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Historical reconstruction of anthropogenic mercury input from sedimentary records: Yeongsan Estuary, South Korea

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ABSTRACT

The rapid economic growth of the Republic of Korea (S. Korea) within the last half-century has resulted in a pronounced increase in anthropogenic Hg emission from coal combustion, oil refining, cement production, and waste incineration. The record of increasing atmospheric sources have been investigated with a historical reconstruction of Hg accumulation in 30 sediment cores collected from the Yeongsan Estuary. Within the last several decades, this region has undergone severe anthropogenic alteration, including the construction of an estuarine dam forming the Yeongsan Lake, and installation of numerous seawalls that eliminated vast tidal flats and restricted estuarine circulation. Total mercury concentrations (T-Hg) measured in sediments deposited after 1980 (23.2 ± 9.6 ng g^{-1}; n = 273), were significantly higher than those reported for pre-industrial sediments (i.e. background values: 8.6 ± 2.7 ng g^{-1}; n = 274). An extensive survey of surface samples show that T-Hg concentrations are highest above the dam, with a gradient to lower values further offshore. The concomitant timing of enrichment of T-Hg within the sedimentary record and increased National emissions in Korea suggests that regional sources dominate the input to the Yeongsan Estuary. This indicates that with sufficient regional historic emission data, T-Hg might be utilized as a geochronologic tool to aid in corroborating traditional radioisotopic methods.

1. Introduction

Mercury (Hg) is found in the environment from both natural and anthropogenic sources, and has been shown to severely deteriorate ecosystem and human health under sufficiently high concentrations (Driscoll et al., 2012; Karagas et al., 2012; Mergler et al., 2007). Industrialization over the last two centuries has caused global Hg inventories to increase rapidly (Schuster et al., 2002; UNEP, 2013). Previous estimates of total annual anthropogenic inputs of Hg vary depending on calculation method, particularly emission factors, with estimates for the years 1990–2010 ranging from 1010 to 4070 ton yr^{-1} (Muntean et al., 2014; Pacyna et al., 2010; Pacyna and Pacyna, 2001; UNEP, 2013). In 2005, relative contributions of global anthropogenic Hg emissions were estimated at 45.6% from fossil fuel combustion, 18.2% from gold production, 10.4% from other metals production, and 9.8% from cement production combined with all other sources (AMAP/UNEP, 2008). Once emitted to the atmosphere, the behavior and transport of anthropogenic Hg depends highly on speciation (Schroeder and Munthe, 1998; Selin, 2012; Swartzendruber and Jaffe, 2012; UNEP, 2013). Gaseous elemental mercury (Hg^0) comprises >90% of atmospheric Hg, and has a high volatility and low water solubility (Han et al., 2014). Depending on environmental conditions, Hg^0 can be deposited locally, or remain in the atmosphere for up to a year allowing global transport (Pirrone and Mason, 2009; Schroeder and Munthe, 1998). More reactive forms, such as gaseous oxidized (Hg^{+2}) and particle bound (Hg^P) mercury, have shorter atmospheric residence times (hours-days) and are typically deposited close to their emission source (Han et al., 2014; Pirrone and Mason, 2009; Rothenberg et al., 2010; Swartzendruber and Jaffe, 2012).

Currently, nearly 40% (1960 ton yr^{-1}) of global anthropogenic Hg emissions are attributed to East and Southeast Asian countries (UNEP, 2013). However, within S. Korea there is a paucity of historical atmospheric Hg measurements to evaluate emissions from local sources, with the majority of records coming from urban areas near Seoul (Kim and Kim, 2000, 2002; Kim et al., 2013). Generally,

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these studies report higher values of total gaseous mercury ($Hg^0 + Hg^{+2}$) concentrations (0.2–150 ng m^{-3}) near highly urbanized regions than within rural areas (0.26–10.8 ng m^{-3}) (Han et al., 2014; Kim et al., 2013), although within the last decade concentrations have been decreasing due to increased emission regulation (Kim et al., 2013). Long-range transport of anthropogenic and natural Hg to Korea has also been observed from China, Japan, and Russia (Choi et al., 2009; Fang et al., 2008; Nguyen et al., 2010). Recently, a comprehensive study evaluated Hg emission factors and sectorial concentrations from the major anthropogenic sources in S. Korea and determined that of the total average of 12.8 ton yr^{-1} (6.5–20.2 ton yr^{-1}), approximately 26% was emitted from coal fired power plants, 25% from oil refineries, 21% from cement kilns, 20% split between medical, sludge, industrial, and municipal waste incinerators, 7% from iron manufacturing, and the remaining 1% combined from glass, pulp/paper, and nonferrous metal manufacturing (Kim et al., 2010).

