Natural archives of long-range transported contamination at the remote lake Letšeng-la Letsie, Maloti Mountains, Lesotho

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Abstract

Naturally accumulating archives, such as lake sediments and wetland peats, in remote areas may be used to identify the scale and rates of atmospherically deposited pollutant inputs to natural ecosystems. Co-located lake sediment and wetland cores were collected from Letšeng-la Letsie, a remote lake in the Maloti Mountains of southern Lesotho. The cores were radiometrically dated and analysed for a suite of contaminants including trace metals and metalloids (Hg, Pb, Cu, Ni, Zn, As), fly-ash particles, stable nitrogen isotopes, polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants such as polychlorinated biphenyls (PCBs), polybrominated flame retardants (PBDEs) and hexachlorobenzene (HCB). While most trace metals showed no recent enrichment, mercury, fly-ash particles, high molecular weight PAHs and total PCBs showed low but increasing levels of contamination since c.1970, likely the result of long-range transport from coal combustion and other industrial sources in the Highveld region of South Africa. However, back-trajectory analysis revealed that atmospheric transport from this region to southern Lesotho is infrequent and the scale of contamination is low. To our knowledge, these data represent the first palaeolimnological records and the first trace contaminant data for Lesotho, and one of the first multi-pollutant historical records for southern Africa. They therefore provide a baseline for future regional assessments in the context of continued coal combustion in South Africa through to the mid-21st century.

Keywords: contamination; fly-ash; lake sediments; Lesotho; long-range transport; persistent organic pollutants; trace metals; wetlands

1. Introduction

Southern Africa possesses a wealth of natural landscapes from the mountainous terrain and upland tarns of the Drakensberg and Great Escarpment to coastal lagoons, and from open savannah to evergreen and cycad forests. These wide-ranging habitats have resulted in a diverse endemic fauna and flora and globally important biodiversity hotspots (Myers et al., 2000; CEPF, 2011). However, a range of pressures detrimentally affect these natural landscapes, and especially freshwater ecosystems. These include expanding urbanisation; an increase in water abstraction and invasive species (Driver et al., 2012); a rapid increase in the release of pollutants to the environment from industrial emissions (Monna et al., 2006; Josipovic et al., 2011) including a continued reliance on fossilfuels (Marais et al., 2019); ongoing use of DDT to control malarial vectors (Sereda and Meinhardt, 2005; Humphries, 2013); direct inputs to waters from acid mine drainage (Tutu et al., 2008; McCarthy, 2011) and agricultural practices. Freshwaters in southern Africa are therefore experiencing a period of unprecedented threat. This is likely to be exacerbated by predicted changes to precipitation and increases in temperature of 0.3-3.6 °C by 2036-2065 over a 1961-1990 baseline (Davis, 2011; SAWS, 2017), making southern Africa one of the world's most climatically vulnerable regions. There are, therefore, significant implications for aquatic biodiversity, human health, and ecosystem service provision to dependent rural communities.

Lesotho is a land-locked country, entirely surrounded by South Africa and over 80% of the country lies over 1800 m above sea level (a.s.l) (Schmitz and Rooyani, 1987). The Maloti Mountains, part of the Drakensberg range and considered part of the Afromontane zone, form a high alpine basalt plateau across the southern and eastern parts of the country, incised by deep valleys which drain into the Senqu River, known as the Orange River in South Africa (Schmitz and Rooyani, 1987; Marake et al., 1998). The population of Lesotho is estimated at just over 2 million (Lesotho Bureau of Statistics, 2016) and Maseru, the capital, along with the main agricultural areas lie in the west (Letšela, 2008). The economy is based on agriculture, livestock, manufacturing and mining, while water and diamonds are the significant natural resources. The Lesotho Highlands Water Project (LHWP), which started in 1986, is designed to store and transfer water from the Senqu/Orange River system to South Africa's Free State province and Johannesburg (Letšela, 2008). Water from Lesotho provides around 35% of the water supplied by the Vaal Water Supply System, which supplies the Gauteng and Mpumalanga urban and industrial complex, including mines, industries and most coal-fired power stations (Le Maitre et al., 2018). Completion of the first phase of the LHWP has contributed significantly towards Lesotho's self-sufficiency in the production of electricity. However, electricity demand currently outstrips supply, and Lesotho imports 37% of its annual electricity needs from South Africa (Thamae et al., 2015). Peak demand is expected to grow to over 500 MW by 2050 (Senatla et al., 2018).

By contrast, South Africa is one of the major industrial countries of the southern hemisphere and the largest industrialised economy in Africa (Venter et al., 2017). It has significant mining and metallurgical activities and is one of the top coal-producing countries in the world (Chelgani, 2019). It has rich coal deposits in the north-east of the country and as a consequence the majority of South Africa's coal-fired plants are located here, in the Highveld area of Mpumalanga province. One estimate suggests South Africa accounted for 43% of the total generating capacity for the continent in 2012 (Marais et al., 2019). Over 85% of all electricity generated in South Africa in 2016 was from coal (StatsSA, 2018) and there is a programme of large, coal-fired power station construction in the Highveld coalfields and in the Lephalale area of Limpopo province, near the border with Botswana. The scarcity of major combustion sources in other parts of the country results in strong spatial gradients of emissions from east to west and from north to south (Josipovic et al., 2011). However, deposition monitoring for fossil-fuel associated contaminants is limited and so long-range transported pollution gradients are assumed to follow patterns in sulphur and nitrogen deposition modelling studies (Lamarque et al., 2013), which indicate highest deposition in the north-east, declining to the south and west. By contrast, local sources of pollutants, such as agricultural pesticide use, and biomass burning due to prescribed management or accidental fires, may affect catchments anywhere in the country.

Contamination of South African aquatic environments by trace metals and persistent organic pollutants (POPs) is widely acknowledged. The presence of metals and organochlorine pesticides (principally DDT and its derivatives, but also polychlorinated biphenyls (PCBs), dioxins and furans (PCDD/Fs)) have been reported for riverine plants, fish, sediments and otters (Mason and Rowe-Rowe, 1992; Roux et al., 1994; Grobler et al., 1996; Vosloo and Bouwman, 2005) with “elevated” accumulations of metals in fish from the Olifants River, Mpumalanga (Kotze et al., 1999). In the lacustrine environment, metals and organohalogen compounds (including DDT, PCBs and brominated flame retardants such as polybrominated diphenyl ethers (PBDEs)) have been reported in fish, crayfish, sediments and aquatic birds (Greichus et al., 1977; Bezuidenhout et al., 1990; Sereda and Meinhardt, 2005; Bouwman et al., 2008; Nakayama et al., 2010; Wepener et al., 2012; Humphries, 2013). Evidence for bioconcentration in higher trophic levels resulting in eggshell thinning has been shown for the aquatic-feeding African darter (*Anhinga rufa*) due to intake of DDE (a dehydrochlorinated product from DDT) and PCBs (Bouwman et al., 2008). Yet, despite this evidence for adverse effects, to our knowledge, there are no equivalent data for Lesotho and very few data exist on the scale and rate of change of contaminant inputs to freshwater systems anywhere in southern Africa.

In other parts of the world, naturally accumulating archives such as lake sediments and wetland peats have been used extensively to identify the impacts of environmental pollutant inputs to natural ecosystems. These archives have been used to identify directions of change (e.g. improvement or deterioration), the scale of anthropogenic enrichment of contaminants over natural baselines and, perhaps most importantly, the changing rate of inputs. However, while high-resolution lake sediment records of trace metals and POPs are widely used, particularly in Europe and North America, in southern Africa such techniques have so far only been applied to a very limited number of sites although this is, in part, due to the rarity of natural, permanent standing waters. To date, only two eutrophic urban lakes, Zeekoevlei in the western Cape (Das et al., 2008a,b) and North End Lake in Port Elizabeth (García-Rodríguez et al., 2007) and a single peat core from the Witwatersrand industrial area (McCarthy and Venter, 2006) have been analysed in this way. Hence, there are no assessments of regional contaminant patterns and no record of atmospherically deposited contamination in remote and non-urban freshwater systems.

Remote mountain lakes can act as sentinels for environmental change as their contaminant sources are usually solely atmospherically derived. Their archives can therefore provide a means to determine regional patterns and baselines for future change not usually possible in lowland systems. In this study we assess the historical record of contamination in the remote lake, Letšeng-la Letsie, located in the Maloti Mountains of Lesotho. This is the only RAMSAR Convention site (www.ramsar.org) in Lesotho, designated as a high altitude wetland, and for IUCN-classified vulnerable bird species including Wattled cranes (*Grus carunculatus*, Lesser kestrel (*Falco naumanni*), Bald ibis (*Geronticus calvus*), Cape vulture (*Gyps coprotheres*), and the Yellow-breasted pipit (*Anthus chloris*). The Maloti minnow (*Pseudobarbus quathlambae*), which may occur at the site, is considered critically endangered and rare (Motanya, 2003). While potential threats from over-grazing and catchment soil erosion are recognised (Matope, 2014) there is no information on the scale of contamination.

Letšeng-la Letsie provides a unique opportunity to study a paired lake sediment and wetland archive in Lesotho. The aims of this study were to analyse these historical records for a suite of contaminants, including trace metals and metalloids (Hg, Pb, Cu, Ni, Zn, As) (hereafter 'trace metals'), spheroidal carbonaceous fly-ash particles (SCPs), stable nitrogen isotopes and organic pollutants including PAHs and POPs, to determine the scale of contamination at this remote site, and its likely sources. In so doing, the study provides the first palaeolimnological records for Lesotho and, more broadly, the first high resolution, multi-pollutant records for southern Africa. An additional aim, therefore, is to add to the sparse southern hemisphere dataset for these pollutants and provide a baseline for future regional assessments in the context of continued coal combustion in South Africa through to the mid-21st century. Given the contrast in the scale of emissions between South Africa and Lesotho, we hypothesise that any contaminants in this remote area are likely derived by the long-range transport of emissions from industrial sources in north-eastern South Africa.

2. Methods

2.1. Site description

Letšeng-la Letsie (30°18'39.7"S; 28°09'59.3"E) is a 0.38 km^2 lake in the Maloti Mountains of Lesotho, lying at 2400 m a.s.l., about 200 km south-east of Maseru and close to the border between Lesotho and Eastern Cape Province, South Africa (Fig. 1). The 413.9 km^2 catchment area was declared the Letšeng-la Letsie Protected Area by the Principal Chief of the Area together with the Prime Minister of Lesotho in 2001 and formed part of the 'Conserving Mountain Biodiversity in Southern Lesotho' area (CMBSL) (Motanya, 2003). The lake has a mean depth of about 1 m and a maximum recorded depth of 1.4 m (Fig. 2). It was impounded in 1968 by a small dam across the Mohlakeng River, which forms the lake's outflow. This flows via the Quthing River to form a tributary of the Senqu River becoming the Orange River in South Africa. The dam was already reported to be in a poor state of repair in 1988 (Skofteland, 1988) and although the water-level of the lake undoubtedly remains raised, the effectiveness of the dam was limited during the field sampling in 2018 with a steady flow of water by-passing it on either side.

