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Lanthanum and lanthanides in atmospheric fine particles and their apportionment to refinery and petrochemical operations in Houston, TX

Pranav Kulkarni[a], Shankararaman Chellam[a,b,*], Matthew P. Fraser[c]

[a]Department of Civil and Environmental Engineering, University of Houston, 4800 Calhoun Road, Houston, TX 77204-4003, USA
[b]Department of Chemical Engineering, University of Houston, Houston, TX 77204-4004, USA
[c]Department of Civil and Environmental Engineering, Rice University, Houston, TX 77005, USA

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Abstract

A study was conducted in Houston, TX focusing on rare earth elements (REEs) in atmospheric fine particles and their sources. $PM_{2.5}$ samples were collected from an ambient air quality monitoring site (HRM3) located in the proximity of a large number of oil refineries and petrochemical industries to estimate the potential contributions of emissions from fluidized-bed catalytic cracking operations to ambient fine particulate matter. The elemental composition of ambient $PM_{2.5}$, several commercially available zeolite catalysts, and local soil was measured after microwave assisted acid digestion using inductively coupled plasma—mass spectrometry. Source identification and apportionment was performed by principal component factor analysis (PCFA) in combination with multiple linear regression. REE relative abundance sequence, ratios of La to light REEs (Ce, Pr, Nd, and Sm), and enrichment factor analysis indicated that refining and petrochemical cat cracking operations were predominantly responsible for REE enrichment in ambient fine particles. PCFA yielded five physically meaningful $PM_{2.5}$ sources: cat cracking operations, a source predominantly comprised of crustal material, industrial high temperature operations, oil combustion, and sea spray. These five sources accounted for 82% of the total mass of atmospheric fine particles (less carbon and sulfate). Factor analysis confirmed that emissions from cat cracking operations primarily contributed to REE enrichment in $PM_{2.5}$ even though they comprised only 2.0% of the apportioned mass. Results from this study demonstrate the need to characterize catalysts employed in the vicinity of the sampling stations to accurately determine local sources of atmospheric REEs.

Keywords: Rare earth elements; $PM_{2.5}$; ICP-MS; Factor analysis; Catalyst; Industrial emissions

1. Introduction

The Port of Houston is the second largest in the United States (and sixth in the world) in terms of total tonnage of both imports and exports, which includes petroleum/petroleum products, iron and steel, organic/inorganic chemicals, plastics, cereals

*Corresponding author. Department of Civil and Environmental Engineering, University of Houston, 4800 Calhoun Road, Houston, TX 77204-4003, USA. Tel.: +713 743 4265; fax: +713 743 4260.
E-mail address: chellam@uh.edu (S. Chellam).

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and cereal products, crude fertilizers, minerals, etc. The region around the Port of Houston and the Houston Ship Channel is home to an extensive industrial complex that contains 49% of the petrochemical manufacturing capacity in the United States (Greater Houston Partnership, 2003). Direct quantification of the $PM_{2.5}$ emissions from Houston's petrochemical complex, which is also the second largest worldwide, has not yet been done. Prior work has focused on the organic compounds (Fraser et al., 2003; Zhao et al., 2004) as well as elements from the main groups and first three transition series (Buzcu et al., 2003) for fine particle source identification and apportionment in Houston, TX. To focus on catalyst emissions specific to petroleum refining and petrochemical manufacturing, it is necessary to measure lanthanum and lanthanides (Olmez and Gordon, 1985; Dzubay et al., 1988; Olmez et al., 1988).

Fluidized-bed catalytic cracking (FCC) is a widely utilized operation during petroleum refining and petrochemical manufacturing. FCC operations typically employ zeolite catalysts enriched in rare earth elements (REEs), a portion of which may escape to the atmosphere (Mizohata, 1986; Dzubay et al., 1988). The term "rare earth elements" refers to the elements Y, La, and the lanthanides (Ce–Lu) (Cotton et al., 1999). Kitto et al. (1992) quantified selected REEs (La, Ce, Nd, Sm, Eu, Gd, Tb, Yb, and Lu) in several catalysts and demonstrated a direct association between catalyst composition and FCC stack emissions. Given their high economic impact, catalyst chemical characteristics are being continuously changed to enhance their performance in terms of metal tolerance and product selectivity (Richardson, 1989). However, to our knowledge, the only detailed reports of catalysts composition including their emissions as fine particle from FCC operations are ~15–20 years old (Mizohata, 1986; Kitto et al., 1992). To update the existing and potentially outdated information on catalysts composition, several currently employed FCC catalysts were analyzed to determine the concentrations of all REEs, including *Y* and the previously unreported lanthanides (Pr, D*y*, Ho, Er, and Tm).

In addition to petrochemical industries, emissions from motor vehicles and entrainment of crustal material can also potentially contribute to atmospheric concentrations of REEs. Hence, we also analyzed local soil, $PM_{2.5}$ collected from a local highway tunnel, as well as an automobile catalyst to evaluate possible interferences.

The objectives of this research are to (1) provide comprehensive data on the elemental composition of several currently employed zeolite catalysts, (2) quantify REEs present in trace ($ng\,m^{-3}$) and ultra trace ($pg\,m^{-3}$) amounts in atmospheric fine particulate matter, and (3) determine the relative contribution of loss of catalyst from FCC operations to $PM_{2.5}$ in the Houston, TX area. Ambient fine particles were collected at an air quality monitoring site located adjacent to the Houston Ship Channel to identify and apportion all possible local sources. Microwave assisted acid digestion at high temperature and high pressure was first employed to dissolve $PM_{2.5}$, catalysts, and soil. Next, concentrations of 42 elements were measured using inductively coupled plasma-mass spectrometry (ICP-MS).

2. Methods

2.1. FCC catalysts

Samples of five different FCC zeolites (designated as SMR1–SMR5) employed in a wide range of refining operations in the Houston area were obtained from the world's leading catalyst manufacturer (Grace Davison Inc., Columbia, MD). All fresh catalysts were odorless and white to brown in color, in the form of a fine powder with bulk densities between ~0.45 and 1.00 $g\,cm^{-3}$. During cat cracking, catalysts get poisoned by metals such as Ni, V, Cu, and Fe, due to high temperature fractionation and also by coke deposition (Richardson, 1989). In other words, catalyst composition changes upon usage. Hence, a sample of used zeolite catalyst was also obtained from Shell Deer Park Refining Company's Fluid Catalytic Cracking Unit (FCCU), located in the Houston Ship Channel industrial complex. This sample was obtained in June 2003 and consisted of the spent catalyst collected from cyclone separators that had removed it from the FCCU product stream. The spent catalyst was also an odorless fine powder but was dark gray in color.

2.2. Ambient $PM_{2.5}$

Ambient fine particulate matter was sampled from an air quality-monitoring site (HRM3) located near the Houston Ship Channel. A total of 25 samples were obtained between 25 May 2001 and 4 September 2001. $PM_{2.5}$ samples were collected on