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Mid-twentieth century increases in anthropogenic Pb, Cd and Cu in central Asia set in hemispheric perspective using Tien Shan ice core

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HIGHLIGHTS

- Major/trace element records (1908–1995) were retrieved from central Asian ice core.
- Pb, Cd and Cu reveal anthropogenic contributions beginning in the 1950s.
- Pb, Cd and Cu reflect anthropogenic emissions from the Soviet Union and China.
- Anthropogenic sources include non-ferrous metals, coal and phosphate fertilizers.

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ABSTRACT

High-resolution major and trace element (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Li, Mn, Na, Pb, S, Ti, and V) ice core records from Inilchek glacier (5120 m above sea level) on the northwestern margin of the Tibetan Plateau provide the first multi-decadal ice core record spanning the period 1908–1995 AD in central Tien Shan. The trace element records reveal pronounced temporal baseline trends and concentration maxima characteristic of post-1950 anthropogenic emissions. Examination of Pb, Cd and Cu concentrations, along with non-crustal calculation estimates (i.e. excess (ex) and enrichment factor (EF)), reveal that discernable anthropogenic inputs began during the 1950s and rapidly increased to the late-1970s and early 1980s, by factors up to of 5, 6 and 3, respectively, relative to a 1910–1950 means. Pb, Cd and Cu concentrations between the 1950s-1980s are reflective of large-scale Soviet industrial and agricultural development, including the growth of production and/or consumption of the non-ferrous metals, coal and phosphate fertilizers. NOAA HYSPLIT back-trajectory frequency analysis suggests pollutant sources originating primarily from southern Kazakhstan (e.g. Shymkent and Balkhash) and the Fergana Valley (located in Kazakhstan, Uzbekistan and Kyrgyzstan). Inilchek ice core Pb, Cd and Cu reveals declines during the 1980s concurrent with Soviet economic declines, however, due to the rapid industrial and agricultural growth of western China, Pb, Cd and Cu trends increase during the 1990s reflecting a transition from primarily central Asian sources to emission sources from western China (e.g. Xinjiang Province).

1. Introduction

Rapid twentieth century growth of industry and agriculture has led to large-scale increases in heavy metal concentrations in air, water and soil, threatening natural ecosystems and human health (Pacyna and Pacyna, 2001; Järup, 2003). Major anthropogenic

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sources include non-ferrous metal production, fossil fuel combustion (e.g. leaded gasoline, oil and coal), fertilizers and waste incineration. Human exposure to these heavy metals (e.g. Pb and Cd) can result in both acute and chronic ailments including detrimental impacts to the development of the nervous system and severe respiratory, kidney and bone disorders (Järup, 2003). The spatial impacts of heavy metal emissions can vary from local to global, as pollutants can be deposited near the emission source and transported long-distances (Knutson and Tu, 1996; Pacyna and Pacyna, 2001). In recent decades research via various monitoring programs and emission inventories have been conducted to assess the impacts of heavy metals (e.g. Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2001). Unfortunately, these studies are limited to the past few decades and thus are not long enough to determine natural background levels. Considering this limitation, ice core records offer the ideal natural archive for inferring the past atmospheric compositions of anthropogenic pollutants, as they can provide well-preserved, high-resolution, multi-parameter glaciochemical data that predate the instrumental era.

Ice core records have previously been utilized to reconstruct atmospheric heavy metal concentrations in the northern hemisphere (e.g. Boutron et al., 1991; Eichler et al., 2012, 2014; Hong et al., 2009; Kaspari et al., 2009; Li et al., 2006; McConnell et al., 2006; Osterberg et al., 2008; Schwikowski et al., 2004; Shotyk et al., 2005; Van de Velde et al., 2000). These records have captured and revealed the spatial and temporal variability in the rise of atmospheric heavy metal concentrations during the rapid industrialization of the twentieth century, as well as subsequent emission reductions, reflective of regional pollution abatement legislation (i.e. North America and Europe) (Boutron et al., 1991; Fischer et al., 1998; Preunkert et al., 2001; Schwikowski et al., 2004; Van de Velde et al., 2000), and/or declines in industrial production (e.g. Eastern Europe and Soviet Union) (Eichler et al., 2012, 2014).

By the end of the twentieth century, Asia was estimated to be the largest emitter of anthropogenic atmospheric pollutants, including trace elements (Pacyna and Pacyna, 2001). Central Asian countries (e.g. Kazakhstan, Kyrgyzstan, Uzbekistan), along with western China, contain large-scale mining industries and agricultural lands that have severely polluted the regional ecosystems, impacting human health (UNEP, 2003; WHO, 2001). High natural background levels of dust, originating from the arid regions of central Asia and western China (e.g. Kyzyl Kum, Kara Kum, Aral Sea region) and Taklimakan Desert), can conceal anthropogenic inputs and make the distinction between natural and anthropogenic sources more complex. Therefore, high-elevation Asian ice cores, further removed from dust influences, are essential to help determine the impact of atmospheric heavy metal pollutants and assess natural background concentrations.