The catchment is bounded by mountains that rise to 2820 m a.s.l giving a relief of 420 m. The dominant geology is basaltic with dolerite intrusions, while the valley floor including the lake have recent alluvial deposits. The region falls within the Drakensberg Alpine Complex (Carbutt and Edwards, 2004; 2006), with Afromontane and Afroalpine vegetation dominated by grasses, sedges and woody shrubs. There are no trees, as the region is situated above the tree-line (Nüsser and Grab, 2002). Letšeng-la Letsie is located within an area of the Maloti-Drakensberg Mountains known as a "biodiversity hotspot" with over 30% endemism (Lesotho Government National Environment Secretariat, 2000). These include the mountain pipit (*Anthus hoeschi*), while another six species including the Bush blackcap (*Lioptilus nigricapillus*), Buff-streaked chat (*Saxicola bifasciata*), Rudd's lark (*Heteromirafra ruddi*), Orange breasted rockjumper (*Chaetops aurantius*) and Drakensberg siskin (*Serinus symonsi*) are near endemic. The only endemic mammal and amphibian at the site are the ice rat (*Otomys slogetti*) and the aquatic river frog (*Rana vertebralis*), respectively.

Winters can be extreme with temperatures commonly -5 °C and a recorded minimum of -22 °C. Snow falls are common in the austral winter months although snow, sleet or hail can occur at any time of the year (Grab and Nash, 2010; Grab and Linde, 2014). Maximum temperatures of 26 °C have been recorded in January (Lesotho Ministry of Natural Resources, 1996). Highest rainfall occurs at the mountain summits which receive over 1000 mm per annum (Sene et al., 1998). More than 80% of rainfall is received between October and March, and on average, the area receives about 800 mm rainfall each year (Sene et al., 1998; Borg, 2012). Lesotho is amongst the windiest countries in Africa (Mpholo et al., 2012). The strongest winds are experienced in late-winter due to the frontal systems associated with the westerlies and lowest in the wet summer months (Grab, 2002a; 2010). Little climate data exist for this area of Lesotho, but in the Sani Valley to the east, summer winds dominate from the east and northeast, bearing moisture from the Indian Ocean, while the winter winds are predominantly north-westerly (Sene et al., 1998; Grab, 2010).

2.2. Sediment and wetland cores

Three parallel lake sediment cores (LETS1-3) were collected from the deepest part of the lake (1.4 m) to the east of the outflow area (Fig. 2) from an inflatable boat. The 26 – 30 cm cores were taken using an HTH gravity corer fitted with a perspex tube of internal diameter 86 mm (Renberg and Hansson, 2008). The cores were extruded vertically in the field at 0.5 cm intervals. All analyses except those for organic compounds were undertaken on LETS2. The core tube and extruding equipment for LETS3, used for organic compound analyses were *n*-hexane-washed and wrapped in *n*-hexane-cleaned aluminium foil prior to use. The cores were kept cold and dark, and were frozen (-20 °C) as soon as possible. Replicate wetland sediment monoliths were also collected from two locations to the north-west of the lake. The monoliths, ranging from 23 - 34 cm length, were collected from exposed vertical sections in drainage channels using strong plastic tubing following standard techniques (e.g. De

Vleeschouwer et al., 2010). Before sampling, the sediment face was cut back to expose uncontaminated and un-oxidised material. Once collected, the monolith was wrapped and stored at 4 °C before sub-sampling at 0.5 cm intervals. Monolith LETS-W3 was used for all contaminant analyses.

2.3. Lithostratigraphic analyses and core chronologies

Lithostratigraphic analyses (bulk density; water content; loss-on-ignition at 550°C (LOI_{550}) and 950 °C (LOI_{950}) as an estimate of organic matter content and carbonate content respectively) were undertaken on each sample following standard methods (Dean, 1974; Heiri et al., 2001). Core samples were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay using ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detectors. Lead-210 was determined via its gamma emissions at 46.5 keV, and ^{226}Ra by the 295 keV and 352 keV gamma rays emitted by its daughter isotope ^{214}Pb following three weeks storage in sealed containers to allow radioactive equilibration for ^{222}Rn and ^{226}Ra. Cesium-137 and ^{241}Am were measured by their emissions at 662 keV and 59.5 keV, respectively. The absolute efficiencies of the detector were determined using calibrated sources and sediment samples of known activity. Corrections were made for self-absorption of low energy gamma rays within the sample (Appleby et al., 1992). Unsupported ^{210}Pb, from atmospheric deposition, was calculated by subtracting supported ^{210}Pb (which derives from *in situ* decay of ^{226}Ra) from total ^{210}Pb. Final sediment chronologies were determined from ^{210}Pb records using constant rate of supply (CRS) or constant initial concentration (CIC) models (Appleby, 2001), in combination with ^{137}Cs and ^{241}Am profiles. Derived and interpolated sediment accumulation rates (g cm^{-2} yr^{-1}) were used to convert contaminant concentrations into fluxes.

2.4. Sediment and wetland core geochemistry and trace metal analysis

Weighed (4 d.p.) freeze-dried milled sediment (~2 g) was measured using an X-ray fluorescence spectrophotometer (Rigaku NEX CG EDXRF) for trace metals (Pb, Cu, Ni, Zn, As) and other geochemical elements. A certified reference sediment sample of similar mass was included in each analytical run (Canadian Certified Reference Materials Project; LKSD-2) with mean recovery rates of 93.6 (Cu) to 102.5% (Zn). For mercury (Hg) analysis, 0.2 g of freeze-dried samples were weighed into a 50 mL polypropylene DigiTUBE (SCP Science). 8 mL of 'aqua regia' (nitric and hydrochloric acids in a molar ratio of 1:3) were added to each and gradually heated on a hotplate to 100 °C to avoid violent reaction. The sample was then digested for another 1.5 h and allowed to cool. The digested solution was diluted to 50 mL using distilled deionised water. Standard reference stream sediment (GBW07305; certified Hg value 100 ± 10 ng g^{-1}; our measured mean value 100.3 ng g^{-1}; RSD = 4.5 ng g^{-1}; N=15) and sample blanks were digested with every 20 samples. Mercury concentrations were measured by cold vapour-atomic fluorescence spectrometry (CV-AFS) following reduction with $SnCl_2$. Standard solutions and quality control blanks were measured after every five samples to monitor measurement stability.

Trace element enrichment factors (EFs) provide a means by which to determine elevation above uncontaminated background levels and hence estimate anthropogenic inputs to sediments (e.g. Chen et al., 2007). EFs were calculated by normalising trace element concentrations to those of a conservative geochemical element within the measured sample and then to the same ratio within basal (uncontaminated) sediments using the following equation:

$$EF = ([M_{samp}]/[R_{samp}]) / ([M_{back}])/([R_{back}]) \quad (1)$$

where M_{samp} is the metal concentration in the sample for which the EF is being calculated, R_{samp} is the concentration of the reference element (here, Ti), while M_{back} and R_{back} are the equivalent concentrations in the basal sample. EFs of 1 - 3 represent minor anthropogenic contamination; 3 - 5 moderate; 5 - 10 moderate to severe; 10 - 25 severe; 25 - 50 very severe and > 50 extremely severe contamination (Chen et al., 2007).

2.5. Spheroidal carbonaceous fly-ash particles (SCPs)

Spheroidal carbonaceous particles (SCPs) are a component of fly-ash, produced solely from the high-temperature combustion of coal-series and fuel oils (Rose, 2001). They have no natural sources and therefore provide an unambiguous indicator of atmospherically deposited industrial contamination. Although particulate, SCPs are able to travel hundreds to thousands of kilometres (Rose et al., 2012) with diffusing industrial plumes before being dry or wet deposited depending on meteorological conditions. For both lake and wetland core samples, SCP analysis involved sequential treatments of nitric, hydrofluoric and hydrochloric acids to remove organic, siliceous and carbonate fractions, resulting in a suspension in water (Rose, 1994). A known fraction of this suspension was then evaporated onto a coverslip, mounted onto a glass slide, and the number of SCPs counted using a light microscope at 400 times magnification. Standard criteria for SCP identification were followed (Rose, 2008). SCP concentrations were calculated as the number of particles per gram dry mass of sediment (gDM^{-1}) and SCP fluxes calculated as the product of SCP concentration and bulk dry sediment accumulation rate (number of particles per cm^2 per year; cm^{-2} yr^{-1}). Analytical blanks and SCP reference material (Rose, 2008) were included with all sample digestions. The detection limit for the technique is typically less than 100 gDM^{-1} and calculated concentrations generally have an accuracy of c. ± 45 gDM^{-1}.

2.6. Stable isotopes of nitrogen

Samples were analysed for their $\delta^{15}N$ signatures using a Flash EA 1112 and a Delta V continuous-flow gas-isotope-ratio mass spectrometer (Thermo Scientific®) in the Bloomsbury Environmental Isotope

Facility, UCL. Samples of 10-20 mg were accurately weighed into tin capsules which were dropped into a furnace held at 1020 °C and burned with a pulse of oxygen at about 1800 °C. The released gases were carried in a stream of helium through an oxidant (granular chromium oxide combustion reagent) to complete combustion; silvered cobalt chemical traps to remove sulphur and halogens; a copper reduction furnace to trap excess oxygen and to convert the formed NOx to N_2 for analysis; a magnesium perchlorate drying tube which also contained some Carbosorb to remove CO_2. Finally, the gases pass through a gas chromatograph (GC) column before passing through a Thermal Conductivity Detector (TCD, to obtain TN%) to then enter the mass spectrometer via a CONFLO IV interface. The results were calibrated against laboratory and international standards (i.e. IAEA-600, IAEA-N1, IAEA-N2, USGS40, OEA alanine). Nitrogen isotope ratios are reported in the conventional delta-notation, in per mil (‰) with respect to atmospheric N_2 (Air).

2.7. Organic pollutants

2.7.1. Sample extraction and fractioning of PAHs and POPs

The analytical procedure for the determination of polychlorinated biphenyl (PCBs), brominated diphenyl ethers (BDEs), hexachlorobenzene (HCB) and polycyclic aromatic hydrocarbons (PAHs) was based on a UNEP method (1992) as modified by Bícego et al. (2006). Approximately 15 g dried sediment was Soxhlet extracted for 8 h with 80 mL of a *n*-hexane and dichloromethane (DCM) mixture (1:1, v/v), copper (for the removal of elemental sulphur), boiling glass spheres and 100 µL of a surrogate standards mixture containing acenaphthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12} (2.5 ng μL^{-1}) for PAHs, and PCB 103 and PCB 198 (1 ng μL^{-1}) for POPs. The extract was reduced to 4 mL using rotary evaporation and divided into two portions of 2 mL. The first portion was subjected to a clean-up and fractionation procedure using a glass column containing 3.2 g of silica, 1.8 g of alumina (both 5% deactivated with Milli-Q® water) and sodium sulphate. The column was first eluted with 10 mL of *n*-hexane to remove a first fraction containing aliphatic hydrocarbons (data not presented), and then with 15 mL of a DCM and *n*-hexane mixture (3:7, v/v), to remove a second fraction (PAHs). Subsequently, these fractions were concentrated by rotary evaporation and transferred to calibrated glass vials with a final volume of 250 µL. Before instrumental analysis, 50 µL of the internal standard benzo[*b*]fluoranthene-d_{12} (2.5 ng μL^{-1}) was added to each PAH extract and adjusted to 250 µL. The second 2 mL portion was purified using a glass column containing 3.2 g of 5% deactivated aluminium oxide, and subsequently eluted with 20 mL of a DCM and *n*-hexane mixture (3:7, v:v), to obtain the POPs fraction. The eluate was spiked with 50 µL of the internal standard tetra-chloro-*m*-xylene (TCMX, 1 ng μL^{-1}) and concentrated to 250 µL for POPs analysis.

