Research article

Distribution trend of trace elements in digestate exposed to air: Laboratory-scale investigations using DGT-based fractionation

Andreina Laera[a,b], Rémy Buzier[b,*], Gilles Guibaud[b], Giovanni Esposito[c], Eric D. van Hullebusch[d]

[a] University of Paris-Est, Laboratoire Géomatériaux et Environnement (EA 4508), UPEM, 77454, Marne-la-Vallée, France
[b] University of Limoges, PEIRENE, Equipe Développement d'indicateurs ou prévision de la qualité des eaux, URA IRSTEA, 123 Avenue Albert Thomas, 87060, Limoges Cedex, France
[c] University of Napoli "Federico II", Department of Civil, Architectural and Environmental Engineering, via Claudio 21, 80125, Napoli, Italy
[d] Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Université Paris Diderot, UMR 7154, CNRS, F-75005, Paris, France

ARTICLE INFO

ABSTRACT

The use of digestate as amendment for agricultural soils has already been proposed as an alternative to mineral fertilizers or undigested organic matter. However, little information is available concerning the effect of digestate atmospheric exposure on trace elements speciation and, consequently, on their mobility and bio-accessibility when digestate is stored in open tanks or handled before land spreading. In this study, we investigated at laboratory-scale the effect of digestate aeration on the distribution of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se and W using the diffusive gradients in thin films technique (DGT)-based fractionation. For this purpose, experiments were performed to assess the variation in distribution between the labile, soluble and particulate fractions over time in digested sewage sludge during passive and forced aeration. Results showed that aeration promoted a dissolution of Al, As, Co, Cr, Cu, Fe, Mn, Mo and Pb, suggesting a possible increase in their mobility that may likely occur during storage in open tanks or handling before land spreading. Labile elements' fraction increased only during forced aeration (except for Fe and Mn), suggesting that their short-term bio-accessibility can increase only after significant aeration as the one assumed to occur when land spreading takes place.

1. Introduction

The use of digestate, a by-product of anaerobic digestion of organic residues (Möller and Müller, 2012), as amendment for agricultural soils and substitute of mineral fertilizers (Riva et al., 2016) is gaining importance as a result of the increasing use of biogas plants running on different organic feedstock (Scarlat et al., 2018). However, the presence of potentially hazardous trace elements (TEs) (*e.g.* cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn)) in digestate, may prevent its use in agriculture (Kupper et al., 2014; Tampio et al., 2016). The bio-accessibility of TEs not only depends on their total concentration but also on their speciation (Hooda, 2010). Therefore, screening of TEs speciation is required to assess the harm or benefit associated with digestate before land spreading (van Hullebusch et al., 2016).

According to the spreading season, digestate could be stored for several months (Plana and Noche, 2016) in open tanks (Boulamanti et al., 2013; Liebetrau et al., 2010). During storage in open tanks and handling before land spreading, digestate will be exposed to air. Such

exposure will alter the anaerobic status of digestate which in turn may alter the speciation of TEs and consequently affect their mobility and bio-accessibility in the environment. Although no information is available, to the best of our knowledge, for digestate, Øygard et al. (2007) demonstrated that atmospheric exposure impacts on TEs' distribution in municipal solid waste landfill leachates. Therefore, new investigations are needed to assess the potential impact of digestate aeration on TEs speciation for risk assessment before land application.

Total element content in digestate is commonly determined after solubilization (usually acid digestion) with conventional methods for TEs analysis in liquids such as ICP-MS (Dragicevic et al., 2018a) and ICP-OES (Cao et al., 2018). The mobility and bio-accessibility of TEs in digestate are usually studied using different techniques such as sequential extractions like the modified Tessier method (Ortner et al., 2014) or extraction with deionized water only (Dragicevic et al., 2018b). Alternatively, the diffusive gradients in thin films technique (DGT) can be used to screen the presence of labile elements (*i.e.* the most readily bio-accessible form of TEs) (Zhang and Davison, 2015)

---

into the environmental matrix. In particular, DGT-based fractionation was recently validated for digestate matrix (Laera et al., 2019). Compared to conventional fractionation techniques, DGT has the advantage of measuring the targeted elements *in situ* without affecting the sample and speciation of TEs (Vrana et al., 2005). Moreover, DGT technique increases the sensitivity of TEs monitoring compared to total acid-soluble measurements (Laera et al., 2019).

