Environ Sci Pollut Res (2015) 22:10047–10057
DOI 10.1007/s11356-015-4131-5

RESEARCH ARTICLE

Investigation of biosolids degradation under flooded environments for use in underwater cover designs for mine tailing remediation

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Received: 12 November 2014 / Accepted: 14 January 2015 / Published online: 14 February 2015

Abstract To evaluate the potential suitability of digested sewage sludge (frequently termed biosolids) for use as underwater cover material for mine waste tailings, the degradability of biosolids at 20−22 °C under flooded anaerobic conditions was evaluated during incubation for 230 days. Leaching of elements from the flooded anaerobic system was also evaluated. Biosolid degradation was confirmed by the generation and accumulation of CH_4 and CO_2. Specifically, approximately 1.65 mmoL gas/g biosolids was generated as a result of incubation, corresponding to degradation of 7.68 % of the organic matter, and the residue was stable at the end of the laboratory experiment. Under field conditions in northern Sweden, it is expected that the degradation rate will be much slower than that observed in the present study (Nason et al. Environ Earth Sci 70:30933105, 2013). Although the majority of biosolid fractions (>92 %) were shown to be recalcitrant during the incubation period, long-term monitoring of further degradability of residue is necessary. The leaching results showed that most of the metals and metalloids leached from the biosolids at day 230 were below the limit value for non-hazardous waste, although Ni was the only element approximately three times higher than the limit value for inert material at the landfill site. In conclusion, biosolids have potential for use as covering material for underwater storage of tailings based on their biodegradability and leaching of elements.

Responsible editor: Philippe Garrigues

Highlights • Biosolids are anaerobically degradable under flooded anaerobic conditions
• During 230-day incubation, 1.65 mmoL gas/g biosolids is generated
• Overall, 7.68 % of biosolids organic matter is degraded
• Elements were leached at levels below non-hazardous waste limits
• Biosolids are rather stable at day 230 of incubation

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Keywords Acid rock drainage · Digested sewage sludge · Metal leaching · Long-term evaluation · Methane release · Water saturation

Introduction

A large volume of mine waste tailings are generated during mining. These materials need to be either stockpiled or stored underwater, which may cause environmental hazards. Mine wastes often contain pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$, where x is from 0.125 to 0), which are unstable and oxidize in the presence of water and oxygen, leading to the generation of acid rock drainage (ARD) (Gerhardt et al. 2004; Johnson and Hallberg 2005; Lottermoser 2010). Uncontrolled ARD can contaminate surface water and groundwater and have an adverse impact on terrestrial and aquatic flora and fauna (Gray 1997; Johnson and Hallberg 2003). In Sweden, which is one of the most active mining countries in Europe, mining industry generates approximately 59 million tons of reactive sulfidic mine tailings annually (Statistics-Sweden 2008).

A number of factors, including mineralogical, geochemical, and hydrogeological conditions in the project and periphery areas, influence the severity and length of ARD, and it has the potential to last for hundreds to thousands of years (Öhlander et al. 2012). Accordingly, long-term remediation of mine waste tailings can be a great challenge. Mine waste remediation can be achieved at the source or along the subsequent ARD pathway. Geochemical stabilization is commonly conducted by controlling the oxygen and water through application of a dry or a wet cover, as well as application of liming to the mine waste (Höglund and Herbert Jr 2004; Johnson and Hallberg 2005; Lu et al. 2013).

Water covers differ in their remedial approach as they are a form of preventative in situ (PIS) remediation and require a tailing repository with a raised groundwater table to be effective. Water covers prevent reactive oxygen formed during the oxidation of pyrite from reaching the underlying tailings. Specifically, the covers function by limiting oxygen diffusivity based on the principle that oxygen diffusivity through water (2×10^{-9} m^2/s) is significantly lower than in air (1.78×10^{-5} m^2/s), and the concentration of O_2 in water is 33 times less than in air (Nicholson et al. 1989; Mbonimpa et al. 2003). In addition to the water column, a thin layer of, e.g., clay till at the water-to-tailings interface (<1 mm) known as the diffusive boundary layer (DBL) limits oxygen ingress by only allowing molecular diffusion of oxygen (Elberling and Damgaard 2001; Awoh et al. 2013). Sedimentation can occur either naturally after remediation or be introduced immediately upon flooding, and can reduce oxidation rates of tailings by one order of magnitude. It has been shown that even a thin layer (<1 cm) of sediment applied above tailings can be even more effective than uncovered tailings (where covered by only protective layer) at limiting oxygen diffusion through the sealing cover of low permeability (Höglund and Herbert Jr 2004). The sealing layer application is advantageous because the water depth of the cover can be reduced, which can reduce costs.

Depending on their availability and transport distance, use of industrial waste residue material to replace natural material such as till in covering mine waste tailings can be a promising solution enabling disposal of the two wastes simultaneously (Pérez-López et al. 2011). Using an organic substrate may be more advantageous than natural sedimentation because sulfate reduction, metal-hydroxide precipitation, and biodegradation could further limit oxygen ingress, promoting metal immobilization and limiting the formation of ARD (Peppas et al. 2000; Nason 2013). Novel materials such as treated sewage sludge derived from wastewater treatment plants have been shown to be effective substitutes for conventionally harnessed glacial till for use as dry cover materials (Peppas et al. 2000; Nason et al. 2014). Characterized by high alkalinity (approximately 3000 mg/L $CaCO_3$), municipal biosolids can neutralize the acidity produced from oxidation of sulfidic tailings (He et al. 1992; Peppas et al. 2000). However, organic substrates such as digested sewage sludge have the potential to biodegrade in the natural environment. To be a satisfactory sediment substrate for underwater disposal of tailings, the material must be stable (physically, chemically, and biologically) over a long period of time (e.g., 100 years).