2.7.2. Instrumental analysis of PAHs and POPs

The instrumental analyses for PCBs, PBDEs, HCB and PAHs were performed by Agilent 7890A gas chromatography (GC) coupled with an Agilent 5975C inert MSD with a Triple-Axis Detector Mass Spectrometer (MS). The GC column was an HP-5 fused silica column (length: 30 m, 0.25 mm ID, film thickness: 0.25 µm). The oven temperature for PCBs, PBDEs and HCB was programmed to begin at 75 °C for 3 min, increasing at 15 °C min^{-1} up to 150 °C, then at 2 °C min^{-1} up to 260 °C, and finally at 20 °C min^{-1} to up to 300 °C (holding for 10 min), in a total time of 75 min. The oven temperature for PAHs was: 40 °C to 60 °C at 20 °C min^{-1}, then to 250 °C at 5 °C min^{-1} and, finally, to 300 °C at 6 °C min^{-1} (held for 20 min). For all analyses, the injector temperature was adjusted to 280 °C, splitless injection mode was adopted and the detector and ion source temperatures were adjusted to 300 °C and 230 °C, respectively. Helium was used as the carrier gas at a constant flow rate of 1 mL min^{-1} while data acquisition was obtained using Selected Ion Monitoring (SIM) mode, and quantification was based on the integration of specific fragment ion (m/z) peaks area using an Agilent Enhanced Chemstation (G1701 CA) program. The PAHs were identified by matching the retention time and specific m/z with the results obtained from the standard mixtures (Z-014G-FL, AccuStandard, USA), and with a calibration curve ranging from 0.10 to 2.00 ng μL^{-1} ($r^2 > 0.995$). The concentration of individual PCBs and PBDEs was obtained through the internal standard peak area method and an 8-point analytical curve for individual components (1, 5, 10, 20, 50, 80 and 100 pg µL^{-1}, $r^2 > 0.995$) from the standard mixtures (PCBs: C-WNN and C-WCFS; PBDEs: BDE-CM, from AccuStandard, USA). The final concentrations were expressed as ng g^{-1} in dry sediment for all compounds detected.

The following compounds were investigated: (i) low-chlorinated PCBs: 8, 18, 28, 31, 33, 44, 49, 52, 56/60, 66, 70, and 74; (ii) high-chlorinated PCBs: 87, 95, 97, 99, 101, 105, 110, 114, 118, 123, 128, 132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 170, 174, 177, 180, 183, 187, 189, 194, 195, 201, 203, 206, and 209; (iii) BDEs: 28, 47, 99, 100, 153, 154 and 183; (iv) hexachlorobenzene (HCB); (v) PAHs: (a) alkyl-PAHs including methyl (C_1), dimethyl (C_2) and trimethyl (C_3) naphthalenes, methyl phenanthrenes; (b) unsubstituted PAHs (2–3 rings) such as naphthalene (C_0), phenanthrene (C_0), anthracene, fluorene, acenaphthene and acenaphthylene; (c) PAHs (4–6 rings) such as fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b+k+j*]fluoranthene, benzo[*a+e*]pyrene, perylene, indeno[1,2,3-*c,d*]pyrene, dibenz[*a,h*]anthracene and benzo[*g,h,i*]perylene.

2.7.3. Quality assurance for organic pollutants

Quality assurance was based on blank extraction (in 15 g of sodium sulphate) and the recoveries of surrogate standards. Procedural blanks were undertaken for each group of ten samples and when necessary (e.g. values greater than 3 times detection limits), the values found in the blanks were removed from the samples. The mean PAH surrogate recoveries in the extracted samples were: (i) PAH: 55 ± 10 % for acenapthene-d_{10}, 78 ± 14 % for phenanthrene-d_{10} and 83 ± 12 % for chrysene-$d_{12;}$ (ii) PCB: 95 ± 22 % for PCB 103 and 73 ± 16 % for PCB 198. Surrogate recoveries in the samples were in the acceptable range (40 - 120%; Denoux et al., 1998) for 100% of samples analysed. Precision ranged from 3.2 to 10.4% for individual PAHs and from 0.2 to 11.4 % for individual PCBs. Method accuracy was checked by the extraction of duplicate standard reference material (SRM) for sediment IAEA 417 (International Atomic Energy Agency, Vienna, 1999). The results were within the upper and lower ± 30% confidence interval reference values for 81% of PAHs and 91 % of PCBs in accordance with criteria proposed by Wade and Cantillo (1994). The instrumental detection limits named as detection limits (DL) adopted in this study were 0.50 ng g^{-1} for the PAHs and 0.03 ng g^{-1} for the PCBs and PBDEs. These data are based on the lowest sensitive PAH / PCB concentration (0.03 ng μL^{-1} / 0.002 ng μL^{-1}) multiplied by the final extracted volume (250 µL) and divided by the sediment weight (15 g) before extraction. The analysis of duplicate samples was used to verify precision which was < 15 % for the individual compounds analysed.

2.8. Back trajectory analysis

The origin of air flowing over Letšeng-la Letsie was investigated with NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al., 2015), using global NCEP reanalysis data. Back trajectories were run for 72 hours, with point of origin 1500 metres above ground level at Letšeng-la Letsie. Trajectories were calculated twice a day (at 00:00 and 12:00 UTC) at ten-year intervals, from 1950 to 2010. Predominant transport pathways were identified using the HYSPLIT model's trajectory cluster analysis, which minimises the total spatial variance between the mean of a cluster and all the trajectories assigned to that cluster (Draxler et al., 2012).

2.9. Emissions from coal combustion

The amount of coal burnt per annum for electricity generation in South Africa was obtained from Eskom's annual reports, to determine to what extent the trends in pollutants observed in the lake sediments can be ascribed to trends in emissions. Eskom's stations accounted for about 75% of all coal used for power generation in South Africa in the 1940s. In the late-1940s, Eskom procured several additional power stations, so that by the 1950s the bulk of coal-fired generation capacity in South Africa was operated by them. The coal used for power generation accounts for the majority of coal use in South Africa and, between 2006 and 2015, coal-fired power stations consumed on average 66%

of all coal consumed in the country (Ratshomo and Nembahe, n.d.). Sulphur dioxide (SO_2) emissions were obtained from Eskom's annual reports (Eskom, 2019); SO_2 emissions were calculated with a station-specific emission factor, based on the sulphur content of the coal, from 1927 to 1981, and with mass balance calculations using daily measurements of the sulphur content in the coal thereafter. Mercury emissions were calculated from mass balance, based on the mercury in coal measurements reported in Garnham and Langerman (2016) for currently operating stations and a national mercury-in-coal concentration average value of 0.31 ppm (UN Environment, 2017) for older stations for which there are no measurements. It was assumed that the abatement technology installed at a power station reduces mercury emissions by 25% for an electrostatic precipitator or cyclone, and by 50% for a fabric filter plant (UN Environment, 2017).

3. Results

3.1. Core chronologies

The radiometric dating for both the lake and wetland cores are shown in Supplementary Information (SI1). The ^{210}Pb and ^{137}Cs records provide chronologies extending to 1933 ± 16 (85 years) and 1899 ± 23 (119 years) respectively. Both show records of continuous accumulation before and after the construction of the impoundment in 1968. The lake sediment core (LETS2) shows little change in sediment accumulation as a result of impoundment although the rate appears to become more stable afterwards. For the wetland core (LETS-W3) there is a continuous trend of increasing sediment accumulation rate from the base of the core through to the present, which appears to accelerate from the late-1980s. The dry weight and loss-on-ignition (550 °C and 950 °C) profiles for the sediment cores LETS2 and LETS3 show excellent agreement (Supp. Info. SI1) and were used to apply dates to the otherwise undated LETS3 core.

3.2. Trace metals, SCPs and stable isotopes of nitrogen

The concentrations of the trace metals and metalloids (Ni, Cu, Zn, Pb, Hg and As; hereafter 'trace metals') are shown in Fig. 3. There is little change in metal concentration over the period covered by the cores. Only Hg shows evidence for an increase with concentrations in the lake core increasing unidirectionally from mid-30s ng g^{-1} at the base of core to > 50 ng g^{-1} in recent sediments. Due to this lack of significant change in metal concentration, metal fluxes follow the historical trends in sediment accumulation rates (Supp. Info. SI2). As a result, metal fluxes for LETS2 show some degree of variability through the 1950s and 1960s but become more stable from the start of the 1970s at the time of the impoundment. By contrast, the increasing sedimentation rates in the wetland core result in increasing metal fluxes from the start of the record, such that peak metal inputs occur in the most recent period. Enrichment factors (Fig. 3) of trace metals also show little change, remaining around 1.0 throughout the dated periods for both cores indicating no clear inputs from anthropogenic sources. Again, the only exception is Hg, which increases slightly from 1.0 in the 1970s to a maximum of 1.3 in the surface sediments of the lake core and indicating recent minor enrichment (Cevik et al., 2009).

Concentrations of geochemical elements and trace metals (Mg, Al, Si, S, K, Ca, Ti, Mn, Fe, Br, Rb, Sr, Ti, V, Cr, Ni, Cu, Zn, As, Pb, Hg) in the LETS2 sediment core along with LOI_{550} as an estimate of organic matter were standardised (z-scores) prior to principal components analysis (PCA) to explore relationships between these data. PCA axis 1 explained 38.5 % of the total variance, and described high loadings of minerogenic elements and some trace metals (e.g. Al, Ti, Rb, Ni, Cu) against negative loadings of Hg and Mn (Supp. Info. SI2). PCA axis 2 eigenvalues (28.7% variance) corresponded to the difference in loadings between organic (LOI_{550}, Br) and minerogenic elements (Sr, K). Axis 3 explains 10.3% of the total variance and, along with axes 1 and 2, describes cumulatively 77% of the variation in these element concentration data. Component weightings of the variables for the first 3 PC axes are also shown in Supp. Info. SI2. Stratigraphically, the bi-plot is reflected in the co-increase of Hg with organic matter and Mn against the relatively unchanging concentrations of other trace metals and minerogenic-associated elements.