Here, the effects of aeration of digested sewage sludge on mobility and bio-accessibility of fourteen TEs were investigated to assess their fate before land spreading. The TEs investigated in this study are either under EU regulation for application of sewage sludge in agriculture (European Commission, 2016) (*i.e.* Cd, Cr, Cu, Ni and Pb), or selected based on previous studies (Dragicevic et al., 2018b; Hamnér and Kirchmann, 2015; Laera et al., 2019; Øygard et al., 2007) (*i.e.* Al, As, Co, Fe, Mn, Mo and Se). Antimony (Sb) and W were included because they could be present in sewage sludge (Fu and Tabatabai, 1988; Healy et al., 2016; McBride, 2003) and generate environmental issues due to their accumulation in plants (Arai, 2010; Charter et al., 1995).

In this study, the conventional particulate/soluble fractionation indicating potential TEs' mobility was implemented with a DGT-based fractionation procedure to monitor the most bio-accessible species. Experiments were performed at laboratory-scale to assess the time variation of labile, soluble and particulate TEs during passive and forced aeration of digestate. Results were discussed assuming that the experimental work can mimic digestate oxidation during storage in open tanks or handling before land spreading.

2. Material and methods

2.1. Digestate sample

Digested sewage sludge was collected from a municipal wastewater treatment plant located in Limoges (France). The digestate derived from activated sludge treated by a mesophilic anaerobic digestion process. About 18 L of sample was collected directly from a pipe before discharge in an open storage tank. The sample was collected in a polypropylene (PP) bucket up to maximum capacity and closed with a lid to limit sample exposure to open air. Once in the laboratory, the sample was stored at 4 °C for less than 24 h before starting the experiment.

2.2. DGT preparation

We used Chelex-DGTs for cationic species (Al, Cd, Co, Cr (III), Cu, Fe, Mn, Ni and Pb) and zirconia-DGTs (Zr-DGTs) for anionic species (As, Mo, Sb, Se and W). Each DGT consisted of a binding gel (Chelex or Zr), a diffusive gel and a filter membrane enclosed in a piston type holder (purchased from DGT Research, Lancaster, UK). Chelex binding gels were prepared according to the procedure described by Zhang et al. (1998), whereas Zr binding gels were made according to Devillers et al. (2016). Diffusive gels were standard polyacrylamide gels (15% acrylamide and 0.3% agarose-derived cross linker, 0.77 mm thick) prepared according to Zhang et al. (1998) and filter membranes were made of cellulose acetate (0.2 μm pore size, 0.12 mm thickness, Whatman, UK).

2.3. Experimental set-up

About 18 L of digested sludge were poured into a laboratory-scale PP tank placed under a fume hood and continuously stirred with an overhead plastic propeller at 30 rpm (Fig. S1) in order to control experimental conditions. Stirring allows optimizing air transfer within the digestate and therefore represents a "worst case scenario" compared to unstirred real scale tanks. A Tinytag data logger (TG-4100, Gemini Data Loggers, UK) was used to record the temperature in the sample every 10 min. The surface of the sample was exposed to air to promote oxidation of the sample during 10 weeks. The surface to volume ratio varied from $0.39 \, dm^{-1}$ ($7.1 \, dm^2$:18 L) to $0.51 \, dm^{-1}$ ($7.1 \, dm^2$:14 L)

during the experiment because of multiple sample collection (see below). Therefore, passive aeration was progressively favored while the experiment continued. Then, aeration was enhanced during 2 supplementary weeks by introducing 4 micro-bubble air diffusers in the digested sludge. All diffusers were connected to air pumps (Newair or Optima) having airflow rates from 60 to 200 L/h.