Factors such as the biodegradability, nutrients level, and leachability of metals and metalloids are also important to the application of biosolids (Forsberg and Ledin 2006; Fitzmorris et al. 2009; Nason et al. 2013). The anaerobic degradation of biosolids by generation of methane (CH_4) and carbon dioxide (CO_2) can change the physical structure of the degradation residue, leading to loss of structure and more voids in the biosolid residue. Another potential problem is the presence of bacteria, fungi, protozoa, and viruses in the biosolids (Peppas et al. 2000; Wang et al. 2008; Fitzmorris et al. 2009). Most sludges contain trace amount of organic pollutants such pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAH), and dioxins, which can also have adverse effects on humans (Peppas et al. 2000; Hundal et al. 2008; Fitzmorris et al. 2009).

Conventionally, anaerobic digestion is employed for waste treatment, which generates CH_4 and CO_2. Optimal anaerobic digestion of sewage sludge is normally accomplished under mesophilic- (30−37 °C) and thermophilic (45−60 °C) conditions (Verstraete et al. 1996; Kim et al. 2002). Digestion is assisted by microorganisms which can be classified into various types: *Clostridia*, *Bacilli*, *Planctomycetia*, *Methanomicrobia*, and *Methanobacteria* (Karakashev et al. 2005; Cheon et al. 2008; Kobayashi et al. 2008; Bertin et al. 2011; De la Rubia et al. 2013). Although their properties are generally similar to those of mesophilic homologies, the growth rates of thermophilic bacteria and *Archaea* are higher than those of mesophilic organisms (Öztürk 1991; Kiyohara et al. 2000; De la Rubia et al. 2013). Under ambient atmospheric temperature ranges in the field (psychrophilic, <20 °C), the degradation kinetics are expected to be much slower (Tyagi et al. 1996; Avery et al. 2014; Scaglia et al. 2014).

Previous investigations of the unsaturated anaerobic digestion of biosolids have revealed that degradation of the total organic fraction was incomplete before application (Jia et al. 2014). Consequently, the material has the ability to degrade further after application, which may compromise and reduce the primary function and volume of the material when used for mine tailings remediation.

Earlier field studies showed that 85 % of the total organic matter in biosolids applied as a sealing layer over mine tailings in Kristineberg, northern Sweden, had degraded 8 years after application due to aerobic and anaerobic degradation processes (Nason et al. 2013). Furthermore, laboratory studies conducted under anaerobic conditions at 20−22 °C showed that 27.8 % of the total organic matter in biosolids had been degraded after 230 days of incubation (Jia et al. 2014; for more information see "Short summary of previous laboratory 20−22 °C unsaturated anaerobic batch" section).

Although the behavior of metals in biosolid-amended soil has been extensively studied over many decades (Ashworth and Alloway 2007), few studies of how sludge-derived metals migrate from surface and subsurface biosolids have been conducted (Nason et al. 2013, 2014). Furthermore, there is little information regarding the feasibility and potential problems associated with use of biosolids for covering underwater-stored tailings (Peppas et al. 2000). To investigate the applicability of biosolids for use in water covers under flooded anaerobic conditions, it is necessary to evaluate the modifications of the material in a flooded anaerobic environment from a long-term perspective. Therefore, the present study was conducted to (i) investigate the degradability of the biosolids under flooded anaerobic conditions, (ii) quantify the mobilization of sludge-borne metals under these conditions, and (iii) compare biodegradation of biosolids under unsaturated anaerobic (Jia et al. 2014) and flooded anaerobic (saturated, the present study) conditions. The results presented herein provide geochemical and biochemical evidence of the suitability and applicability of biosolids for use in underwater flooded tailing repositories for effective ARD mitigation.

Materials and methods

Source, physicochemical characteristics, and organic contents of biosolids

Fresh biosolid samples applied in the Boliden mine at the site named Gillervattet tailing impoundment in northern Sweden were originating from the Skellefteå Biogas plant in northern Sweden. The biosolids were a mixture of aerobic and anaerobically digested waste residues generated from slaughterhouse and domestic wastes that would have been used to produce biogas. During the field campaign, spot samples were collected from Gillervattnet tailing impoundment immediately after application. The samples, which were 20−30 kg each, were thoroughly homogenized with a shovel and then stored at 4 °C before use in the experiments. An earlier study showed that these fresh biosolids had a pH, electrical conductivity (EC), and redox potential (E_h) of 7.3, 18.5 ms/cm, and 189 mV, respectively (Table 1; Jia et al. 2014). The biosolids contained approximately 60 % organic matter, with the main organic groups being lignin [48 % in total solid (TS)] and carbohydrate (11.8 % in TS), equating to approximately 60 % of total organic matter (TOM). Cellulose and hemicellulose represented 6.6 % (in TS) and 5.2 % (in TS) of the carbohydrate fraction, respectively. The total organic carbon content was approximately 40 %. The volatile fatty acids, fat, and neutral lipids contents were negligible (Jia et al. 2014). Toxic organic matter such as PCB, PAH, pesticide, and dioxins were not considered as an issue in the present study based on the results of long-term biosolid site monitoring conducted by Boliden Mineral AS (Lundkvist, personal communication).