Previous Asian trace element ice core records that span multiple decades suggest that onsets of discernable anthropogenic inputs vary. Pb, Cd and Cu begin between the 1930s and 1940s at Belukha (Eichler et al., 2012, 2014), Bi, U, Cs, As, Mo, Sn, and Sb from Everest (Himalayas) (Kang et al., 2007; Kaspari et al., 2009; Hong et al., 2009) and Sb, Bi, Pb from Muztagh Ata (eastern Pamir) begin increasing between the 1950s and 1970s (Y. Li et al., 2006). Minor contributions of Sb, Bi, and Pb have been suggested at Miaoergou glacier (eastern Tien Shan) between 1953 and 2004 (Liu et al., 2011).

In the central Tien Shan, previous studies on trace elements have been limited, with the longest available records representing only a few years (1992–1998) (Kreutz and Sholkovitz, 2000). Here we present the first high-resolution multi-decadal (1908–1995) trace element records from Inilchek glacier (42.26°N, 80.42°E, 5120 m a.s.l; Fig. 1a), located in the central Tien Shan, focusing on Pb, Cd and Cu concentrations. Inilchek Glacier serves as an excellent archive to reconstruct the regional evolution of anthropogenic pollutants, due to its proximity to major Soviet and Chinese (western province of Xinjiang) industrial and agricultural centers that developed rapidly during mid-late twentieth century.

2. Methodology

2.1. Ice core collection and chemical analysis

In the summer of 2000, a collaborative ice core drilling expedition from the Climate Change Institute (University of Maine), the University of Idaho and the University of New Hampshire was conducted on the Inilchek glacier (42.26°N, 80.42°E, 5120 m a.s.l), located in the Tien Shan in Kyrgyzstan. Two ice cores were retrieved during the expedition using the ECLIPSE solar powered electromechanical drill (Blake et al., 1998; Gerasimoiff and Wake, 2001) and were returned frozen to the U.S. for analysis (Kreutz et al., 2003). Borehole temperature profiles were constant and were recorded at −12 °C between 10 m and 50 m and −11.2 °C at 100 m and 160 m, and stratigraphy profiles revealed negligible snowmelt (Aizen et al., 2001). This paper presents the methodology and data from the higher elevation core, Core 2 (160.48 m, 5120 m a.s.l.).

Core 2 was processed using a discrete sampling (DS) method. Samples were sectioned on a modified band-saw set (stainless-steel blades; tabletops and saw guides covered with teflon) and were regularly cleaned with ethyl alcohol and deionized (DI) water (>18.2 MΩ). Sample resolutions between 8 and 160 m depth were 0.10 m. Each individual sample outer surface was scraped in a clean cold room using a clean plastic lathe with pre-cleaned ceramic blades wearing a non-particulating tyvek suit, face mask and wrist-length polypropylene (PP) gloves. Samples were then placed into Whirlpak bags and melted at room temperature. A total of 1510 co-registered samples were collected into high-density polyethylene (HDPE) vials and polypropylene (PP) vials for analysis of stable water isotopes ($\delta^{18}O$ and δD) and trace elements (e.g. Al, As, Ca, Cd, Co, Cr, Cu, Fe, Li, Mn, Na, Pb, S, Ti, V). Vial-cleaning procedures for elemental analysis followed Osterberg et al. (2006). Stable water isotopes were analyzed at the Climate Change Institute (CCI) and the University of Idaho using a Micromass Isoprime ion chromatograph, a VG/Micromass SIRA and Isoprime magnetic sector SIRA (Stable Isotope Ratio Analysis) mass spectrometer configured in continuous flow mode with an Eurovector Pyr-OH peripheral with LAS (Liquid Auto Sampler). Analysis of major and trace elements were conducted at CCI using a Thermo-Finnigan Element 2 inductively coupled plasma sector field mass spectrometer (ICP-SFMS), respectively. The ICP-SFMS is coupled with a microflow nebulizer/desolvation introduction system to reduce potential spectroscopic interferences (Field and Sherrell, 2003; Gabrielli et al., 2006). ICP-SFMS samples were acidified to 1% with double-distilled HNO_3 and spiked with 1 ppb of indium as an internal standard under a class 100 High Efficiency Particle Air (HEPA) clean bench, and allowed to react with the acid for ten days before being frozen. Samples were melted at room temperature approximately 24 h prior to analysis. A statistical summary of major and trace elements is presented in Table 1. In addition, Core 2 was analyzed at Lamont-Doherty Earth Observatory for ^{137}Cs at approximately 1 m sample resolution using outer ice core cuts.

2.2. Inilchek time-scale

The Inilchek (Core 2) was annually dated to 1908 AD at a depth of ~160 m. The depth-age scale was based primarily on the annual layer counting (ALC) of clear sub-annual (seasonal) variation of stable water isotopes ($\delta^{18}O$ and δD) (Fig. 2a.). Although the majority of precipitation in the Inilchek Valley occurs during the summer