Labile TEs were sampled by deploying three DGTs probes composed either of Chelex or Zr for 24 h in the digested sludge. We choose a 24 h deployment because it was shown previously to be a good compromise for the studied elements in digestate (Laera et al., 2019).

DGTs were deployed according to the following sequence (Fig. S1): every day for the 6 first consecutive days; once per week from week 2–10; twice per week for weeks 11 and 12. Blanks DGT devices were also prepared in duplicate and treated alongside exposed devices every week.

After DGTs' retrieval, we measured dissolved O_2, redox potential (E_h) and pH. Additionally, we collected an aliquot of sample to measure total and volatile solids (TS and VS), total and volatile suspended solids (TSS and VSS) and soluble TEs. Additionally, we monitored sulfate (SO_4^{2-}) concentration.

2.4. Analytical procedures

2.4.1. Physicochemical analysis

pH and E_h were measured with a Mettler Toledo pH meter and a Radiometer electrode, respectively. Dissolved oxygen was measured using a ProODO™ optical sensor (YSI). Each sampling time, about 90 mL of sample was collected in duplicate to measure the total solids (TS), volatile solids (VS), total suspended solids (TSS) and volatile suspended solids (VSS) according to the French standard AFNOR NF T90-105 method.

The supernatant recovered during the TSS and VSS analysis was conserved to determine soluble TEs (see Section 2.4.2.).

2.4.2. Sample treatment and trace elements analysis

Total elements' content was determined at the beginning and at the end of the experiment using 5 g of raw sample. Each sampling time, soluble elements' concentration was determined from the supernatant recovered during TSS determination. Supernatants and raw samples in duplicate were acid digested with 6 mL of 69% HNO_3 and 3 mL of 37% HCl in a microwave oven (Multiwave GO, Anton Paar GmbH) at 180 °C for 60 min.

TEs were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700 ×) except for Fe which was analyzed by microwave plasma atomic emission spectroscopy (MP-AES, Agilent 4210). Blanks and quality controls at 5 and 10 μg/L were analyzed every 10 samples. The recovery was equal or above 86% for each element, except for Sb and W which was equal or above 79% and 76%, respectively, among all analyses.

2.5. Element's fractionations calculation

The fractionation procedure is presented in Fig. 1. Particulate elements' concentration was calculated by subtracting the soluble to the initial total elements content.

After retrieval from the digested sludge, DGT samplers were rinsed with ultrapure water and disassembled to recover the binding gels and determine labile elements concentration. The accumulated mass (m) was determined following elution of binding gels in 2 mL of 1 M HNO_3 or 5×10^{-3} M NaOH and 0.5 M H_2O_2 for 24 h for Chelex and Zr-binding gels, respectively (see Table S1 for elution yields). The concentration of labile TEs, C_{DGT}, was then derived using Eq. (1) based on Fick's first law (Zhang and Davison, 1995):

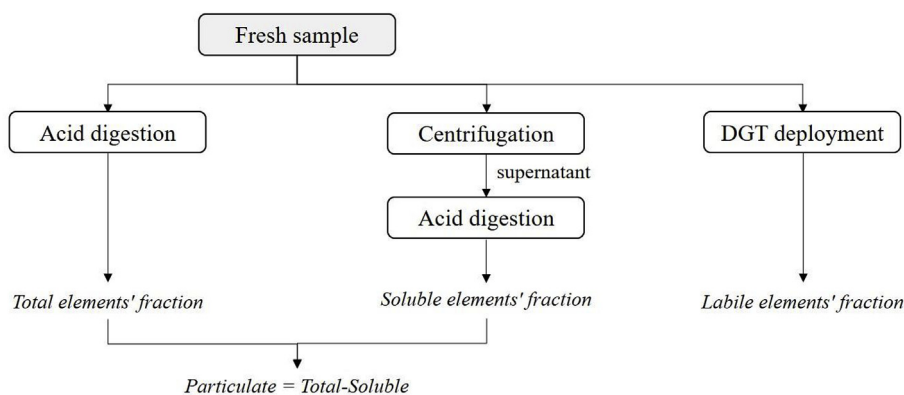$$C_{DGT} = \frac{m \times \Delta_{MDL}}{D \times t \times A} \tag{1}$$