Table 1 Physicochemical characterization of the biosolids after flooded anaerobic laboratory incubation at the end of the experiment. For comparison, the relevant parameters for the original biosolids are also presented (Jia et al. 2014)

	pH	EC (mS/cm)	E_h (mV)
Original biosolids	7.30±0.02[a]	18.48±0.46[a]	189±1[a]
Sample (after exp)	7.94±0.43	3.37±0.63	266.5±26.2
Control (after exp)	7.41	6.11	257.5

[a] Jia et al. (2014)

Microcosms

Prior to the experiment, 500-mL transparent glass infusion flasks, 32-mm airtight rubber stoppers, and aluminum rings were rinsed with Milli-Q water and then sterilized in a Varioklav 500 autoclave (H+P Labortechnik, Oberschleiβheim, Germany), at 120 °C for 4 h.

Preparation of control samples

The biosolids used as control samples were oven-dried at 105 °C for 24 h, and then cooled to room temperature before being placed in a desiccator for drying. The samples were removed from the desiccators the next day and crushed into small pieces (<2 mm in size) using a mortar and pestle. The aim of the control was to study the effect of the dry-rewet process on biodegradability of the biosolids.

Incubation under flooded anaerobic condition at 20− 22 °C

A single-batch incubation was conducted at ambient temperature to investigate simulated flooded anaerobic conditions. Triplicates of 15 g dry mass portions of the fresh biosolids (see “Source, physicochemical characteristics, and organic contents of biosolids” section) were transferred into a 500-mL sterilized glass infusion flask. An L/S ratio of 10 mL/g of Milli-Q water was supplied to the flasks, which were then closed with rubber stoppers and tightened using aluminum rings. A needle connected to a three-way stopcock (in a closed position unless sampling) was placed on the septum.

Flooded anaerobic conditions were created via purging the incubation flask with helium for 20 min to expel oxygen from the flask and simultaneously allow helium to exist in the headspace, after which incubation was initiated. One control microcosm containing 15 g dry mass biosolids (see “Preparation of control samples” section) was mixed with Milli-Q water to achieve similar incubation conditions as for the fresh sample (i.e., an L/S ratio of 10 mL/g). All incubations were carried out in the dark.

Gas sampling and measurements

Each 22-mL vial was purged with 2.5 bar helium for 2 min and then sealed with rubber septa before gas measurement. Overpressure was released when necessary to maintain the internal atmospheric pressure. Sampling was conducted on days 5, 10, 20, 40, 90, 130, 180, and 230 for the flooded anaerobic batch. After each gas sampling, the flasks were shaken vigorously to achieve a re-distribution of the biosolids in the microcosm, after which the shaking process for the flasks was repeated.

At each scheduled gas sampling event, gas was withdrawn from the experimental flasks. The gas amount was then adjusted and 11 mL of gas was transferred to the vial. The total amount of gas that represented the overpressure was withdrawn using a 100-mL Auswechselbar interchangeable glass syringe, after which the overpressure was released until atmospheric pressure was obtained in the gas collecting vials. The gas (CO_2, CH_4, and H_2S) concentrations were measured by injecting the sample from the vial into a stream of helium flowing through a gas chromatograph (GC, Clarius 580, PerkinElmer) with a built-in syringe auto-sampler.

Chemical analysis

Inorganic elements

Elemental analysis of the original biosolids with moisture was performed using a handheld XRF analyzer (Olympus Innov-x systems, USA) with a detection limit of 0.3 %. Instrument calibration was carried out using a known standard (Alloy 316 stainless steel) prior to analysis. The instrument was run in beam mining mode for the biosolid samples. The measured values were normalized while considering the moisture content (76.02 %) of the biosolids. The analyzed elements were Ca, Fe, K, Mg, Na, Si, Al, As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, P, Pb, Zn, and S.

Elements in remaining solution from flooded anaerobic experiment

The remaining solution in the biosolids microcosm in the samples after termination of the flooded anaerobic experiment (230 days) was filtered using a syringe with a micro-cellulose 0.45 μm filter and then transferred to a 60-mL plastic bottle to analyze the pH, E_h, and EC.

The pH was measured using a Metrohm 704 portable pH meter after calibration with buffers of pH 7 and 10. The redox potential was measured using a pH/ion meter (Radiometer) with an Ag/AgCl electrode. The observed redox potential was converted to E_h by adding a correction factor of 207 mV at room temperature. The EC was measured using a HI8733 Multi-Range Conductivity Meter (Henna Instruments).

The filtered sample was sent to an accredited commercial laboratory (ALS Scandinavia AB, Luleå, Sweden) for metal and elemental analysis (Al, Ca, K, Na, Fe, S, Mg, Si, As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, and Zn). Elemental sulfur was analyzed after the samples had been acidified with nitric acid (Super®) 1:100 vol/vol and digested in an autoclave at 120 °C for 3 min.

