Environmental Research 156 (2017) 394–403

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Assessment of mobility and bioavailability of mercury compounds in sewage sludge and composts☆

Beata Janowska*, Kazimierz Szymański, Robert Sidełko, Izabela Siebielska, Bartosz Walendzik

Koszalin University of Technology, Faculty of Civil Engineering, Environmental and Geodetic Sciences, Department of Waste Management, ul. Śniadeckich, 75-453 Koszalin, Poland

ARTICLE INFO

Keywords:
Mercury
Fractionation
Bioavailability
Sewage sludge
Compost
Mobility factor

ABSTRACT

Content of heavy metals, including mercury, determines the method of management and disposal of sewage sludge. Excessive concentration of mercury in composts used as organic fertilizer may lead to accumulation of this element in soil and plant material. Fractionation of mercury in sewage sludge and composts provides a better understanding of the extent of mobility and bioavailability of the different mercury species and helps in more informed decision making on the application of sludge for agricultural purposes. The experimental setup comprises the composing process of the sewage sludge containing 13.1 mg kg^{-1} of the total mercury, performed in static reactors with forced aeration. In order to evaluate the bioavailability of mercury, its fractionation was performed in sewage sludge and composts during the process. An analytical procedure based on four-stage sequential extraction was applied to determine the mercury content in the ion exchange (water soluble and exchangeable Hg), base soluble (Hg bound to humic and fulvic acid), acid soluble (Hg bound to Fe/Mn oxides and carbonates) and oxidizable (Hg bound to organic matter and sulphide) fractions. The results showed that from 50.09% to 64.55% of the total mercury was strongly bound to organo-sulphur and inorganic sulphide; that during composting, increase of concentrations of mercury compounds strongly bound with organic matter and sulphides; and that mercury content in the base soluble and oxidizable fractions was strongly correlated with concentration of dissolved organic carbon in those fractions.

1. Introduction

Management and disposal of sewage sludge being the product of sewage treatment is in highly industrialised countries a logistic, economic, and primarily, environmental problem. Sewage sludge is considered as dangerous waste as it contains high organic load, chemical pollutants including heavy metals, pesticides and other dangerous organic compounds (Białobrzewski et al., 2015; Dong et al., 2013). Sewage sludge also makes sanitary hazard due to the occurrence of pathogenic bacteria, viruses and other pathogenic organisms (Bień, 2002; Iacovidou et al., 2012). The main disposal processes of sewage sludge is its use in agriculture and degraded land reclamation. The disposal processes comprise composting, incineration and deposition (Ramdani et al., 2015; Samolada and Zabaniotou, 2014; Fonts et al., 2012).

Sewage sludge intended for agriculture application and soils reclamation should comply with the requirements pertaining to its chemical composition, including heavy metals content and sanitary conditions. Excessive heavy metals concentration limits the use of sewage sludge for fertilization due to its toxic action and ability to bioaccumulate in plant material (Dong et al., 2013; Ingelmo et al., 2012; Ramdani et al., 2015). The process of sewage sludge composting could be used for producing organic fertilizer, biofuel and other forms of renewable energy sources (Fonts et al., 2012; Iacovidou et al., 2012). However, heavy metals content, including mercury, in composts and biofuel limits the possibility of the use of this material in agriculture and energy generation. One criteria for assessing the quality of compost is the content of heavy metals, including mercury compounds in such material (Hseu et al., 2010; Janowska and Szymański, 2009; Confesor et al., 2008; Szymański et al., 2005).

Mercury is one of the most dangerous environmental pollutants, featuring high chemical and biological activities that create compounds

Abbreviations: EX, exchangeable fraction; BS, base soluble fraction; AS, acid soluble fraction; OX, oxidizable fraction; PE, population equivalent; HgT, total mercury concentration; TOC, total organic carbon; DOC, dissolved organic carbon; Mf, mobility factor; r, Pearson's correlation coefficient

☆ This research work was financed by the Polish State Committee for Scientific Research within the project No. N N523 743840.

* Corresponding author.
E-mail addresses: beata.janowska@tu.koszalin.pl (B. Janowska), kazimierz.szymanski@tu.koszalin.pl (K. Szymański), robert.sidelko@gmail.com (R. Sidełko), izabela.siebielska@tu.koszalin.pl (I. Siebielska), bartosz@wilsig.tu.koszalin.pl (B. Walendzik).

http://dx.doi.org/10.1016/j.envres.2017.04.005
Received 30 July 2016; Received in revised form 28 February 2017; Accepted 4 April 2017

of diversified properties (AMAP, 2013, Syversen and Kaur, 2012). Biogeochemical mercury circulation depends not only on its concentration but, primarily, on its forms of occurrence.

Mercury may occur in nature in the form of volatile alkylated compounds, particularly as methyl mercury and ethyl mercury, or in the elemental form Hg^0 (Kabata-Pendias, 2010; Mao et al., 2016). It can also form water-soluble complex compounds where ligands can be chlorides or sparingly soluble organic complexes (Hutchison and Atwood, 2003; Kabata-Pendias, 2010; Han et al., 2003; Wang et al., 2012; Xu et al., 2015). Mercury shows strong affinity to compounds containing sulphur and chlorine as well as to organic compounds and organic matter (Hutchison and Atwood, 2003; Kabata-Pendias, 2010; Xu et al., 2015).

Organomercury species such as methyl mercury are more mobile than inorganic mercury forms, and thus more easily bioaccumulated and considered as more toxic to humans than either elemental Hg^0 or Hg salts. Mercury readily chelates with organic matter in the form of humic and fulvic acids, forming stable complexes (Hutchison and Atwood, 2003; Kabata-Pendias, 2010; Xu et al., 2015).