Fig. 1. Fractionation procedure adopted in this study to estimate total, soluble, particulate and labile elements' fractions.

where Δ_{MDL} is the thickness of the material diffusion layer (*i.e.* diffusive gel plus membrane, 0.89 mm), t is the time of DGT samplers' exposure in the sludge (24 h), D is the coefficient of diffusion of the considered element and A is the geometric area of the DGT holder window (3.14 cm²). D values were taken from literature (Table S2) and corrected for the average temperature recorded during each deployment using Stokes–Einstein relation (Zhang and Davison, 1999).

The method's limits of detection and quantification (namely MLD and MLQ for total and soluble elements or MLD_{DGT} and MLQ_{DGT} for labile elements) are displayed in Tables S3 and S4.

3. Results and discussion

3.1. Sample characterization

The characteristic of the digested sewage sludge (TS, VS and water concentration) are presented in Fig. S2. The results show that the water concentration and the VS content is nearly constant throughout the experiment. In particular, the average water content was 96.2% ± 1.6 and the average VS content was 63.9% ± 1.3. Moreover, the average pH of the digested sludge was 7.8 ± 0.3 and the E_h was below −50 mV, whatever the aeration of the sludge. The latter is shown in Fig. S3.

The total elements concentration in the digested sludge is shown in Table S5. Except for Cd, Mo and Ni, the concentration of total elements is not significantly different (p > 0.05) at the beginning and at the end of the experiment. For total Cd, Mo and Ni content the difference was significant and could derive from an artifact caused by multiple sampling during the experiment if these elements were not homogenously distributed in the sludge.

3.2. Particulate and soluble concentrations of elements

Soluble concentrations of Cd, Ni, Sb, Se and W were below the method's limits of detection or quantification (*i.e.* lower than 12, 721, 102, 1077 and 69 µg/L, respectively) during the whole experiment and the impact of aeration on their distribution cannot be discussed. For the other elements (Fig. S4), three different trends were observed. An example of each trend is given in Fig. 2. Fe and Mn showed limited variations of their particulate and soluble concentrations during the first 15 days of passive aeration. Then, their soluble concentrations doubled up to the 66th day of aeration with a limited influence on their particulate concentration. From the 76th day of passive aeration and during the two weeks of forced aeration, the soluble concentration of Fe and Mn rapidly doubled. This rapid release in solution generated a slight decrease in particulate Fe (*i.e.* 4% less) and Mn (*i.e.* 5% less). Soluble concentrations of Al, Co, Cr, Cu, Mo and Pb were below MLD or MLQ during most of the passive aeration sequence (Fig. 2, Fig. S4). However, during forced aeration, the soluble concentration of these elements

increased above the detection limits and was followed by a decrease of their particulate concentration. In particular, the soluble Mo concentration prevailed in its total content during forced aeration (Fig. S4). Finally, As displayed a slightly different behavior. Although its soluble concentration is nearly constant during the first 22 days of passive aeration, a marked increase was observed from day 29. This increase is followed by a decrease of its particulate concentration. Unlike other elements, forced aeration had no significant impact on As soluble concentration.

Overall, aeration induces a release in solution of all quantified elements (*i.e.* Al, As, Co, Cr, Cu, Fe, Mn, Mo and Pb). This release was likely caused by direct oxidation of sulfur precipitates in presence of oxygen from the air (Fermoso et al., 2015). However, oxidation performed by indigenous microorganisms such as sulfur oxidizing bacteria (*i.e. Acidithiobacillus* species) (Jain and Tyagi, 1992) is not excluded, though this hypothesis needs further investigations. In both cases, sulfide oxidation leads to metal sulfide precipitates dissolution (*e.g.* FeS, CoS, Cu₂S, PbS) (Maharaj et al., 2018; Möller and Müller, 2012) as well as the release of sulfate. Indeed, a significant increase of sulfate concentration was measured after the 57th days of passive aeration and during forced aeration (Fig. S5). These results are in agreement with the soluble sulfate in sludge suspension found by Carbonell-Barrachina et al. (1999) under oxidizing conditions. Regarding particulate As, it can be hypothesized that it is initially co-precipitated with Fe sulfides (Savage et al., 2000) and consequently released in solution after their dissolution upon oxidation. This is consistent with the slight increase of soluble Fe observed from the 29th day of passive aeration.