Data analysis

Gas concentration (%) was converted to millimoles per gram of biosolids using the ideal gas law. At 0 °C (273 K), the ideal gas volume was assumed to be 22.4 L/mol. Based on this volume, the calculated volume at 20 °C was adjusted to 24 L/mol. Gas sampling and subsequent GC analysis of the gas composition were performed at room temperature. The collected data were compiled as instantaneous and cumulative gas production, as well as mass balance curves based on the volume and calculated amount of organic matter in the biosolid samples. The CH_4 to CO_2 ratio was then calculated based on the gas composition.

Calculation of gas formation potential

In each experimental batch, the organic matter was assumed to be homogenous and to have the same content of organic fractions as distributed in all samples. Additionally, microbial organisms were assumed to be distributed evenly in each microcosm.

Theoretical gas formation potential, G_p (mL/g), was calculated by the equation (Tabasaran 1976):

$$G_p = 1.868 C_0 {*} (0.014\,T + 0.28) \tag{1}$$

where C_0 is the degradable carbon in the waste (mg/g) and T is the temperature (°C).

Short summary of previous laboratory 20−22 °C unsaturated anaerobic batch

The incubation experiments showed that 61.0 mL gas/g biosolids were produced during anaerobic incubation at 20−22 °C (Fig. 1a) and that a plateau to the biodegradation rate was approached. The results showed that the original biosolid consisted of approximately 60 % TOM, including 48.0 % lignin and 11.8 % carbohydrates that had not been fully degraded. The accumulated H_2S was 0.65 μmoL/g of biosolid at 230 days. Based on the model results following equation $G_t = G_e(1\text{-}e^{-kt})$ (Tabasaran 1976), where G_t is accumulated gas generation until time t ($mL{*}g^{-1}$), G_p is gas formation potential ($mL{*}g^{-1}$), k is degradation constant (day^{-1}), $k = ln(2)/t_{1/2}$, and t is time (day). Mean residence time (MRT, day) can be described by MRT=1/k, the degradation constant was 0.0125 (per day). The calculated theoretical gas formation potential was approximately 50 % higher than the modeled results based on the average degradation rate (Jia et al. 2014), indicating that a fraction of organic matter (e.g., lignin) in the biosolids was not easily biodegradable.

Results and discussion

Degradation under flooded anaerobic condition

The accumulated gas in the flooded anaerobic batch was as low as 36.9 mL gas/g biosolids on day 230 (Fig. 1b). The

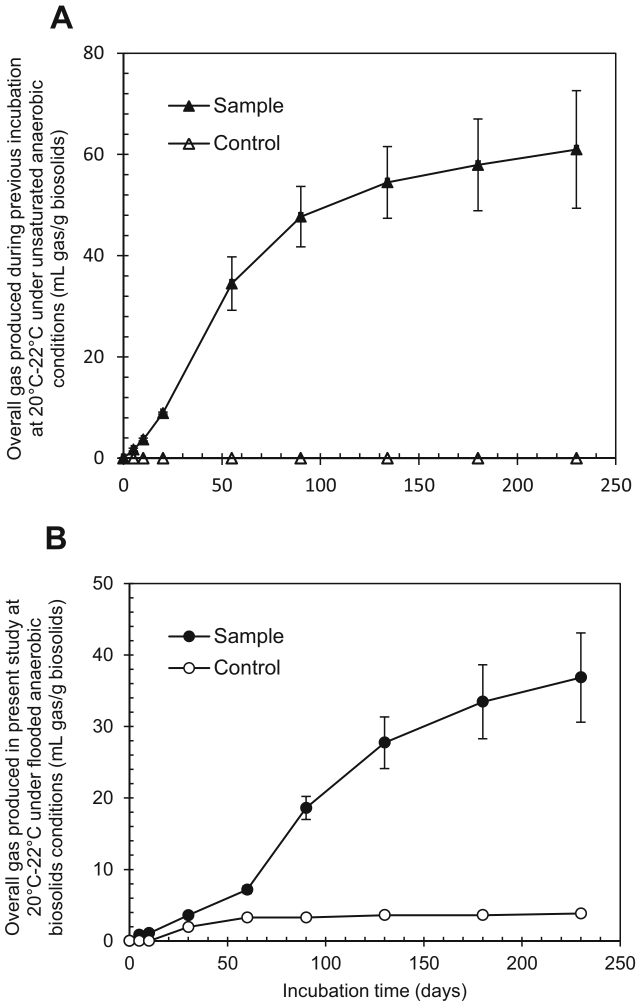

Fig. 1 Accumulated gas overpressure for the flooded anaerobic batches at 20−22 °C during the incubation period (**a**). For comparison, previous laboratory batch results for the biosolids incubated anaerobically under unsaturated anaerobic conditions at 20−22 °C (Jia et al. 2014) are presented in (**b**). *Error bars* indicate the standard deviation (*n*=3 for the samples; *n*=1 for the control). In some intances, *error bars* are smaller than *symbols*

calculated cumulative concentrations of CO_2 and CH_4 per gram of biosolid as a function of time are shown in Fig. 2a. The results also showed a lag phase from the initiation of incubation until day 60, which might reflect the time required for the microorganisms to adapt flooded anaerobic conditions.

