal to produce energy at its many coal-fired power stations, where mercury is potentially released into the environment at our coal-fired power plants. These mercury emissions then enter our water ecosystems through wet and dry deposition, making it crucial to monitor and manage mercury in the South African environment. Results obtained from the national survey reveal elevated concentrations of total mercury (TotHg) and methylmercury (MeHg) at specific sites. These sites are located in the vicinity of coal-fired power plants, in an area impacted by artisanal gold mining activities, and at a previously Hg-contaminated area (Somerset *et al.* 2009b).

Analytical facilities and equipment

The Stellenbosch facility has state-of-the-art equipment for the analysis of water, sediment, biota (invertebrates and fish) and air samples for total mercury and methylmercury. Using the methods recommended by the US Environmental Protection Agency, TotHg and MeHg in water samples can be analysed to the nanogram per litre (or ppt) range, and in sediment and biota samples to the nanogram per gram (or ppb) concentration range.

The following instruments are available in the laboratory:

- A Tekran® Model 2500 Cold Vapour Atomic Fluorescence Spectrophotometric (CVAFS) detector that is used with an analytical system capable of producing mercury vapour in an Argon inert gas stream, followed by detection with the instrument.
- A Tekran® Series 2600 system that allows the analysis of ultra-trace levels of TotHg in water (or liquid) samples.
- A Tekran® Model 2537 Mercury Vapour Analyzer that provides continuous analysis of total gaseous mercury (TGM) in air at sub-ng/m^3 (parts per trillion (ppt) and parts per quadrillion (ppq)) levels.
- A Milestone® Direct Mercury Analyser (DMA-80) for the determination of TotHg in sediment and biological tissue, allowing effortless of solid samples with no sample preparation.

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