3.3. DGT-labile elements concentration

Labile concentrations of Cd, Cr(III), Cu and Pb were lower than 0.02, 0.2, 2, 0.6 µg/L, respectively, during the whole experiment. The labile concentrations of Mo, Sb and W were close or below the MLD_{DGT} during most of the passive aeration experiment (Fig. S5). Labile concentrations of the other elements are given in Fig. S5 and typical examples are displayed in Fig. 3. Labile Al, As, Co, Fe and Mn rapidly decreased during the first 3–5 days of passive aeration and later their concentration remained rather constant until the 57th day of aeration at least. Conversely, no initial decrease was observed for Ni and Se.

Under forced aeration, several elements (*i.e.* Al, Mo, Ni, Sb, Se and W) displayed a rapid increase of their DGT-labile concentrations followed by a decrease, except for Mo and W. As and Co slightly decreased immediately after forced aeration and their concentration increased again at the 85th day. After 57 days of passive aeration Fe and Mn behavior differs from the other elements since their labile concentrations continued to decrease, even under forced aeration.

The decrease of labile Al at the beginning of passive aeration may be explained by the presence of negatively charged hydroxide complexes (*e.g.* Al(OH)₄⁻) at pH 7.8 ± 0.3 that are not efficiently sampled by
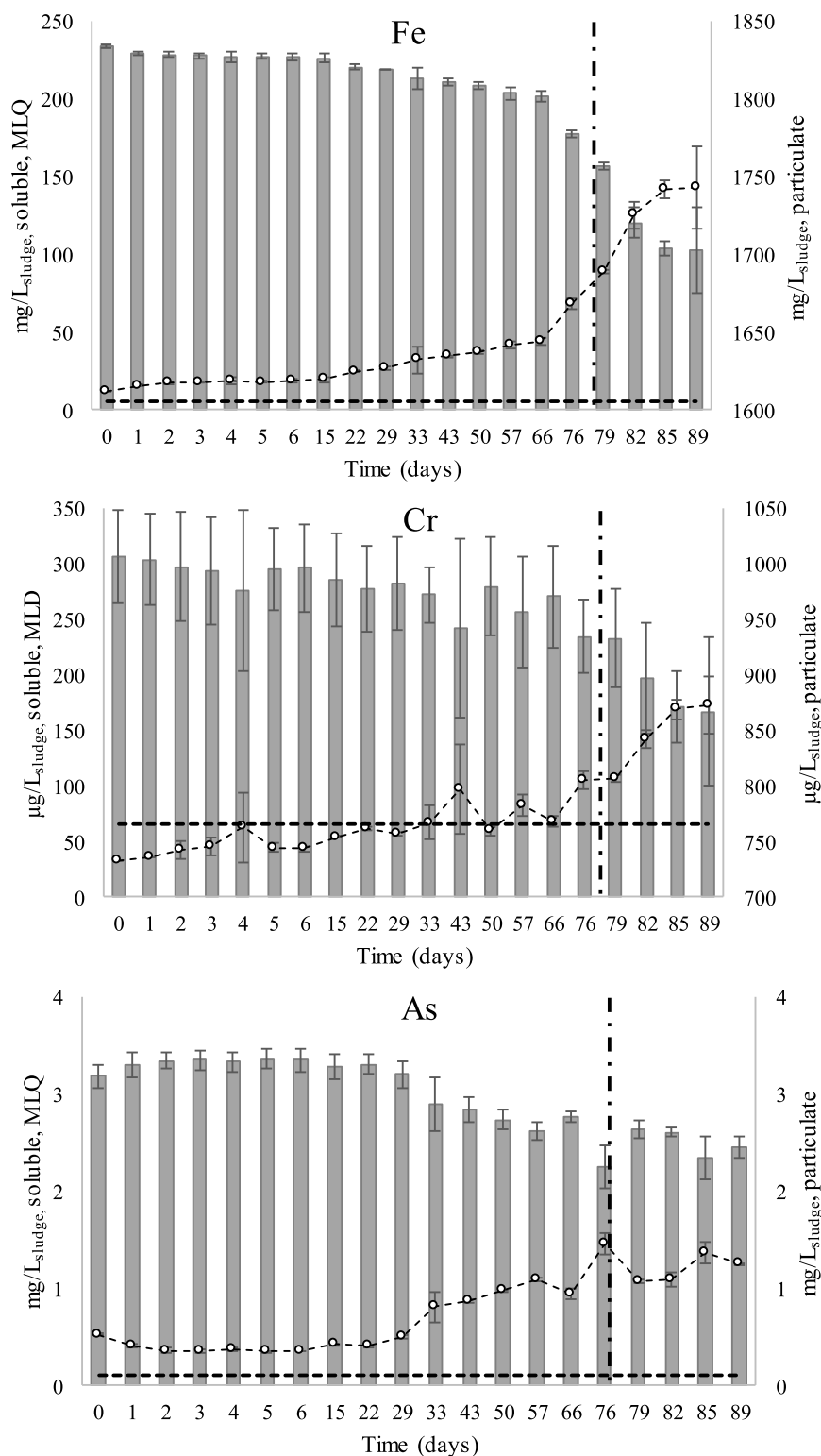
Fig. 2. Examples of soluble (dashed line with circles) and particulate (bars) elements' concentration over time. The bold horizontal dashed line is the method limit of detection (MLD) or quantification (MLQ) for soluble elements whereas the vertical dashed line indicates the beginning of forced aeration.