Under flooded anaerobic conditions, the lag phase could be longer than under unsaturated anaerobic conditions because the microorganisms in the aquatic environment cannot easily utilize the substrates as when they are in a pore-water niche (Maier et al. 2000). However, after the microorganisms had adapted to the environment, they utilized substrate more efficiently than under unsaturated anaerobic conditions.

Assuming 1 mol gas at 20 °C is 24 L ("Data analysis" section) and that a complete microbial catalyzed reaction can be expressed by generating 3 mol of CH_4 and 3 mol of CO_2, the accumulated gas in overpressure in the microcosm was 0.553 L at day 230 of incubation, which required 0.69 g organic matter as glucose. Overall, approximately 60 % of 15 g of TS biosolids (i.e., 9 g) was organic matter; thus, 7.68 % TOM was degraded under flooded anaerobic conditions in the microcosm experiment. If the same approach is used to analyze data from a previous unsaturated anaerobic study conducted by Jia et al. (2014), it can be calculated that 25.5 % of TOM in the biosolids was degraded during the 230-day unsaturated-anaerobic incubation period. The value shown here is slightly lower (2.3 %) than that reported in Jia et al. (2014), where 22 L/mol was assumed.

A much lower amount of accumulated gas was recorded for the flooded anaerobic batch (under saturated conditions) in the present study relative to the previous unsaturated anaerobic experiment (Jia et al. 2014) at the same incubation temperature 20−22 °C. These findings imply that the increased amount of water filled pores, inhibiting biodegradation of biosolids, similar to the mechanism observed in soil (Khalil and Baggs 2005). These results indicate that the investigated method has potential for widespread application since a slower degradation process can prolong the lifetime of the biosolids when they are used as sealing material over tailings.

Moreover, if the tailings covered by the biosolids are stored under water (in lakes, such as wet cover material) or under saturated conditions in non-flooded conditions, the oxygen diffusion to the tailings can also be greatly reduced. Alternatively, CH_4 may be oxidized before the dissolved O_2 is depleted in the liquid phase. Thus the oxidization of the tailings can also be mitigated.

Though detectable, most measured H_2S was approaching the detection limit, with concentrations at the end of the experiment being as low as 27 ppm/g biosolids. The accumulated H_2S was thus calculated to be 1.2 μmol/L/g biosolids (Fig. 2b). This value is approximately twice as high as that obtained in the unsaturated anaerobic batch (0.65 μmol/L/g biosolids; Jia et al. 2014). Since the sulfate content in the biosolids is as high as 1.76 g SO_4^{2-}/kg biosolids (Jia et al. 2014), the potential release of H_2S under flooded anaerobic conditions over time should be considered. H_2S is highly toxic and can lead to erosion of the biosolid sealing layer (APHA 1998; Dhar et al. 2011); accordingly, the release of H_2S from the biosolids should be monitored from a long-term perspective.

In the flooded anaerobic batch, the accumulated gas produced in the treated control represents 10.4 % of the produced gas relative to the sample at day 230. The kinetic curve in the flooded anaerobic batch showed that a plateau was achieved in the microcosm, although the variation increased (standard deviation) with time.

In contrast, the gas produced in the control for the previous unsaturated anaerobic batch was negligible. The difference between the current flooded anaerobic control and previous unsaturated anaerobic control is considered to be due to the