It has been well documented that through wet and dry deposition, atmospheric Hg is ultimately accumulated within sediments, typically transported associated with fine particles and organic matter (Chakraborty et al., 2014; Connan et al., 2013; Lasorsa et al., 2012; Sanei and Goodarzi, 2006; Sanei et al., 2014; Weiss-Penzias et al., 2011; Zhang et al., 2012). Numerous studies have investigated the historical record of Hg input to sedimentary systems throughout the world, and the impact of localized deposition and varying source input is apparent in the wide range of timing for onset of increased Hg and peak concentrations (Table 1). While in some regions the increase in total global anthropogenic Hg due to industrialization (mid 1800's) is recorded, many studies have not reported increases above background levels until well into the 20th century. Furthermore, considerable variation exists in background and maximum total Hg concentration (Al Mukaimi, 2013; Alonso-Hernández et al., 2012; BuTayban and Preston, 2004; Donovan et al., 2013; Jha et al., 2003; Kading et al., 2009; Leonardo et al., 2006; Li et al., 2013; Lim et al., 2012; Louchouarn and Lucotte, 1998; Louchouarn et al., 2012; Mil-Homens et al., 2013; Ram et al., 2003; Sanders et al., 2006; Shi et al., 2010; Stupar et al., 2014; Yang and Rose, 2003). Several studies have investigated Hg (and other heavy metal) contamination within estuaries, rivers, and lakes of S. Korea; however, they have been primarily focused on surface sediment concentration and distribution (Choi et al., 2012; Joo et al., 2000; Kim et al., 2014, 2011; Lee et al., 2008; Lim et al., 2013; Oh et al., 2010), with few reporting historical inputs from core data (Lim et al., 2012; Park et al., 2012b). The variation within these data indicates that the type and proximity of Hg source are strong controls on the historical record of inputs to the sedimentary record.

Without significant policy intervention, estimates of global Hg emissions are projected to increase significantly (up to 98%) by 2050 (Pacyna et al., 2010; Rafaj et al., 2013; Streets et al., 2009). In order to understand the implications of future increased anthropogenic Hg emissions, the sedimentary record of deposition and the relative influence of long-range transport and local sources must be evaluated regionally. The rapid development and industrialization of Asian countries, particularly China and Korea, within the last few decades has caused a significant increase in sources of atmospheric Hg (Muntean et al., 2014; Pacyna et al., 2010; UNEP, 2013). Thus, this study aims to determine 1) the sedimentary record of historical inputs of anthropogenic Hg to the Yeongsan Estuary, 2) the distribution of Hg concentrations in surface sediments, and 3) the potential utility of Hg as a geochronological tool in this region. The results herein provide a case study on how an anthropogenically altered estuary has recorded increasing anthropogenic Hg throughout the last half-century. These findings are not only significant regionally, as many depositional environments in East Asia have been accumulating anthropogenic Hg, but have global implications for the fate of anthropogenic Hg with continued industrialization in developing countries.

2. Regional setting/background

The Yeongsan Estuary is separated respectively into the Yeongsan Lake, Inner Estuary, Outer Estuary, and Coastal zones (Fig. 1). Located on the southwestern tip of the Korean Peninsula, the Yeongsan River has a drainage basin area of 3468 km^2 and a total length of 137 km, making it the sixth longest river in the country. The estuary has undergone significant coastal construction within the last century, including the construction of an estuarine dam in 1981 and the addition of approximately 90 km of seawalls/embankments. The estuarine dam resulted in cessation of tidal

Table 1
Summary of numerous studies investigating the historical input of anthropogenic Hg to the sedimentary record. The timing of initial significant increase in detected Hg ($t_{INT.}$), the timing of peak concentrations (t_{Peak}), average background value (T-$Hg_{Bkg.}$), and maximum reported concentration (T-Hg_{MAX}) are indicated. Note: this list is not comprehensive of all investigations.

Location	$t_{INT.}$	t_{Peak}	T-$Hg_{Bkg.}$ (ng g^{-1})	T-Hg_{MAX} (ng g^{-1})	Source
N. America					
San Francisco Bay, USA	<1900	1960's	<60	434	Donovan et al. (2013)
Galveston Bay, USA	1940's	1971	30	2375	Al Mukaimi (2013)
St. Lawrence Estuary, Canada	1940's	1965	30	6000	Louchouarn and Lucotte (1998)
Sagua la Grande Estuary, Cuba	1970's	1985	35	312	Alonso-Hernández et al. (2012)
S. America					
Guaratuba Bay, Brazil	1950's	2000	15	44	Sanders et al. (2006)
Laguna del Plata, Argentina	1970's	1993	13	131	Stupar et al. (2014)
Europe					
United Kingdom	1850's	1970's	20	1606	Yang and Rose (2003)
Portuguese Margin	1850's	1990's	50	594	Mil-Homens et al. (2013)
Straight of Sicily	1950's	1975	38	202	Leonardo et al. (2006)
Asia					
Pearl River Estuary, China	1950's	1960's	<80	201	Shi et al. (2010)
Shanghai, China	1940's	1990's	43	867	Li et al. (2013)
Jinhae-Masan Bay, Korea	1940's	1940's	19	150	Lim et al. (2012)
Thane Estuary, India	1950's	1975	70	10,500	Jha et al. (2003)
Ulhas Estuary, India	1960's	1991	60	20,000	Ram et al. (2003)
Africa/Arabia					
Berg Estuary, S. Africa	1970's	2003	22	48	Kading et al. (2009)
Kuwait Bay, Kuwait	1960's	1985	15	36,500	BuTayban and Preston (2004)