At Letšeng-la Letsie, spheroidal carbonaceous fly-ash particles (SCPs) are first recorded in the lake sediment core in the late-1970s and in the wetland core in the late-1980s. Peak concentrations agree well, reaching 900 gDM^{-1} in 2015 in the lake record and 500 gDM^{-1} in wetland surface sediments (Fig. 3). These SCP concentrations are similar to those found in recent levels of a peat core (200 – 350 gDM^{-1}; unpublished data) taken from Sani Top (29°35'8.12"S; 29°15'56.68"E - Fig. 1; Fitchett et al., 2017) 140 km to the northeast of Letšeng-la Letsie For both cores, SCP flux records reinforce the concentration patterns and trends (Supp. Info. SI2) in showing a steady increase in contamination through to the present although recent fluxes in the wetland core (326 cm^{-2} yr^{-1}) are approximately double those of the lake (148 cm^{-2} yr^{-1}).

The δ^{15}N data for both lake and wetland cores are also shown in Fig. 3. For the lake core, δ^{15}N values range between 5.5 and 5.9 ‰ from basal sediments (1930s) through to the late-1970s, when they increase gradually to maximum values of around 6.5 ‰ in most recent sediments. By contrast, δ^{15}N values in the wetland core are higher, remaining between 7.5 and 8.1 ‰ from the base of the core (1890s) through to the early-2000s where they decline slightly, reaching a minimum of 6.7 - 7.0 ‰ in surface sediments.

3.3. Organic pollutants

Concentrations of total PAHs, total 16 United States Environmental Protection Agency (USEPA) PAHs, total high molecular weight (HMW; 4-6 rings) and total low molecular weight (LMW; 2-3 rings) PAHs in LETS2 all follow very similar historical trends (Fig. 3c). Concentrations are low, with total PAH concentrations not exceeding 250 ng g^{-1}. Concentrations for all these groups of compounds remain largely unchanged through the core except for two minima around 1970 and the early-2000s, and a peak in the late-1990s. The agreement between these different groups suggests similar sources for both HMW and LMW compounds. However, concentrations for some individual HMW PAHs e.g. benzo[*a*]pyrene, indeno[1,2,3–*c,d*]pyrene and benzo[*g,h,i*]perylene only exceed the limit of detection after the mid-1970s, with concentrations increasing from this time through to surface sediments. High molecular weight PAHs are preferentially industrially-derived (Tobiszewski and Namieśnik, 2012; Thang et al., 2019) suggesting increasing inputs from these sources over the last 40 years. This is confirmed by the flux data for these compounds which reaches a peak of 4.6 ng cm^{-2} yr^{-1} in surface sediments. Concentration ratios of PAH compounds may also be used to provide information on sources. The ratio between non-alkylated phenanthrene and total (alkylated and non-alkylated) phenanthrene (C_0-P/(C_0 + C_1)-P) and the ratio between fluoranthene and the sum of fluoranthene and pyrene (Fl/Fl + Py) can both provide an indication as to the strength of the role played by various combustion sources. For both ratios, values > 0.5 indicate combustion of biomass and / or coal (Yunker et al., 2002) while those 0.4 - 0.5 indicate combustion of petroleum. Ratios exceed 0.4, and mostly 0.5, throughout the core (Suppl. Info. SI3) indicating combustion as the only detected source of PAHs.

Concentrations of total PCBs and the total of the 7 'indicator' congeners (PCBs 28, 52, 101, 118, 138, 153, 180; hereafter PCB_7) are both low and only increase to above detection limits in the 1970s (Fig. 3c). As indicators of anthropogenic industrial contamination, independent of PAHs, these data provide additional evidence for deposition from industrial sources at Letšeng-la Letsie. Concentrations of total PCBs and PCB_7 increase through to the early-2000s but then show neither significant increase nor decrease in the last two decades. Of the polybrominated flame retardants, only BDE47 is detected in Letšeng-la Letsie, but concentrations are close to analytical detection limits. A BDE47 'peak' concentration of 0.05 ng g^{-1} is observed in surface sediments. Hexachlorobenzene (HCB) is first detected in sediments dated to the 1950s and highest concentrations and fluxes occur in surface sediments (0.21 ng g^{-1}; 0.03 ng cm^{-2} yr^{-1}).

4. Discussion

4.1. The sediment record at Letšeng-la Letsie

There has been some uncertainty regarding the presence of a permanent waterbody at Letšeng-la Letsie prior to the 1968 impoundment. While a first edition map from 1973, based on South African aerial surveys in 1964 shows no lake in the area, the earliest 1:50,000 topographic maps (Basutoland Sheet 3028AC, surveyed in 1950 and first published by the Directorate of Colonial Surveys, 1952) show the presence of a pond or tarn in part of the present lake. Furthermore, a British Army survey from 1904 describes a "*flat open valley about 3.5 miles long by 1.5 miles broad, surrounded by mountains. There are a number of pools surrounded by boggy land; branch valleys contribute small streams which combine to form the northern source of the Quthing River*" (Dobson, in South Africa 1910) (see Supp. Info. SI4 for comparison).

Neither the wetland nor the lake sediment core indicate any evidence for a hiatus in accumulation before or after the construction of the impoundment in 1968 and the radiometric chronologies for both cores continue through this period. This is to be expected for the wetland core as the sampling location is above the current water level and is therefore likely to have been so throughout the period. Accumulation rates continue a smooth increasing trend before, during and after dam construction and geochemical trends also exhibit no changes (Supp. Info. SI5). For the lake core (LETS2), sediment accumulation rates are more variable prior to 1968 (Supp. Info. SI1) suggesting a more stable accumulating environment after the impoundment, while there is also a marked, although brief, decline in Fe/Mn ratio at the time of its construction (Supp. Info. SI5). Fe/Mn declines in reducing conditions and it maybe that this temporary dip is due to extended inundation of the catchment when the dam was built. However, the Fe/Mn ratio reverts to pre-dam levels after a single datapoint so should be interpreted with caution (Supp. Info. SI5). A small dip in LOI_{550}, and a small peak in K, Mn and Ca also occur, briefly, at this time. It is unclear how significant these changes are as greater, longer-term and monotonic changes in Fe/Mn occur from the 1990s which, since the mid-2000s seems to be driven by an increase in Mn concentration. It seems unlikely that this more extensive recent trend represents a further increase in catchment inundation as the dam has not been raised and the existing structure has been reported to be in a state of poor repair since at least the late-1980s (Skofteland, 1988). Furthermore, it is unlikely that this shallow, wind-stressed lake experiences extended periods of anoxia even at its deepest point where the sediment core was taken. Organic matter content (as LOI_{550}) also increases over this same period, but this is probably due to less diagenesis of organic material in recent sediments. In summary, we conclude it most likely that a shallow lake or wetland has been present at Letšeng-la Letsie over at least the last 85 years with continuous accumulation both prior to, and following, the construction of the dam.

4.2. Historical records of contamination

The lake and wetland cores show continuous sedimentation over 85 ± 16 and 119 ± 23 years respectively and thereby cover a period of increasing emissions within South Africa since the middle of the 20th century. This includes the combustion of coal for the generation of electricity and other industrial processes (Masekoameng et al., 2010). As Lesotho, by comparison, has only very minor emissions and no industrial fossil-fuel combustion, we have hypothesised that any contamination observed at Letšeng-la Letsie would likely be derived from the long-range transport of emissions from South African sources.

Although the scale of contamination at Letšeng-la Letsie is very low, a number of measured lake sediment and wetland parameters indicate an increase in contamination from the 1970s. While most trace metals show no indication of anthropogenic enhancement, Hg concentrations and fluxes increase from the 1970s, while the Hg EF also increases above 1.0 at this time albeit only reaching a level of minor enrichment in surface sediments. Gaseous mercury emitted from industrial sources may have an atmospheric lifetime of around one year and so Hg deposited at Letšeng-la Letsie is potentially derived from anywhere globally (Yang et al., 2010a). However, some studies (e.g. Yang et al., 2016; Panichev et al., 2019) indicate elevated Hg deposition at sites more proximal to emission sources. As coal combustion is a major industrial Hg source, the coal-fired power plants in South Africa, which contribute up to 78% of total Hg emissions in the country (27 - 39 tonnes yr^{-1}; Masekoameng et al., 2010) are likely to be making a significant contribution to Hg deposition, especially given the timing of the deposition increase. SCPs, also produced from the industrial combustion of coal, similarly show a first presence and then a gradual increase from the 1970s in the lake sediment core and 1980s in the wetland core. As these particulates have no natural sources, any presence may be considered an enrichment, and the SCP concentration and flux profiles show good temporal agreement increasing through to the present. SCPs are not able to travel globally prior to deposition, as Hg does, but may travel thousands of kilometres under favourable meteorological conditions (Rose et al., 2012) and well within the range required for transport from coal combustion sources in the Highveld (Fig. 1). The agreement between Hg and SCP records provides a strong indication of South African industrial coal combustion being the source of these contaminants.

The records of industrial organic contaminants and $\delta^{15}N$ also support this conclusion. The PAH ratio data (Supp. Info. SI3) indicate that their source has been from combustion over the last century. However, while historical patterns of total PAH concentrations vary little through time, those of individual HMW compounds only exceed their analytical detection limits from the 1970s suggesting an increase in emissions from industrial combustion sources. Similarly, the concentrations of total PCBs and PCB_7 (Fig. 3) have only become elevated above detection limit since the 1970s, providing independent evidence for the long-range transport and deposition of industrial emissions. Declining trends in $\delta^{15}N$ recorded in lake sediment and ice cores (Holtgrieve at al., 2011) are considered indicative of nitrogen from anthropogenic sources, including industrial fossil-fuel combustion, and so the $\delta^{15}N$ decline over the last two decades in the Letšeng-la Letsie wetland core may reflect an increase in atmospherically deposited nitrogen inputs from these sources (Heaton, 1987). The contrasting increase in $\delta^{15}N$ in the lake sediment core since the 1970s clearly does not support this. However, it may result from the expansion of the waterbody following the impoundment in 1968 and an enrichment from animal-derived nitrogen inputs from newly flooded areas entering the sediment record from this time.

There is clear evidence in the natural archives of Letšeng-la Letsie for an increase in the products of high temperature coal combustion since the 1970s and this reflects the development of the power generation and other heavy industries in South Africa. The 1970s saw a marked increase in electricity generation in South Africa with the commissioning of a number of new, and larger, coal-fuelled power stations mostly in the Highveld / Mpumalanga region. The amount of coal burnt in coal-fired power stations more than doubled from 22 Mt in 1970 to 47 Mt in 1980, reaching a peak of 125 Mt in 2007. This resulted in concomitant increases in the emissions of SO_2 and Hg. Sulphur dioxide emissions increased from 250 ktonnes in the late-1960s to a peak of almost 2000 ktonnes in 2013, while Hg emissions increased from 4.5 tonnes in 1970 to a peak of over 22 tonnes yr^{-1} between 2007 and 2012 (Fig. 4). Importantly, while coal combustion for electricity generation is the major source of Hg emissions, other sources such as coal gasification, cement production and domestic coal burning also contribute and increased through this period (Masekoameng et al., 2010). However, as the scale of contamination is low, further evidence is required to track these contaminants to likely source areas.