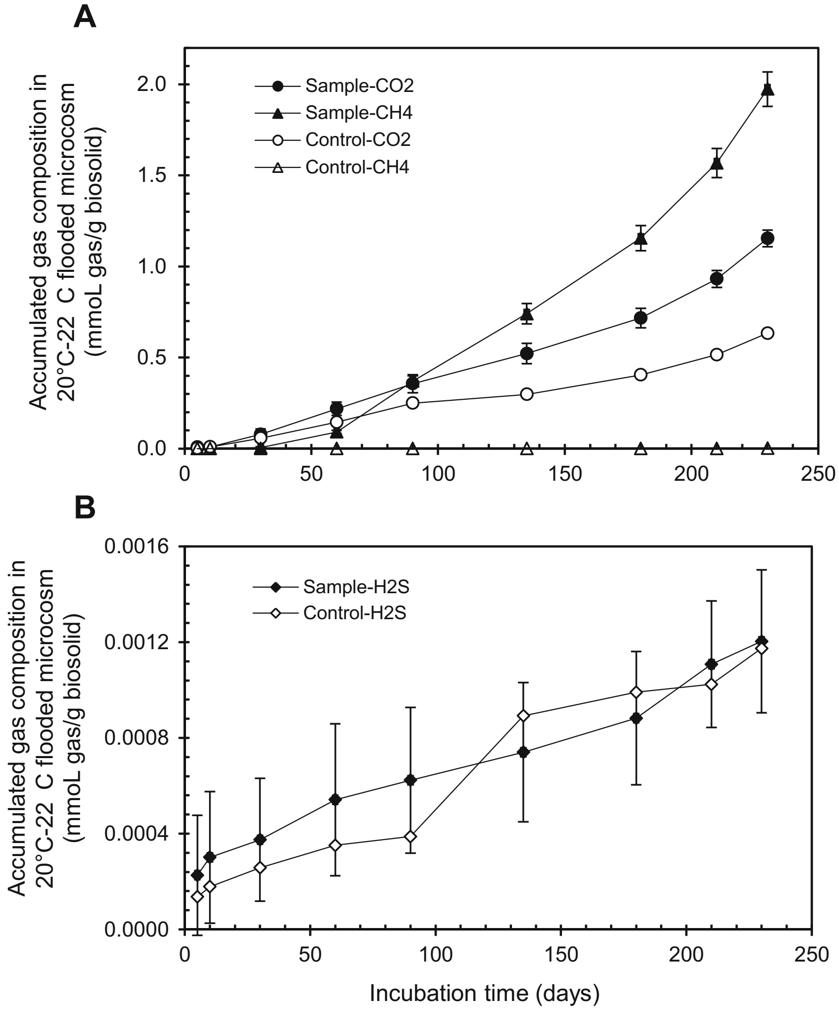

Fig. 2 Composition of accumulated gas under flooded anaerobic laboratory incubation at 20−22 °C using biosolid sample. **a** CO_2 and CH_4. **b** H_2S. Error bars indicate the standard deviation (*n*=3 for the samples); *n*=1 for the control

drying and re-wetting process for the flooded anaerobic control, while only dry process was performed for the unsaturated anaerobic control. The control biosolids were subjected to 105 °C for 24 h before the experiment was initiated under the assumption that the microorganisms would be killed and biodegradation minimized. However, the results indicate that the conditions implemented to sterilize the biosolids were not sufficient, and microbial degradation still persisted. It is likely that the organisms that survived the flooded anaerobic control were redistributed and then utilized the re-wetted biosolids as substrate.

Theoretically, the anaerobic degradation of 1 mol of glucose leads to generation of 6 mol of gas, corresponding to 3 mol of methane and 3 mol of CO_2. However, the results showed that the CH_4-to-CO_2 ratio for the flooded anaerobic batch was around 1.71 after 230 days (Fig. 3), indicating that intermediates were produced under flooded anaerobic conditions, but that some fractions were converted into CH_4 as end products in the later phases of incubation. Biogas generally consists of 60 % CH_4 and 40 % CO_2 (Wang et al. 2008). The ratio of CH_4 to CO_2 is often considered to be >1 due to the amount of intermediates formed under anaerobic conditions (Asgari et al. 2011; Kavuma 2013). The ratio for the previous unsaturated anaerobic batch (Jia et al. 2014) showed a similar trend (Fig. 3).

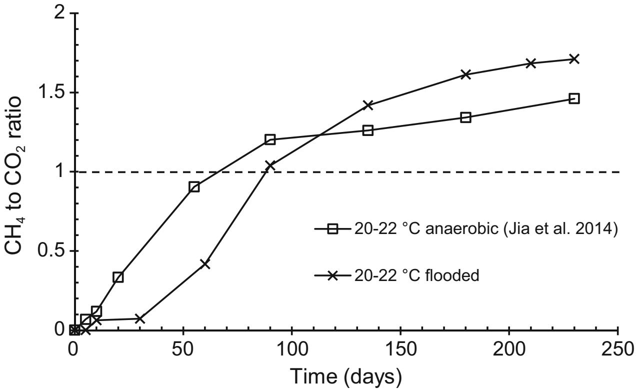

Fig. 3 CH_4-to-CO_2 ratio for the flooded anaerobic batch. The 20 °C−22 °C batch from an earlier study (Jia et al. 2014) is also included for comparison. The average value for the accumulated composition of CO_2 and CH_4 was used in each batch. The *horizontal dashed line* indicates the theortical CH_4-to-CO_2 ratio of 1

More intermediates were assumed to be formed in the first 120 days of incubation in the unsaturated anaerobic experimental microcosms than in the flooded anaerobic experimental microcosms, while in the later stage of incubation period, the opposite conclusion was drawn (Fig. 3).

In contrast, however, in the pilot-scale experiments, it is clear that the system exhibited a release of CO_2 preferentially over CH_4. Nason et al. (2013) indicated that the combination of CO_2 released from aerobic degradation of organic matter in the biosolids from atmospheric oxygen exposure, together with CO_2 released from anaerobic degradation, may create a larger combined CO_2 release. Atmospheric oxygen may have also oxidized CH_4 to form CO_2 which may have resulted in the elevated CO_2 concentration.

The difference between the laboratory results (the present study) and the field results (Nason et al. 2013) could be due to the sealed closed system in the laboratory microcosm compared to the open-system field conditions.

In the present study, sewage sludge from one producer was used as biosolids. Originating from the treatment process of waste water and as the solid residue generated during primary (physical/chemical), secondary (biological), and tertiary (nutrient removal) treatment, the quality of sewage sludge (biosolids) can vary a lot with respect to pH (7.7±0.7) (Pichtel et al. 1994; Fjällborg and Dave 2003; Ahlberg 2006; Andres and Francisco 2008; Wang et al. 2009), saturation level (95±5 %) (Elliot et al. 1997; Ahlberg 2006), moisture content (53±3 %) (Elliot et al. 1997; Andres and Francisco 2008; Wang et al. 2009), and organic matter (58±5 %) (Ahlberg 2006; Wang et al. 2009; Nason 2013). Biosolids originating from other producers may behave differently in terms of biodegradation kinetics and grade. It is thus recommended to perform more work to these topics.

Leaching of elements from biosolids under flooded anaerobic condition

Upon termination of the flooded anaerobic experiment, the pH increased from 7.3 (Jia et al. 2014) to 7.9 (the present study, Table 1), possibly due to a small change in the chemical composition such as dissolution of carbonate in the biosolids. The redox potential increased 78 mV after the experiment (Table 1), indicating a decrease in the reactivity of the biosolids.

