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Leaching of polycyclic aromatic hydrocarbons from oil shale processing waste deposit: A long-term field study

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HIGHLIGHTS

- Spent shale deposit is a source of PAHs for a long period of time.
- The low molecular weight PAHs dominated the emission from the deposit.
- The concentration of PAHs in leachates from aged deposit was higher than from fresh one.
- Content of PAHs in leachates depended on the sampling place and weather conditions.

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ABSTRACT

The leaching behavior of selected polycyclic aromatic hydrocarbons (PAHs) from an oil shale processing waste deposit was monitored during 2005–2009. Samples were collected from the deposit using a special device for leachate sampling at field conditions without disturbance of the upper layers. Contents of 16 priority PAHs in leachate samples collected from aged and fresh parts of the deposit were determined by GC–MS. The sum of the detected PAHs in leachates varied significantly throughout the study period: 19–315 μg/l from aged spent shale, and 36–151 μg/l from fresh spent shale. Among the studied PAHs the low-molecular weight compounds phenanthrene, naphthalene, acenaphthylene, and anthracene predominated. Among the high-molecular weight PAHs benzo[a]anthracene and pyrene leached in the highest concentrations. A spent shale deposit is a source of PAHs that could infiltrate into the surrounding environment for a long period of time.

1. Introduction

Waste deposits could be a source of hazardous substances including persistent organic pollutants, e.g. polycyclic aromatic hydrocarbons (PAHs) to their surrounding environment through direct contact, leaching, or runoff (van der Sloot et al., 1996; Twardowska et al., 2004; Saether et al., 2004). At field conditions a number of site-specific factors play a significant role: temperature, mode of contact with water, remineralization, aging of waste, etc. (van der Sloot et al., 1996; Twardowska and Szczepanska, 2002). Laboratory studies could supply important information on the leachate characteristics, however the adequate identification of the hazard represented by a solid waste only on the basis of laboratory leaching tests, is problematic (Baur et al., 2001; Twardowska and Szczepanska, 2002; Doick et al., 2005). The inconsistency of the data obtained from laboratory leach tests and field conditions have been confirmed in the case studies of coal combustion waste (Twardowska and Szczepanska, 2002), oil shale processing wastes (Kirso et al., 2007, 2011). For proper waste management and beneficial remediation reliable data on the leaching potential of toxins from waste disposal sites under actual field conditions is needed, in addition to standard laboratory testing (Kirso et al., 2007; Susset and Grathwohl, 2011; Twardowska and Szczepanska, 2002).

Among the EU member states only Estonia is currently actively engaged in exploitation of oil shale on a significant scale (EASAC, 2007). About 20% of mined oil shale in Estonia is used for producing shale oil by thermal processing — semi-coking or retorting. At present, two different oil shale retorting technologies are employed in Estonia: the Kiviter-type internal combustion vertical retort and the Galoter type or solid heat carrier (SHC 140) unit (Veiderma, 2003). Retorting of Estonian oil shale produces oil, water, gas and a charcoal-colored, non-decarbonized spent shale waste (also called semi-coke). Solid residues from these two processes are different, due to different temperatures and other parameters used during retorting. Spent shale deposits

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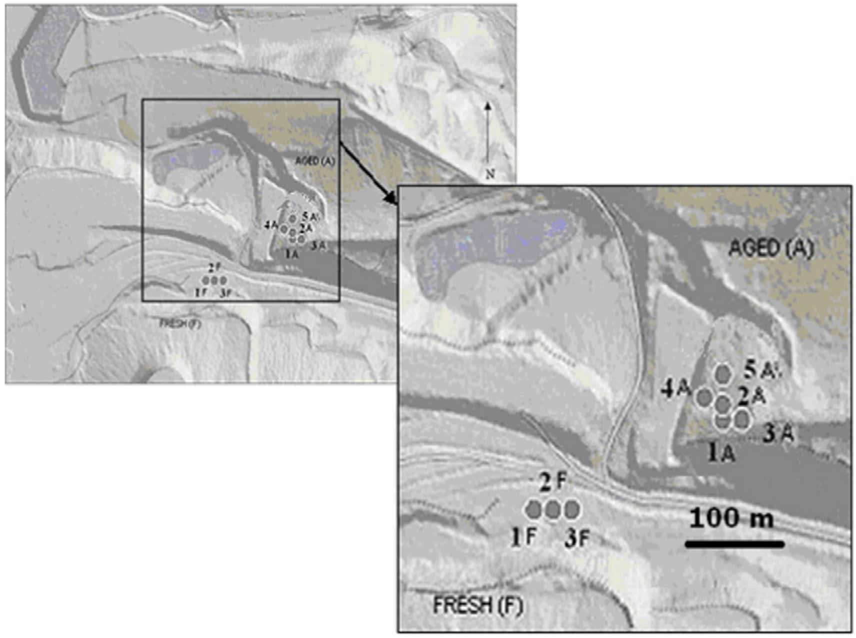