4.3. Tracing the sources of contamination

The deposition of contaminants in the Maloti Mountains of southern Lesotho from suspected industrial sources in the Highveld of South Africa requires long-range transport. Back-trajectory analysis permits the reconstruction of air-mass pathways to a location, and is widely used to determine potential sources in contaminant studies. Air originating over the industrialised Highveld and the Lephalale region is advected over Letšeng-la Letsie, but only infrequently (no more than 7% of the time; Fig. 5) which may explain the low level of contamination experienced at the site. This flow occurs in association with continental anticyclones and the slow-moving air-masses typically take 2-3 days to move from the Highveld to southern Lesotho. By contrast, air masses transported from the south-west and west (occurring 56% of the time), from the east (10%), and from Botswana in the north (26%) are relatively free of contamination from coal combustion. These flow patterns have been broadly similar at least since 1950 (Supp. Info. SI6 for more detailed historical breakdown). Aerosols from industries and biomass burning have previously been measured at Ben Macdhui in Eastern Cape, South Africa, about 45 km to the south-south-west of Letšeng-la Letsie (Piketh et al., 1999; 2002). Trajectory analysis at Ben Macdhui show that peak concentrations of industrial sulphate aerosols occur in association with recirculating, anticyclonic flow which transports pollutants from the Mpumalanga Highveld (Zunckel et al., 1999; Piketh et al., 2002).

Other industrial contaminants, such as PCBs, which show some coincidence with the historical patterns of PAHs, may also be derived from industries in the Highveld region and an assessment of the PCB congeners helps corroborate our hypothesis that these are derived from long-distance transport. PCBs congener distribution was dominated by low-chlorinated forms (fewer than four chlorine atoms), which are more volatile and mainly related to atmospheric transport. Furthermore, the ratio R = ([PCB28] + [PCB52])/([PCB28] + [PCB52] + [PCB138] + [PCB153] + [PCB180]) has been used as an indicator of contaminant transport, where an R value close to 1.0 is considered to be related to atmospheric deposition and long-range transport (Naffrechoux et al., 2015). Here, all calculated R-values were 1.0, as the high-chlorinated forms included in this ratio were not detected. Similarly, the flame retardant BDE47 recorded at the site, is most likely to be derived from urban or commercial sources and so may be transported to Letšeng-la Letsie along the same atmospheric pathways. In southern Africa, global warming is associated with a poleward shift of easterly and westerly wave circulation systems (Sousa et al., 2018), an intensification of subtropical anticyclones, and heightened variability associated with El Niño-Southern Oscillation (ENSO), the Indian Ocean Dipole (IOD) and the Southern Annular Mode (SAM) (Fauchereau et al., 2003; Reason and Roault, 2005; Gaughan et al., 2016). Over time, Letšeng-la Letsie is expected to be less frequently influenced by westerly flow and more frequently influenced by anticyclonic flow, which may result in a marginal increase in transport of polluted air from the industrialised regions to the north.

Hexachlorobenzene (HCB), was widely used as a fungicide but banned under the Stockholm Convention on Persistent Organic Pollutants in 2001. It is a byproduct of the manufacture of certain industrial chemicals and exists as an impurity in several pesticide formulations (UNEP, 2002). As production and use of HCB have been regulated over the past decades an important source of this contaminant is its unintentional release as a byproduct in many chlorination processes in chemical and metals manufacturing. It may also be re-emitted from soils previously contaminated by agricultural use as well as combustion processes including coal burning (Bailey, 2001; Gong et al., 2017). Hexachlorobenzene is found consistently through the lake sediment core since the mid-1970s (Fig. 3). A review of organochlorine compounds in South African freshwaters (Ansara-Ross et al., 2012) demonstrated very few data for HCB except some sediment and soil concentrations in industrial and agricultural areas (Quinn et al., 2009). Its presence has also been detected in the eggs of aquatic, and aquatic-feeding, birds (Bouwman et al., 2008) and some freshwater fish species (Wepener et al., 2012; Gerber et al., 2016) and Fatoki and Awofolu (2004) reported high concentrations (up to 150 ng L^{-1}) in the waters of the Buffalo River in South Africa's Eastern Cape to the south-east of Lesotho. Hexachlorobenzene has been banned in South Africa since 1983 (Bouwman, 2004) and its use is considered limited (Gerber et al., 2016). Potential sources for HCB in Letšeng-la Letsie are, therefore, difficult to identify, although Ansara-Ross et al. (2012) cite accidental spillages, poor management of stocks and poor disposal as possible sources to the environment, in addition to its use for agricultural purposes. Fatoki and Awofolu (2004) suggest that illegal use of pesticides may also be a source. One agricultural application is as a scabicide treatment for sheep, which has been reported elsewhere in

Africa (e.g. Jemaa et al., 1986). Over 60% of households surveyed in the area around Letšeng-la Letsie own grazing animals, including cattle sheep and goats, with sheep being the dominant form of livestock (Lannas and Turpie, 2009). However, while nearly 90% of those surveyed grazed their stock in the wetland area, we have found no evidence that HCB was used as a scabicide there. Another possible source for HCB is as a by-product of coal combustion. Hexachlorobenzene is more volatile than many POPs and is stable in the atmosphere. Consequently, it has a high potential for long-range transport (Jaward et al., 2004; Shen et al., 2005; Pozo et al., 2017) and therefore HCB at Letšeng-la Letsie could be derived from Highveld coal emissions. Further research is certainly warranted to investigate organochlorine compound patterns in the region.

4.4. Scale of contamination

Contamination measured in Letšeng-la Letsie archives is low with many POPs at or below the analytical limit of detection. All trace metal concentrations, except those of Ni and Cu, are well below their consensus threshold effect concentration (TEC), the concentration at which any detrimental biological effect would be expected to occur only rarely (MacDonald et al., 2000; Buchman, 2008). Concentrations of both Ni and Cu are approximately double their TECs (22.7 and 31.6 µg g^{-1} respectively) throughout the lake sediment core and Ni concentrations approach the Probable Effects Concentration (PEC) (48.6 µg g^{-1}), the level at which detrimental biological effects would be expected due to that contaminant alone. However, both Cu and Ni have EFs of around 1.0 throughout the core indicating that these elevated concentrations are most likely natural, as reported for other studies in South Africa (Dalton et al., 2018). By contrast, and for comparison, the peak concentration of HCB in the core is 0.21 ng g^{-1}, two orders of magnitude below the US National Oceanic and Atmospheric Administration (NOAA) lowest effect level (LEL; no TEC reported for HCB) of 20 ng g^{-1} for freshwater sediments. This is defined as the level of sediment contamination that can be tolerated by the majority of benthic organisms (Buchman, 2008).

Comparing coal combustion-related contaminants in Letšeng-la Letsie sediments with those from other remote lakes, the peak SCP flux of 148 cm^{-2} yr^{-1} is up to an order of magnitude higher than equivalent fluxes in Greenland (Bindler et al., 2001) and in Antarctic or sub-Antarctic lake sediments (Rose et al., 2012). They are at a similar level to mountain lakes in Europe (e.g. Rose et al., 1999) (typically 100 - 180 cm^{-2} yr^{-1}) and the Rocky Mountains of North America (Landers et al., 2008) (50 - 100 cm^{-2} yr^{-1}). While equivalent data in Africa are sparse, the peak SCP sediment flux for Lake Bisoke, a volcanic crater lake in the Albertine Rift in Rwanda was similar (179 cm^{-2} yr^{-1}; McGlynn et al., 2019), but higher than peak fluxes in an Ethiopian mountain lake (approximately 50 cm^{-2} yr^{-1}; Bittner et al., in press).

The Hg peak concentration and EF in the Letšeng-la Letsie lake sediment core are 51 ng g^{-1} and 1.3 respectively. This concentration is equivalent to those reported from remote lakes on the Tibetan Plateau (30 - 50 ng g^{-1}; Yang et al., 2010a) but lower than Hg concentrations in sediments taken from lakes in the Rwenzori Mountains in Uganda (100 - 250 ng g^{-1}) (Yang et al., 2010b) and the US Rocky Mountains (100 - 550 ng g^{-1}) as well as lakes from central Alaska (110 - 150 ng g^{-1}) (Landers et al., 2008). The comparison for PAH contamination is similar to that of Hg, with peak concentrations of total PAH and total 16 USEPA PAHs (244 ng g^{-1} and 126 ng g^{-1} respectively) similar to those for Qinghai Lake on the northern Tibetan Plateau (15-341 and 11 - 279 ng g^{-1} respectively) (Wang et al., 2010) and in the same broad range as those reported for marine sediments in the vicinity of Antarctic islands (Sutilli et al., 2019). These PAH concentrations are lower than those for lakes in the Rocky Mountains, where total concentrations for the 16 USEPA PAHs in Lone Pine Lake and Mills Lake were reported as 210 - 280 ng g^{-1} (Usenko et al., 2007) and for European mountain lakes where peak total PAH concentrations varied between 300 ng g^{-1} for Arresjoen on Svalbard and up to 25,000 ng g^{-1} for remote mountain lakes in the Tatra Mountains of Slovakia and Poland (Fernandez et al., 2002). Interestingly, these latter concentrations are similar (9700 – 61,000 ng g^{-1}) to those reported for soils taken from the vicinity of coal-fired power stations in South Africa (Okedeyi, 2013) indicating elevated levels of proximal PAH deposition close to sources.

It is widely accepted that Hg in the global atmosphere at the start of the 21st century had increased by around 3-fold since pre-industrial times although more recent estimates place this increase at 450 % (UNEP, 2019). Hence, Hg enrichments (ratios of modern to background but not necessarily calculated as EFs) in remote lake sediments, not impacted by local or regional sources, are often seen to be around these values. For example, in a review, Fitzgerald et al. (1998) reported enrichments of 2.7 (± standard deviation of 0.9) for lakes in mid-continental North America, 2.3 (± 0.6) in northern Canada and 2.0 - 2.6 in Scandinavia. Similarly, Yang et al. (2010a;b) show Hg enrichments of 2.5 - 2.9 for Rwenzori Mountain lakes and 2.8 - 14.7 (the latter closer to sources) for Tibetan Plateau lakes. The EF for Letšeng-la Letsie is considerably lower than these remote lakes and even selecting the highest and lowest Hg fluxes only provides an enrichment ratio of below 2.0. Although low Hg values have been reported for southern Africa in the past, leading to the suggestion of an African mercury "anomaly" (e.g. Black et al., 2011), this has tended to be related to unexpectedly low Hg levels in biota which would have been expected to biomagnify Hg through the aquatic food-web. However, given the atmospheric life-time of Hg may conceivably be around one year and hence Hg deposited to remote lake sediments could potentially be derived from any global source, an African anomaly may be less relevant. Indeed, such an anomaly might be expected to result in lower Hg concentrations in uncontaminated background sediments, which would then elevate Hg EFs in contemporary samples. This is clearly not the case for Letšeng-la Letsie. It is currently unclear why Hg enrichment at the site is lower than other global 'background' locations.