The leaching results show that metals and metalloids were stable at neutral pH after the biosolids were in contact with the water for 230 days. Similarly, Forsberg et al. (2008) showed that, at a near-neutral pH range, most metals are normally relatively immobile when not bound to dissolved organic carbon (DOC). Although metals can be rapidly released from biosolids used for surface applications (Andres and Francisco 2008; Stehouwer et al. 2006), the results of the present study suggest that metals were not easily released from the biosolids over the long term. This may have occurred because there was an interaction between mine tailings and biosolids in those studies, while biosolids alone were investigated in the present study.

Most metals and metalloids leached from the biosolids after the flooded anaerobic experiment were present at below the limit (Council Decision 2003/33/EC) for inert material at landfill sites, except for Ni, which was present at approximately three times higher than the limit. Nevertheless, none of the metals and metalloids exceeded the limit value for non-hazardous waste (Table 2). This may have occurred because humic substances were produced upon biological degradation, providing complex chemical structures that tend to be more stable when compared to the initial biosolids (Peppas et al. 2000).

Based on these results, biosolids are generally considered to be satisfactory with respect to the leaching of metals and metalloids to the environment. Similarly, Forsberg and Ledin (2006) found that the addition of biosolids to tailings played a minor role in metal leaching in a 20-month column experiment, implying a negligible effect on mine waste remediation.

Conversely, the biosolids consisted of a large quantity of major elements such as Al and Ca, as well as nutritious elements such as K, Na, and P, which can influence underlying layers substantially (Nason et al. 2013). The Ca, K, and Al contents in the biosolids were high in the leachate of the flooded anaerobic sample, reflecting a cation migration process from the biosolids matrix. The lower content of phosphorus in the biosolids used herein (Table 2) could have been due to differences in wastewater processing of the original sludge, such as nutrient consumption in the biogas process prior to the biosolids being disposed of in the Boliden mine site named Gillervattet tailings impoundment.

Prospects for use of biosolids as covering materials under different conditions

Overall, the design, the operation, and the efficiency of an organic cover to prevent oxygen diffusion and mine-waste contaminants from being released may depend on the type of underlying mine wastes (causing ARD or neutral rock drainage (if it contains high levels of carbonates)). The local and regional climate, the characteristics of the biosolid composition (organic and inorganic), and the interaction between the organic cover and the underlying tailings may all govern the potential environmental impact if the biosolid sealing layer were to fail.

Factors such as the shear strength (for the placement on a slope such as hillside and tailings stack), permeability (the guideline value is 10^{-9} m s^{-1} for barrier layer in Sweden (Herrmann et al. 2009)), water retention capacity, saturation degree, particle size distribution, and freeze–thaw processes (especially in cold climates) play an important role in tailings remediation, especially if this material is to be used as a long-term (100-year) amendment.

Table 2 Chemical compositions of metals and metalloids in the original biosolids and biosolids leachates after the flooded anaerobic experiments at an L/S ratio of 10 mL/g at 230 days. For comparison, regulatory concentration limits for inert and non-hazardous waste at the same L-to-S ratio (Council Decision 2003/33/EC) are also presented

Element	Unit	Original biosolids	Leached after experiment	Relative mass released (%)	Leaching limit values at landfills for inert waste	Leaching limit values at landfills for non-hazardous waste
Ca	(g/kg)	33.2	3.4	10.1	NA	NA
Fe	(mg/kg)	17,014	9.5	0.1	NA	NA
K	(g/kg)	18.6	2.5	13.7	NA	NA
Mg	(g/kg)	11.19	0.71	6.4	NA	NA
Na	(mg/kg)	ND	1810	–	NA	NA
Si	(g/kg)	11.1	0.15	1.3	NA	NA
Al	(mg/kg)	7367	0.15	0.002	NA	NA
As	(mg/kg)	22.2	0.29	0.001	0.5	2
Cd	(mg/kg)	80.6	0.00057	0.001	0.04	1
Co	(mg/kg)	153	0.04	0.03	NA	NA
Cr	(mg/kg)	ND	0.0063	–	0.5	10
Cu	(mg/kg)	58.4	0.032	0.03	2	50
Hg	(mg/kg)	ND	0.000077	–	0.01	0.2
Mn	(mg/kg)	292	2.45	0.8	NA	NA
Mo	(mg/kg)	ND	0.01	–	NA	NA
Ni	(mg/kg)	54.2	*1.22*	2.3	0.4	10
P	(mg/kg)	264	192	72.7	NA	NA
Pb	(mg/kg)	40.3	0.067	0.2	0.5	10
Zn	(mg/kg)	213	0.074	0.03	4	10
S	(mg/kg)	1418	40.3	2.8	Sulfate 1000	Sulfate 20,000

The experimentally derived data that exceed the limit value are marked in italic

NA not available, *ND* not detectable

Under natural condition, 80 % of biosolids was degraded after 8 years of field application (Nason et al. 2013). In the previous unsaturated anaerobic laboratory experiment, approx. 25.5 % biosolids was degraded after 230 days of incubation at ambient temperature (Jia et al. 2014). In contrast, in the present flooded anaerobic laboratory study, approx. 7.68 % biosolids was degraded after 230 days of incubation at ambient temperature.