The quantity of this element in sewage sludge generated in wastewater treatment plants depends on the wastewater treatment technology and on the wastewater properties (Balogh and Nollet, 2008; Mao et al., 2016). In the studies by Mukherjee et al., (2004) the average values of the total mercury concentration in sewage sludge were all in the range from 0.6 to 3 mg kg^{-1} (DM).

The environmental mobility and toxicological effects of mercury are strongly dependent on the chemical species present (Kabata-Pendias, 2010). Mercury in sewage sludge and compost could be extracted by means of various chemical reagents in order to determine the different mercury species and partitions, providing useful information about their toxicology, bioavailability and biogeochemical reactivity. Sequential extraction allows for determination of bond strengths and differentiation of chemical species of mercury: elemental mercury Hg°, water-soluble compounds ($HgCl_2$), compounds associated with carbonate, associated with hydrous oxides of Fe and Mn, bound to organic substances and mercury (II) sulphide (Bloom et al., 2003; Boszke et al., 2008; Fernandez–Martinez et al.al., 2006; Fernandez-Martinez and Rucandio, 2013; Han et al., 2003; Han et al., 2006; Issaro et al., 2009; Ram et al., 2009; Reis et al., 2010).

Many research papers were dedicated to mercury speciation in environmental and biological samples. The literature survey presented in Ibanez-Palomino et al. has shown that approximately 80% of the papers pertain to definition of forms of mercury occurring in water, bottom sediments and in aquatic organisms; approximately 12% of the papers refer to determination of mercury forms in biological samples, and 5% of the papers pertain to soil (Ibáñez-Palomino et al., 2012).

Information describing fractionation of mercury in samples of compost and sewage sludge can be found in few publications (Cappon, 1987; Shoham-Frider et al., 2007; Lomonte et al., 2010), although the fractionation of mercury based on sequential extraction allows for definition of mobility and bioavailability of this element. There is a need for further research leading to the definition of the qualitative and quantitative forms of mercury, which findings could help evaluate the fertilizing properties of composts.

In line with this motivation, the objective of the study documented in this article was to examine the relationships between the changes in the organic matter and bioavailability of Hg. The study applied sequential chemical extractions to determine Hg partitioning in sewage sludge and composts. The results were tested on the mixture of sewage sludge and timber shavings during its aerobic bath composting and with an initial C/N ratio of 26.

2. Methods

2.1. Test material

The used sewage sludge was obtained from the wastewater treatment plant of Sianów, Poland, featuring the capacity of 15000 PE (population equivalent). Samples of the sewage sludge were taken from the open air sludge drying bed, in autumn and spring (2011–2012), where it was stored for approximately one year (it was dependent on the weather conditions). This was a mechanical and biological wastewater treatment plant using trickling filter, which was built and put into operation at the beginning of the 1990s. The mechanical system comprised a manually cleaned screen, two-chambers and a trap featuring a trapezoid-shape cross-section. The biological system comprised a trickling filter with sprinkler system. The sediment part of the wastewater treatment plant included the secondary sedimentation tank with sludge scraper, open sludge chambers where the sludge was concentrated, and drying beds. In 2015, the said wastewater treatment plant was closed.

2.2. Composting of sewage sludge

The composting of the sewage sludge was performed in two static bioreactors (KI and KII) with forced aeration, featuring the capacity of 60 L. The bioreactors were enclosed, insulated containers with controlled flow of air and temperature (Siebielska, 2014). The bioreactor feedstock was approximately 50 L. Intense aeration was performed during the first 21 days of the process. During this stage, the volume of air supplied to bioreactors was 2.5 L min^{-1} (Siebielska and Sidełko, 2015).

The material intended for composting was a mixture of sewage sludge with some amount of structural material such as timber shavings. The weight proportion of the sewage sludge to the structural material was 2:1. In order to ensure uniform distribution of air across the entire volume, polypropylene rings were added to the composted biomass; the proportion of weight of the sewage sludge to the polypropylene rings was 10:1.

Each composting cycle lasted for 182 days. During the first composting cycle, composted biomass samples were taken for testing after 3, 7, 10 and 14 days, and subsequently every 7 days, i.e. after 21 and 28 days. For subsequent 6 weeks, the samples were taken every 14 days, every 21 days during the following 12 weeks, and the final sample was taken after 28 days.

2.3. Physico-chemical analyses

Moisture, organic matter content, pH, total organic carbon (TOC), total nitrogen and total mercury content (HgT) were determined in samples of sludge waste intended for composting and taken from the bioreactors. The organic matter content was determined by the loss on ignition of the dry mass at 550 °C. The content of total organic carbon and total nitrogen were determined using the Vario Max CN macro analyser. The total mercury (HgT) content was determined in air-dry samples of the tested material, which was ground and sifted through 0.75 mm mesh sieve. In such prepared samples, the content of HgT was determined using spectrophotometer LECO AMA-245 dedicated to mercury determination.

Mercury fractionation was performed based on the sequential extraction regime presented in Ram's paper, which recommended this method as highly repeatable; extraction solutions and extraction conditions applied prevented mercury loss (Ram et al., 2009).

Mercury compounds contents were determined in the ion exchange (EX), base soluble (BS), acid soluble (AS) and oxidizable (OX) fractions. Air-dried, ground and sifted (0.75 mm) 1 g sample was subjected to sequential extraction, the regime of which is presented in Table 1. After each extraction stage, the samples were centrifuged (MPW – 350