4.5. Wider implications

Estimates of anthropogenic Hg emissions to the atmosphere in South Africa increased in the first decade of the 21st century from approximately 34 tonnes yr^{-1} in 2000 to around 50 tonnes yr^{-1} in 2006 (Masekoameng et al., 2010). Since then, coal combustion has levelled-off and is predicted to decline slightly through to 2030. However, coal remains in South Africa's power generation plans at least through to 2050 (South Africa Department of Energy, 2019) although there is currently no targeted mercury abatement for the country. Coal combustion in the power generation industry remains the largest Hg emission source by far in South Africa and so while predicted Hg emissions are also expected to decline slightly to 2026 (Garnham and Langerman, 2016), emissions of this and other contaminants from coal combustion such as PAHs, SCPs and other particulate matter are likely to continue into the late-21st century being distributed and deposited throughout southern Africa. Currently, deposition of these contaminants in Lesotho would appear to be limited, although comparable data within the country, as for the rest of southern Africa, are remarkably sparse and so it is difficult to ascertain the full scale and extent across the region.

Lesotho is an important water resource area for southern Africa and an estimated 780 million m^3 of water each year is exported to South Africa under the Lesotho Highlands Water Project (LHWP) programme. Despite this, many rural communities still take drinking water directly from springs and wells while urban water supplies experience frequent water scarcity. Maintaining and expanding access to clean and secure water is one of the biggest challenges facing southern Africa in the 21st century. This is likely to be exacerbated by the predicted impacts of climate change on the quantity and timing of rainfall, and increases in temperature, making this area one of the world's most climatically vulnerable regions. Determining the scale of contamination in these source areas is therefore vital for both human and ecological health.

Furthermore, the health of aquatic ecosystems is recognised as an essential prerequisite for sustainable use of water resources and Claassen (2010) states that: "*The biggest threat to a sustainable water supply in South Africa is not a lack of storage but the contamination of available* *water resources through pollution"*. Further deterioration of water quality through increasing levels of contamination could have a serious impact on ecosystem services provided by southern African freshwaters, especially to rural populations. While the situation is already critical, the synergistic effects of increased contaminant loading and climate-related stress are likely to lead to further degradation in water quality and aquatic ecosystems. Such deterioration will also jeopardise the suitability of natural waters for human use (e.g. contaminant intake through fish consumption) (Wepener and Chapman, 2012) and adversely affect ecosystem services for rural communities. Despite this, the scale, extent and rate of freshwater contamination are largely unknown and there is an urgent need to address this. In the absence of monitoring, the analysis of natural archives such as lake and wetland cores is one of the only ways by which to determine trends in the direction (i.e. improvement or deterioration) and rates of change in freshwater contamination. The records presented here which, to our knowledge, are the first high resolution multi-pollutant sediment records for southern Africa therefore provide a valuable baseline, not just for temporal changes in deposition to this background region, but also geographically for comparison to future studies in more contaminated areas of southern Africa.

Authorship contribution statement

Neil Rose: Conceptualization; Data curation; Formal analysis; Funding acquisition; Investigation; Methodology; Project administration; Visualization; Writing - original draft; Writing - review & editing. **Alice Milner:** Conceptualization; Data curation; Funding acquisition; Investigation; Methodology; Writing - review & editing. **Jennifer Fitchett:** Conceptualization; Funding acquisition; Investigation; Project administration; Methodology; Project administration; Visualization; Writing - review & editing. **Kristy Langerman:** Formal analysis; Methodology; Visualization; Writing - review & editing. **Handong Yang:** Formal analysis; Validation; Writing - review & editing. **Simon Turner:** Data curation; Formal analysis; Validation; Writing - review & editing. **Anne-Lise Jourdan:** Formal analysis; Writing - review & editing. **James Shilland:** Formal analysis; Writing - review & editing. **César Martins:** Data curation;

Formal analysis; Methodology; Validation; Visualization; Writing - review & editing. **Amanda Câmara de Souza:** Formal analysis; Methodology; Writing - review & editing. **Christopher Curtis:** Conceptualization; Funding acquisition; Investigation; Project administration; Resources; Writing - review & editing.

Declaration of Competing Interest

The authors declare no competing financial interest.

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References

Ansara-Ross, T., Wepener, V., Van den Brink, P.J., Ross, M.J., 2012. Pesticides in South African fresh waters. Afric. J. Aquat. Sci. 37, 1-16.

Appleby, P.G., 2001. Chronostratigraphic techniques in recent sediments. In: Last, W.N., Smol, J.P. (Eds.), Tracking environmental change through lake sediments. Volume 1: Basin analysis, coring and chronological techniques. Kluwer, Dordrecht, pp. 171-203.

Appleby, P.G., Richardson, N., Nolan, P.J., 1992. Self-absorption corrections for well-type germanium detectors. Nucl. Instr. Methods Phys. Res. Section B - Beam Interactions with Materials and Atoms. 71, 228-233.

Bailey, R.E., 2001. Global hexachlorobenzene emissions. Chemosphere 43, 167–182.

Bezuidenhout, L.M., Schoonbee, H.J. de Wet, L.P.D., 1990. Heavy metal content in organs of the African sharptooth catfish, *Clarias gariepinus* (Burchell), from a Transvaal lake affected by mine and industrial effluents. Part 1. Zinc and copper. Water SA. 16, 125-129.

Bícego, M.C., Taniguchi, S., Yogui, G.T., Montone, R.C., Silva, D.A.M., Lourenço, R.A., Martins, C.C., Sasaki, S.T., Pellizari, V.H., Weber, R.R., 2006. Assessment of contamination by polychlorinated biphenyls and aliphatic and aromatic hydrocarbons in sediments of the Santos and São Vicente Estuary System, São Paulo, Brazil. Mar. Pollut. Bull. 52, 1804–1816.

Bindler, R., Renberg, I., Appleby, P.G., Anderson, N.J., Rose, N.L., 2001. Mercury accumulation rates and spatial patterns in lake sediments from west Greenland: a coast to ice margin transect. Environ. Sci. Technol. 35, 1736-1741.

Bittner, L., Bliedtner, M., Grady, D., Gil-Romera, G., Martin-Jones, C., Lemma, B., Mekonnen, B., Lamb, H., Yang, H., Glaser, B., Szidet, S., Salazar, G., Rose, N.L., Opgenoorth, L., Miehe, G., Nauss, T., Zech, W., Zech, M. (in press). Revisiting afro-alpine Lake Garba Guracha in the Bale Mountains of Ethiopia – rationale, chronology, geochemistry and paleoenvironmental implications. J. Paleolimnol.

Black, F.J., Bokhutlo, T., Somoxa, A., Maethamako, M., Modisaemang, O., Kemosedile, T., Cobb-Adams, C., Mosepele, K., Chimbari, M., 2011. The tropical African mercury anomaly: lower than expected mercury concentrations in fish and human hair. Sci. Tot. Environ. 409, 1967-1975.

Borg, C., 2012. Mechanisms controlling valley asymmetry development at Abisko Northern Sweden and Sani Pass, Southern Africa. Geotrycheriet Uppsala University: Uppsala.

Bouwman, H., 2004. South Africa and the Stockholm Convention on persistent organic pollutants: science policy. South African J. Sci. 100, 323-328.

Bouwman, H., Polder, A., Venter, B., Skaare, J.U., 2008. Organochlorine contaminants in cormorant, darter, egret, and ibis eggs from South Africa. Chemosphere. 71, 227-241.

Buchman, M.F., 2008. NOAA Screening Quick Reference Tables, NOAA ORandR Report 08-1, Seattle WA, Office of Response and Restoration Division, National Oceanic and Atmospheric Administration, 34 pp. https://response.restoration.noaa.gov/environmental-restoration/environmental-assessment-tools/squirt-cards.html. Accessed 31st March 2020.

Carbutt, C. and Edwards, T.J., 2004. The flora of the Drakensberg Alpine Centre. Edinburgh J. Botany. 60, 581-607.

Carbutt, C. and Edwards, T.J., 2006. The endemic and near-endemic angiosperms of the Drakensberg Alpine Centre. South African J. Bot. 72, 105-132.

Cevik, F., Göksu, M.Z.L., Derici, O.B., Findik, O., 2009. An assessment of metal pollution in surface sediments of Seyhan dam by using enrichment factor, geoaccumulation index and statistical analyses. Environ. Monit. Assess. 152, 309–317.

Chelgani, S.C., 2019. Investigating the occurrences of valuable trace elements in African coals as potential byproducts of coal and coal combustion products. J. Afric. Earth Sci. 150, 131-135.

Chen, C-W., Kao, C-M., Chen, C-F., Dong, C-D., 2007. Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. Chemosphere. 66, 1431–1440.

Claassen, M., 2010. How much water do we have? In: CSIR Perspective on Water in South Africa. Council for Scientific and Industrial Research (CSIR) Report: CSIR/NRE/PW/IR/2011/0012/A.

Critical Ecosystem Partnership Fund (CEPF), 2011. Maputaland-Pondoland-Albany Ecosystem Profile Summary. Critical Ecosystem Partnership Fund / Conservation International, Arlington.

Dalton, A., Feig, G.T., Barber, K., 2018. Trace metal enrichment observed in soils around a coal fired power plant in South Africa. Clean Air J. 28, 1-9.

Das, S.K., Routh, J., Roychoudhury, A.N., 2008a. Sources and historic changes in polycyclic aromatic hydrocarbon input in a shallow lake, Zeekoevlei, South Africa. Org. Geochem. 39, 1109-1112.

Das, S.K., Routh, J., Roychoudhury, A.N., Klump, J.V. 2008b. Major and trace element geochemistry in Zeekoevlei, South Africa: a lacustrine record of present and past processes. Appl. Geochem. 23, 2496-2511.

Davis, C.L., 2011. Climate Risk and Vulnerability: A Handbook for Southern Africa. CSIR: Pretoria, 92.

Dean Jr, W.E., 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: Comparison with other methods. J. Sed. Petrol. 44, 242-248.

Denoux, G.J., Gardinali, P., Wade, T.L., 1998. Quantitative determination of polynuclear aromatic hydrocarbons by gas chromatography/mass spectrometry - selected ion monitoring (SIM) mode. NOAA Technical Memorandum NOS ORCA 130, 129-139.

De Vleeschouwer, F., Chambers, F.M., Swindles, G.T., 2010. Coring and sub-sampling of peatlands for palaeoenvironmental research. Mires and Peat, 7.

Draxler, R.R., Stunder, B., Rolph, G., Stein, A., Taylor, A., 2012. HYSPLIT_4 User's Guide, NOAA Air Resources Laboratory, Silver Spring, Maryland. http://www.arl.noaa.gov/documents/reports/hysplit_user_guide.pdf.

Driver, A., Sink, K.J., Nel, J.L., Holness, S., van Niekerk, L., Daniels, F., Jonas, Z., Majiedt, P.A., Harris, L., Maze, K., 2012. National Biodiversity Assessment 2011: An assessment of South Africa's biodiversity and ecosystems. South African National Biodiversity Institute, Pretoria.

ESKOM, 2019. Annual reports http://www.eskom.co.za/sites/heritage/Pages/Annual-Reports.aspx and statements http://www.eskom.co.za/OurCompany/Investors/IntegratedReports/Pages/Annual_Statements.aspx Accessed 22nd November 2019.