It was difficult to maintain similar conditions between the laboratory microcosm and the field conditions. The closed microcosm provided a quantitative estimate of anaerobic degradation rates, whereas the field experiment may represent a combination of aerobic and anaerobic degradation processes due to open-field conditions. Nevertheless, it is notable that the gas diffusion pathways in these two systems can be different and the microbial communities can also be different in comparison to the laboratory microcosm with the field samples. A number of environmental factors may affect field degradation rates and the sealing layer was found to be highly water saturated in the spring-melt and autumn storm events.

Moreover, the comparison of unsaturated anaerobic and flooded anaerobic experiments showed that water saturation was a crucial factor when biosolids are used as a sealing material over tailings.

In principle, biosolids have a wide variety of potential uses in sulfide mine tailing remediation such as sealing layer materials, organic barrier layers, wetland applications, and surface applications (Peppas et al. 2000; Andres and Francisco 2008; Neuschütz and Greger 2010; Nason et al. 2013). One prominent use is for surface applications, such as substrate for vegetation planted directly above sulfide mine tailings (Gardner et al. 2010; Nason et al. 2014). However, surface applications of biosolids have been shown to cause rapid oxidation of the original reduced fractions of sludge, such as metals and organic matter (Cravotta 1998). This process can also lead to reduction of the high content of macro-nutrients such as K, Ca, N, P, and organic matter, which can promote plant growth (Huapeng et al. 2012; Wang et al. 2010). However, application of biosolids as a vegetation substrate can considerably modify the underlying soil by reducing soil bulk density, tailings, and groundwater geochemistry (Ashworth and Alloway 2004; Ahlberg et al. 2006; Gardner et al. 2010).

The issues associated with the design, the operation and the efficiency with which an organic dry cover prevents O_2

diffusion and mine waste contaminants from being released has been discussed in detail in previous study (Jia et al. 2014). In addition, hydro-geological and geotechnical aspects have been discussed to some extent in Jia et al. (2014). Aerobic laboratory experiments are currently in progress to provide information regarding the behavior of biosolids under conditions in which air infiltration is not limiting. Comprehensive anaerobic and aerobic investigations in the closed system (microcosm isolated from the atmospheric air) are expected to provide insight into extreme cases in comparison with the field (considered as an open system) experimental data. Due to the origin of municipal biosolids, their chemical compositions and properties can differ dramatically (Peppas et al. 2000). In the present study, one type of biosolids was investigated for its long-term biodegradability and mobilization of elements. However, it is recommended that more types of biosolids be tested to gain more detailed knowledge regarding this subject and determine the effects of biosolid composition on biodegradability and leaching capacity.

A number of critical parameters such as annual precipitation rate, biosolid thickness, initial moisture, and moisture under saturation conditions can play a major role in the performance of an organic cover (Peppas et al. 2000). Therefore, these factors should also be monitored throughout the covering period.

The establishment of organic covers is generally considered one of the best oxygen limiting factors for the purpose of controlling ARD (Peppas et al. 2000). Under field conditions in northern Sweden, which has a sub-Arctic climate with a mean annual temperature and precipitation of 0.7 °C and 600 mm/year (Axelsson et al. 1991), it is expected that the degradation rate will be much slower than that observed in the present study. Although the majority of the recalcitrant fraction of biosolids (>92 %) was shown to undergo degradation during the incubation period (230 days), further long-term monitoring of the degradation of residues is necessary. Conversely, even if all organic fractions would be degraded eventually, the biosolid residue would still likely function as a non-reactive barrier. However, there is uncertainty regarding the results of increases in pore voids, which would alter the O_2 diffusion pathway.

Conclusions

In the present study, biosolids were evaluated as a sealing layer covering material of water cover or flooded dry cover for mine tailings. After 230 days of incubation under flooded anaerobic conditions at ambient temperature, approximately 7.68 % of the organic matter in the biosolids had been degraded. The experimental results indicate that the biosolids were biochemically stable at the end of the experiment. The flooded biosoild cover systems show less degradation than the unsaturated anaerobic biosolid covers. Although the degradation under the flooded (saturated) anaerobic conditions was low, the accumulated gas was still as high as 36.9 mL gas/g biosolids. The accumulated H_2S was of minor importance in the batch investigated. The leaching of metals and metalloids from biosolids was not a critical issue after 230 days of flooding at an L/S ratio of 10 mL/g based on the limit values for the non-hazardous waste at landfill sites not being exceeded. Nevertheless, the large metal and metalloids reservoir in the biosolids might become mobile when environmental conditions change. However, microbial activities and biodegradation of biosolids are expected to be much slower under field conditions in northern Sweden relative to those observed in the present study. In general, biosolids are considered a promising candidate in covering tailings underwater with respect to biodegradation and leaching of elements. Nevertheless, further microbial breakdown of biosolids residue as well as a number of other factors including H_2S generation should be monitored in long-term programs.

Acknowledgments The authors thank the GEORANGE program and the Center of Advanced Mining and Metallurgy (CAMM) for the financial support. We also thank Anton Lundkvist from Boliden Mineral AS for field assistance during biosolid sample collection and Désirée Nordmark, Jingying Xu, and Tommy Wikström for their laboratory assistance.

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