Fig. 1. Sampling points in spent shale deposit (scale bar 100 m, courtesy of Google Maps).

consist of heterogeneous layers with variable properties and composition, which undergo mineralogical and chemical transformations along with alteration of their physical properties (Veiderma, 2003; Mõtlep et al., 2007; Sedman et al., 2012; Trikkel et al., 2004). Spent shale deposit sites are a major concern in oil shale industry, because of the large volume of disposed waste (70–80 million tonnes according to Saether et al., 2004) and the potentially harmful compounds contained in the waste. It is officially classified as hazardous waste in Estonia. Spent shale contains considerable amounts of organic compounds (7–24 wt.%) including PAHs, as well as tar and other bituminous substances (Orupõld et al., 2008; Otsa and Tang, 2003; Saether et al., 2004; Trikkel et al., 2004).

Although spent shale has been reported to contain numerous organic compounds, the authors found only limited information on the fate and transport of persistent organic pollutants such as PAHs for spent shale deposits (Kirso et al., 2007; Jefimova et al., 2012). Determination of mobile PAHs in the spent shale is important because of their possible carcinogenic and/or mutagenic properties. Consequently, deposits of oil shale processing wastes may be detrimental to the environment as well as to human health because of mobilization of PAHs. Generally, PAHs are very hydrophobic organic compounds. They have a high affinity for organic matter, and when present in waste, soil or sediments they tend to remain bound to solid particles (Roskam and Comans, 2009). PAHs can persist, transport and accumulate in the environment to the extent that the potential for adverse environmental effects is considerable (Alexander, 1995; Enell et al., 2004). Therefore the long-term fate of PAHs in the environment represents a subject of interest. Many studies have pointed out the importance of determining the mobility and bioavailability of contaminants in the risk analysis of solid materials both in utilization and deposit sites (Yang et al., 2007; Roskam and Comans, 2009; Witt et al., 2009; van der Sloot and Kosson, 2012).

In a waste deposit, the interactions between water and waste constituents lead to generation of leachates. Lack of data concerning the actual leaching potential of PAHs from spent shale deposits studied in-situ is available. At the same time, the assessment of long-term influence of industrial wastes to the surrounding environment requires reliable data on the fate of pollutants at field conditions. The focus of the present study is investigating the long-term leaching behavior of 16 priority EPA PAHs by monitoring both aged and fresh spent shale at field conditions, with emphasis on PAH behavior at current field conditions.

2. Materials and methods

2.1. Study site and sample collection

The studied waste deposit is located at Kohtla-Järve (Northeast Estonia) close to an oil shale retorting plant (*Viru Keemia Grupp*). Leachate water samples were taken from both the closed part of the deposit (aged waste, A) and from the active part of the site currently in use

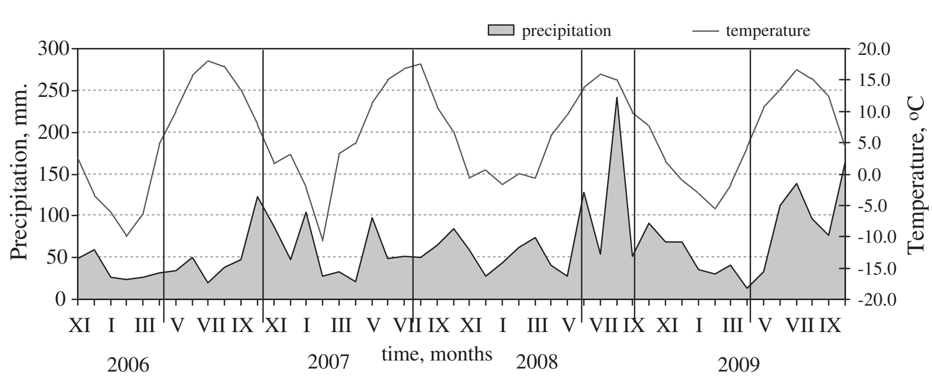

Fig. 2. Sample collection periods (vertical lines), monthly average precipitation and temperature data recorded at Jõhvi weather station, EIMH in 2005–2009.