Fatoki, O.S., Awofolu O.R., 2004. Levels of Organochlorine Pesticide Residues in Marine-, Surface-, Ground- and Drinking Waters from the Eastern Cape Province of South Africa. J. Environ. Sci. Health B. 39, 101-114.

Fauchereau, N., Trzaska, S., Rouault, M., Richard, Y., 2003. Rainfall variability and changes in southern Africa during the 20th century in the global warming context. Natur. Hazards. 29, 139-154.

Fernández, P., Rose, N.L., Vilanova, R.M., Grimalt, J.O., 2002. Spatial and temporal comparison of polycyclic aromatic hydrocarbons and spheroidal carbonaceous particles in remote European lakes. Wat. Air Soil Pollut. Focus. 2, 261-274.

Fitchett, J.M., Bamford, M.K., Mackay, A.W., Grab, S.W., 2017. *Chrysocoma cilliata* L. (Asteraceae) in the Lesotho Highlands: an anthropogenically introduced invasive or niche coloniser? Biol. Invas. 19, 2711-2728.

Fitzgerald, W.F., Engstrom, D.R., Mason, R.P., Nater, E.A., 1998. The case for atmospheric mercury contamination in remote areas. Environ. Sci. Technol. 32, 1-7.

García-Rodríguez, F., Anderson, C.R., Adams, J.B., 2007. Paleolimnological assessment of human impacts on an urban South African lake. J. Paleolimnol. 38, 297-308.

Garnham, B.L., Langerman, K.E., 2016. Mercury emissions from South Africa's coal-fired power stations. Clean Air J. 26, 14-20.

Gaughan, A.E., Staub, C.G., Hoell, A., Weaver, A. and Waylen, P.R., 2016. Inter-and Intra-annual precipitation variability and associated relationships to ENSO and the IOD in southern Africa. Internat. J. Climat. 36, 1643-1656.

Gerber, R., Smit, N.J., Van Vuren, J.HJ., Nakayama, S.M.M., Yohannes, Y.B., Ikenaka, Y., Ishizuka, M., Wepener, V., 2016. Bioaccumulation and human health risk assessment of DDT and other organochlorine pesticides in an apex aquatic predator from a premier conservation area. Sci. Tot. Environ. 550, 522-533.

Gong W., Fiedler H., Liu X., Wang, B., Yu, G., 2017. Emission factors of unintentional HCB and PeCBz and their correlation with PCDD/PCDF. Environ. Pollut. 230, 516–522.

Grab, S., 2002. Characteristics and palaeoenvironmental significance of relict sorted patterned ground, Drakensberg plateau, southern Africa. Quat. Sci. Rev. 21, 1729-1744.

Grab, S.W., 2010. Alpine turf exfoliation pans in Lesotho, southern Africa: Climate-process-morphological linkages. Geomorphology. 114, 261-275.

Grab, S.W., Nash, D.J., 2010. Documentary evidence of climate variability during cold seasons in Lesotho, southern Africa, 1833-1900. Clima. Dynam. 34, 473-499.

Grab, S.W., Linde, J.H., 2014. Mapping exposure to snow in a developing African context: implications for human and livestock vulnerability in Lesotho. Natur. Hazards. 71, 1537-1560.

Greichus, Y.A., Greichus, A., Amman, B.D., Call, D.J., Hamman, D.C., Pott, R.M., 1977. Insecticides, polychlorinated biphenyls and metals in African lake ecosystems. I. Hartbeespoort Dam, Transvaal and Voëlvlei Dam, Cape Province, Republic of South Africa. Arch. Environ. Contam. Toxicol. 6, 371-383.

Grobler, D.F., Badenhorst, J.E., Kempster, P.L., 1996. PCBs, chlorinated hydrocarbon pesticides and chlorophenols in the Isipingo Estuary, Natal, Republic of South Africa. Mar. Pollut. Bull. 32, 572-575.

Heaton, T.H.E., 1987. 15N/14N ratios of nitrate and ammonium in rain at Pretoria, South Africa. Atmos. Environ. 21, 843-852.

Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. J. Palaeolim. 25, 101-110.

Holtgrieve, G.W., Schindler, D.E., Hobbs, W.O., Leavitt, P.R., Ward, E.J., Bunting, L., Chen, G., Finney, B.P., Gregory-Eaves, I., Holmgren, S., Lisac, M.J., Lisi, P.J., Nydick, K., Rogers, L.A., Saros, J.E., Selbie, D.T., Shapley, M.D., Walsh, P.B., Wolfe, A.P., 2011. A coherent signature of anthropogenic nitrogen deposition to remote watersheds of the northern hemisphere. Science. 334, 1545-1548.

Humphries, M.S., 2013. DDT residue contamination in sediments from Lake Sibaya in northern KwaZulu-Natal, South Africa: Implications for conservation in a World Heritage Site. Chemosphere. 93, 1494-1499

Jaward, F.M., Farrar, N.J., Harner, T, Sweetman, A.J., Jones, K.C., 2004. Passive air sampling of PCBs, PBDEs and organochlorine pesticides across Europe. Environ. Sci. Technol. 38, 34–41.

Jemaa, Z., Sabbah, S., Driss, M.R., Bouguerra, M.L., 1986. Hexachlorobenzene in Tunisian mothers' milk, cord blood and foodstuffs. In: Morris, C.R., Cabral, J.R.P. (Eds.), Hexachlorobenzene: Proceedings of an International Symposium. IARC Sci. Publ. 77. Lyon, 139-142.

Josipovic, M., Annegard, H.J., Kneen, M.A., Pienaar, J.J., Piketh, S.J., 2011. Atmospheric dry and wet deposition of sulphur and nitrogen species and assessment of critical loads of acidic deposition exceedance in South Africa. S. Afric. J. Sci. 107, 1-10.

Kotze, P., Du Preez, H.H., Van Vuren, J.H.J., 1999. Bioaccumulation of copper and zinc in *Oreochromis mossambicus* and *Clarias gariepinus*, from the Olifants River, Mpumalanga, South Africa. Water SA. 25, 99-110.

Lamarque, J.F., Dentener, F., McConnell, J., Ro, C.U., Shaw, M., Vet, R., Bergmann, D., Cameron-Smith, P., Dalsoren, S., Doherty, R. and Faluvegi, G., 2013. Multi-model mean nitrogen and sulfur deposition from the atmospheric chemistry and climate model intercomparison project (ACCMIP): evaluation of historical and projected future. Atmos. Chem. Phys. 13, 7997-8018.

Landers, D.H., Simonich, S.L., Jaffe, D.A., Geiser, L.H., Campbell, D.H., Schwindt, A.R., Schreck, C.B., Kent, M.L., Hafner, W.D., Taylor, H.E., Hageman, K.J., Usenko, S., Ackerman, L.K., Schrlau, J.E., Rose, N.L., Blett, T.F., Erway, M.M., 2008. The fate, transport, and ecological impacts of airborne contaminants in Western National Parks (USA). EPA/600/R-07/138. U.S. Environmental Protection Agency, Office of Research and Development, NHEERL, Western Ecology Division, Corvallis, Oregon. 350pp.

Lannas, K.S., Turpie, J.K., 2009. Valuing the provisioning services of wetlands: contrasting a rural wetland in Lesotho with a peri-urban wetland in South Africa. Ecol. Soc. 14(2), 18.

Le Maitre, D., Seyler, H., Holland, M., Smith-Adoa, L., Nel, J., Maherry, A., Witthuser, K., 2018. Identification, delineation and importance of the strategic water source areas of South Africa, Lesotho and Swaziland for Surface Water and Groundwater. Report No. TT 743/1/18, Water Research Commission, Pretoria.

Lesotho Bureau of Statistics,, 2016. 2016 Lesotho Population Census. Ministry of Development Planning. Maseru, Kingdom of Lesotho.

Lesotho Government, National Environment Secretariat, 2000. Biological Diversity in Lesotho. Department of Environment. Kingdom of Lesotho. Maseru. 142pp

Lesotho Ministry of Natural Resources, 1996. Water Resources Management: Policies and Strategies. Government of Lesotho.

Letšela, L.M.S., 2008. A participatory sustainability assessment framework for biodiversity conservation in rural areas. PhD Thesis submitted to the University of the Free State: Bloemfontein.

MacDonald, D.D., Ingersoll, C.G. and Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39, 20-31.

Marais, E.A., Silvern, R.F., Vodonos, A., Dupin, E., Bockarie, A.S., Mickley, L.J., Schwartz, J., 2019. Air Quality and Health Impact of Future Fossil Fuel Use for Electricity Generation and Transport in Africa. Environ. Sci. Technol. 53, 13524-13534.

Marake, M., Mokuku, C., Majoro, M., Mokkitimi, N., 1998. Global change and subsistence rangelands in southern Africa: Resource availability, access and use in relation to rural livelihoods and welfare. National University of Lesotho, Maseru.

Masekoameng, K.E., Leaner, J., Dabrowski, J., 2010. Trends in anthropogenic mercury emissions estimated for South Africa during 2000–2006. Atmos. Environ. 44, 3007-3014.

Mason, C.F., Rowe-Rowe, D.T., 1992. Organochlorine pesticide residues and PCBs in otter scats from Natal. S. Afric. J. Wildlife Res. 22, 29-31.

Matope, T. (2014). Tug of war over Letšeng-la Letsie. Lesotho Times. March 21st 2014. (http://lestimes.com/tug-of-war-over-letseng-la-letsie/). Accessed 30th October 2019.

McCarthy, T.S.,Venter, J.S., 2006. Increasing pollution levels on the Witwatersrand recorded in the peat deposits of the Klip River wetland. S. Afric. J. Sci. 102, 27-34.

McCarthy, T.S., 2011. The impact of acid mine drainage in South Africa. S. Afric. J. Sci. 107, 712

McGlynn, G., Lejju, J., Dalton, C., Mooney, S.D., Rose, N.L., Tompkins, A.M., Bannister, W., Tan, Z.D., Zheng, X., Rühland, K., Taylor, D., 2019. Aquatic ecosystem changes in a global biodiversity hotspot: evidence from the Albertine Rift, central Africa. J. Biogeog. 46, 2098-2114

Monna, F., Poujol, M., Losno, R., Dominik, J., Annegarn, H., Coetzee, H., 2006. Origin of atmospheric lead in Johannesburg, South Africa. Atmos. Environ. 40, 6554-6566.

Motanya, L., 2003. Information Sheet on RAMSAR Wetlands: Letšeng-la Letsie LS1388RIS. Department of Water Affairs, Ministry of Natural Resources, Lesotho.

Mpholo, M., Mathaba, T., Letuma, M., 2012. Wind profile assessment at Masitise and Sani in Lesotho for potential off-grid electricity generation. Energy Cons. Manag. 53, 118-127.

Myers, N., Mittermeier, R.A., Mittermeier, C.G., da Fonseca, G.A., Kent, J., 2000. Biodiversity hotspots for conservation priorities. Nature. 6772, 853-858.

Naffrechoux, E., Cottin, N., Pignol, C., Arnaud, F., Jenny, J-P., Perga, M-E., 2015. Historical profiles of PCB in dated sediment cores suggest recent lake contamination through the "halo effect." Environ. Sci. Technol. 49, 1303–1310.

Nakayama, S.M., Ikenaka, Y., Muzandu, K., Choongo, K., Oroszlany, B., Teraoka, H., Mizuno, N., Ishizuka, M., 2010. Heavy metal accumulation in lake sediments, fish (*Oreochromis niloticus* and *Serranochromis thumbergi*), and crayfish (*Cherax quadricarinatus*) in Lake Itezhi-tezhi and Lake Kariba, Zambia. Arch. Environ. Contam. Toxicol. 59, 291-300.

Nüsser, M., Grab, S., 2002. Land degradation and soil erosion in the eastern Highlands of Lesotho, Southern Africa. Beiträge sur Physischen Geographie. 133, 291-311.

Okedeyi, O.O., 2012. Assessment of polycyclic aromatic hydrocarbon (PAHs) and heavy metals in the vicinity of coal power plants in South Africa. University of South Africa. (Doctoral dissertation)

Panichev, N., Mokgalaka, N., Panicheva, S., 2019. Assessment of air pollution by mercury in South African provinces using lichens *Parmelia caperata* as bioindicators. Environ. Geochem. Health. 41, 2239-2250.

Piketh, S.J., Swap, R.J., Anderson, C.A., Freiman, M.T., Zunckel, M., Held, G., 1999. The Ben Macdhui High Altitude Trace Gas and Aerosol Transport Experiment. S. Afric. J. Sci. 95, 35-43.

Piketh, S.J., Swap, R.J., Maenhaut, W., Annegarn, H.J., Formenti, P., 2002. Chemical evidence of long-range transport over southern Africa. J. Geophys. Res. Atmos. 107(D24), ACH 7-1–ACH 7-3.

Pozo K., Martellini T., Corsolini S., Harner, T., Estellano, V., Kukučka, P., Mulder, M.D., Lammel, G., Cincinelli, A., 2017. Persistent organic pollutants (POPs) in the atmosphere of the coastal areas of the Ross Sea, Antarctica: Indications for long-term downward trends. Chemosphere. 178, 458-465.

Quinn, L., Pieters, R., Nieuwoudt, C., Borgen, A.R., Kylin, H., Bouwman, H., 2009. Distribution profiles of selected organic pollutants in soils and sediments of industrial, residential and agricultural areas of South Africa. J. Environ. Monit. 11, 1647-1657.

Ratshomo, K., Nembahe, R., n.d. South African Coal Sector Report. Department of Energy, Pretoria. http://www.energy.gov.za/files/media/explained/South-African-Coal-Sector-Report.pdf Accessed 5th November 2019.

Reason, C.J.C., Rouault, M., 2005. Links between the Antarctic Oscillation and winter rainfall over western South Africa. Geophys. Res. Lett. 32(7).

Renberg, I., Hansson, H., 2008. The HTH sediment corer. Journal of Paleolimnology 40: 655-659.
Rose, N.L. (1994). A note on further refinements to a procedure for the extraction of carbonaceous fly-ash particles from sediments. J. Paleolim. 11, 201-204.

Rose, N.L., 2001. Fly-ash particles. In: Last, W.M., Smol, J.P., (Eds.) Tracking Environmental Change Using Lake Sediments: Volume 2. Physical and Chemical Techniques. Kluwer Academic Publishers, Dordrecht, The Netherlands. pp. 319 – 349.

Rose, N.L., 2008. Quality control in the analysis of lake sediments for spheroidal carbonaceous particles. Limnol. Oceanogr. Meth. 6, 172 – 179.

Rose, N.L., Harlock, S., Appleby, P.G., 1999. The spatial and temporal distributions of spheroidal carbonaceous fly-ash particles (SCP) in the sediment records of European mountain lakes. Wat. Air Soil Pollut. 113, 1-32.

Rose, N.L., Jones, V.J., Noon, P.E., Hodgson, D.A., Flower, R.J., Appleby, P.G., 2012. Long-range transport of pollutants to the Falkland Islands and Antarctica: Evidence from lake sediment fly-ash particle records. Environ. Sci. Technol. 46, 9881 – 9889

Roux, D.J., Badenhorst, J.E., Du Preez, H.H., Steyn, G.J., 1994. Note on the occurrence of selected trace metals and organic compounds in water, sediment and biota of the Crocodile River, Eastern Transvaal, South Africa. Water SA, 20, 333-340.

Schmitz, G., Rooyani, F., 1987. Lesotho geology, geomorphology, soils. National University of Lesotho: Maseru.

Senatla, M., Nchake, M., Taele, B.M., Hapazari, I., 2018. Electricity capacity expansion plan for Lesotho–implications on energy policy. Energy Policy. 120, 622-634.

Sene, K.J., Jones, D.A., Meigh, J.R., Farquarson, F.A.K., 1998. Rainfall and flow variations in the Lesotho highlands. Internat. J. Climat. 18, 329-345.

Sereda, B.L., Meinhardt, H.R., 2005. Contamination of the water environment in malaria endemic areas of KwaZulu-Natal, South Africa by DDT and its metabolites. Bull. Environ. Contam. Toxicol. 75, 538-545

Shen L., Wania F., Lei Y.D., Teixeira, C., Muir, D.C.G., Bidleman, T.F., 2005. Atmospheric distribution and long-range transport behavior of organochlorine pesticides in North America. Environ. Sci. Technol. 39, 409–420.

Skofteland, E., 1988. Establishment of hydrometric stations within Quthing River basin, Lesotho. A mission report. Norwegian Water Resources and Energy Administration Report 02-88. 25pp.

Sousa, P.M., Blamey, R.C., Reason, C.J., Ramos, A.M. and Trigo, R.M., 2018. The 'Day Zero' Cape Town drought and the poleward migration of moisture corridors. Environ. Res. Lett. 13, 124025.

South Africa Department of Energy, 2019. Integrated Resource Plan. https://www.egsa.org.za/wp-content/uploads/2019/10/IRP-2019_corrected-as-gazetted-18-October-2019-No.-42784.pdf Accessed 29th October 2019.

South African Weather Service (SAWS), 2017. Climate Change Reference Atlas for South Africa. Water Research Commission, Pretoria.

StatsSA, 2018. Electricity, gas and water supply industry, 2016. Statistics South Africa Report No. 41-01-02 (2016). http://www.statssa.gov.za/publications/Report-41-01-02/Report-41-01-022016.pdf. Accessed 5 November 2019.

Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F., 2015. NOAA's HYSPLIT atmospheric transport and dispersion modeling system. Bull. Am. Met. Soc. 96, 2059-2077.

Sutilli, M., Ferreira, P.A.L., Figueira, R.C.L., Martins, C.C., 2019. Depositional input of hydrocarbons recorded in sedimentary cores from Deception and Penguin Islands (South Shetland Archipelago, Antarctica). Environ. Pollu. 253, 981-991.

Thamae, L.Z., Thamae, R.I., Thamae, T.M., 2015. Assessing a decade of regulatory performance for the Lesotho electricity industry. Utilities Policy. 35, 91-101.

Thang, P.Q., Kim, S-J., Lee, S.J., Ye, J., Seo, Y-K., Baek, S-O., Choi, S-D., 2019. Seasonal characteristics of particulate polycyclic aromatic hydrocarbons (PAHs) in a petrochemical and oil refinery industrial area on the west coast of South Korea. Atmos. Environ. 198, 398-406.

Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110-119.

Tutu, H., McCarthy, T.S., Cukrowska, E., 2008. The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand Basin, South Africa as a case study. Appl. Geochem. 23, 3666-3684.

United Nations Environmental Programme (UNEP), 2002. Regionally based assessment of persistent toxic substances. Sub-Saharan Africa Regional Report. 118.

United Nations Environment, 2017. Toolkit for Identification and Quantification of Mercury Sources, Reference Report and Guideline for Inventory Level 2, Version 1.4, December 2017. UN Environment Chemicals Branch, Geneva, Switzerland.

United Nations Environment, 2019. Global Mercury Assessment 2018. UN Environment Programme, Chemicals and Health Branch Geneva, Switzerland. https://www.unenvironment.org/resources/publication/global-mercury-assessment-2018. Accessed 31st March 2020.

United Nations Environmental Programme, 1992. Determinations of Petroleum Hydrocarbons in Sediments. Reference Methods for Marine Pollution Studies. No. 20.

Usenko, S., Landers, D.H., Appleby, P.G., Simonich, S.L., 2007. Current and historical deposition of PBDEs, pesticides, PCBs, and PAHs to rocky mountain national park. Environ. Sci. Technol. 41, 7235-7241.

Venter, A.D., van Zyl, P.G., Beukes, J.P., Josipovic, M., Hendriks, J., Vakkari, V., Laakso, L., 2017. Atmospheric trace metals measured at a regional background site (Welgegund) in South Africa. Atmos. Chem. Phys. 17, 4251-4263.

Vosloo, R., Bouwman, H., 2005. Survey of certain persistent organic pollutants in major South African waters. Report to the Water Research Commission. WRC1213/1/05.

Wade, T.L., Cantillo, Y.A., 1994. Use of standards and reference materials in the measurement of chlorinated hydrocarbon residues. Chemistry Workbook. NOAA Tech. Mem. NOS ORCA 77, Silver Spring, Maryland, 59pp.

Wang, X., Yang, H., Gong, P., Zhao, X., Wu, G., Turner, S., Yao, T., 2010. One century sedimentary records of polycyclic aromatic hydrocarbons, mercury and trace elements in the Qinghai Lake, Tibetan Plateau. Environ. Pollut. 158, 3065-3070.

Wepener, V., Chapman, P.M., 2012. South African ecotoxicology—present status and future prognosis. Afric. J. Aq. Sci. 37, 229-234.

Wepener, V., Smit, N., Covaci, A., Dyke, S., Bervoets, L., 2012. Seasonal bioaccumulation of organohalogens in tigerfish, *Hydrocynus vittatus* Castelnau, from Lake Pongolapoort, South Africa. Bull. Environ. Contam. Toxicol. 88, 277-282.

Yang, H., Battarbee, R.W., Turner, S.D., Rose, N.L., Derwent, R.G., Wu, G., Yang R., 2010a. Historical reconstruction of mercury pollution across the Tibetan Plateau using lake sediments. Environ. Sci. Technol. 44, 2918-2924.

Yang, H., Engstrom, D., Rose, N.L., 2010b. Recent changes in atmospheric mercury deposition recorded in the sediments of remote, equatorial lakes in the Rwenzori Mountains, Uganda. Environ. Sci. Technol. 44, 6570 – 6575.

Yang, H., Turner, S., Rose, N.L., 2016. Mercury pollution in the lake sediments and catchment soils of anthropogenically-disturbed sites across England. Environ. Pollut. 219, 1092-1101.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33, 489–515.

Zunckel, M., Piketh, S., Freiman, T., 1999. Dry deposition of sulphur at a high-altitude background station in South Africa. Wat. Air Soil Pollut. 115, 445-463.