Chelex-DGT (Panther et al., 2012). The increase of labile Al, As, Co, Ni after 57 days of aeration could be a direct consequence of their release form sulfide species as discussed in 3.2. In contrast, the decrease of Fe and Mn labile concentration is not associated with the increase of their soluble fraction, especially at the end of the forced aeration, meaning that part of these soluble elements are DGT-inert (*e.g.* colloids such as Fe(II)-phosphate or strongly complexed with organic functional groups

such as thiol groups (Shakeri Yekta et al., 2014)). Therefore, it can be concluded that oxidation converts a part of labile species of Fe and Mn into soluble non-labile species. Similarly, Øygard et al. (2007) showed a strong decrease of labile Fe (determined with cation exchange SPE cartridge) during the exposition of leachate to oxygen, while particulate and colloidal Fe (*e.g.* iron oxides) increased.

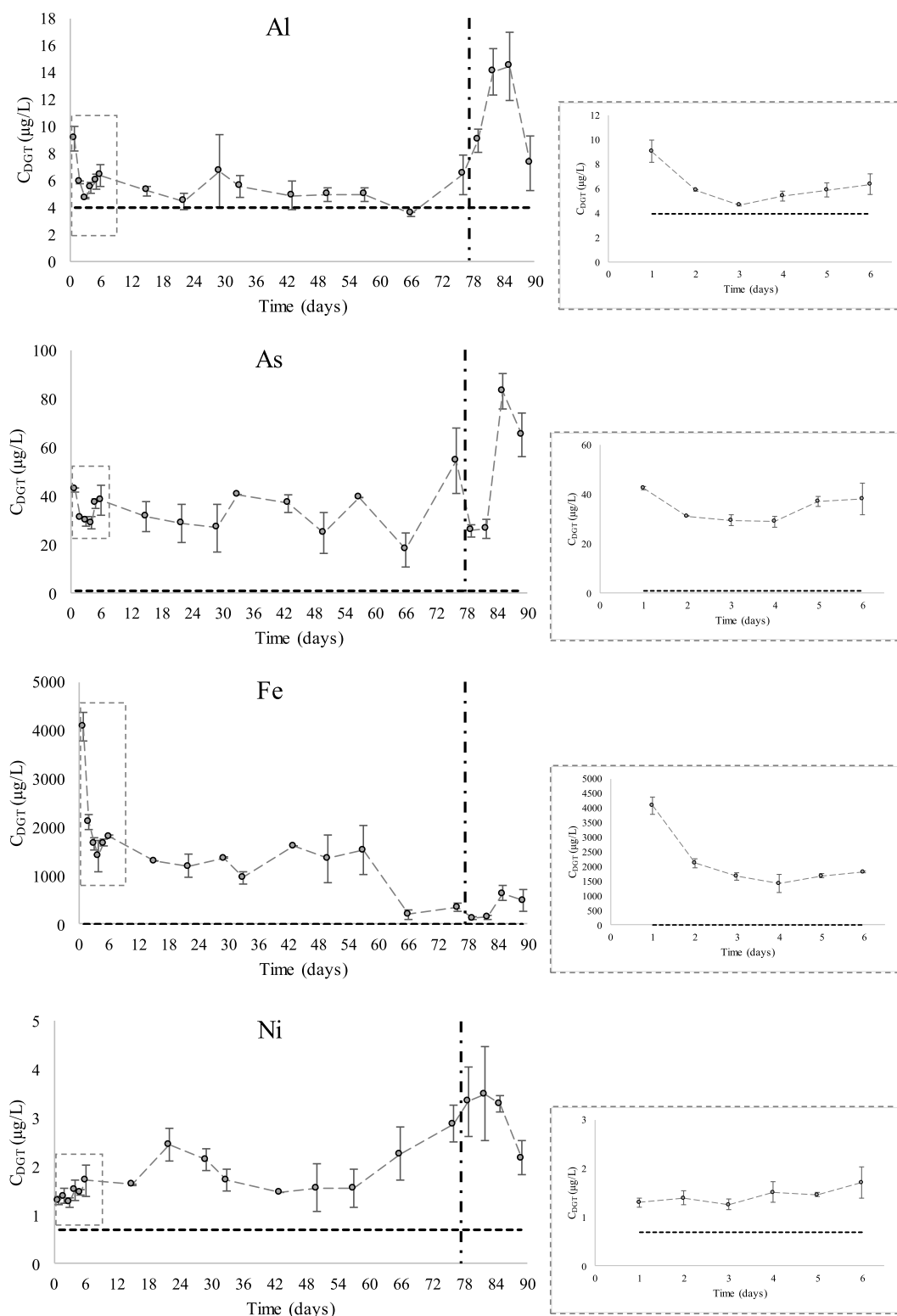Conversely, the delay observed for the increase of labile As and Co

Fig. 3. Examples of labile elements' concentration over time. The bold horizontal dashed line is the MLQ_{DGT} whereas the vertical dashed line indicates the beginning of forced aeration. The inset is an enlargement of the first 6 days of the experiment.

concentration during forced aeration let suppose slow mechanisms of conversion into labile form. Moreover, adsorption onto Fe/Mn colloids could have occurred.

3.4. Environmental impact of digestate aeration

In this study, performed at laboratory-scale in controlled conditions,

it was reported that aeration regime modifies TEs distribution among labile, soluble and particulate fractions. It is assumed that the observed TEs' fractionation can help to anticipate phenomena related to air exposure occurring on field during digestate management. Indeed, the passive aeration experiment could show the phenomena that can be expected during the storage of digestate in open tanks. Usually, the required storage time of digestate before land spreading may range

from 90 days to 10 months depending on the country and digestate spreading season (Plana and Noche, 2016). The variation on TEs' mobility observed during forced aeration is hypothesized to be similar to the one occurring during digestate handling for land application since the contact between air and digestate is significant.

Passive and forced aeration resulted both in a release in solution of Al, As, Co, Cr, Cu, Fe, Mn, Mo and Pb. Therefore, aeration of digestate could increase mobility of TEs over time. Under passive aeration, dissolution was slow during the first four weeks. Consequently, storage of digestate in an open tank could increase only marginally TEs mobility provided the storage duration is limited. However, dissolution increased significantly after approximately 30 days of passive aeration for most elements. Such increase is likely correlated to the increase of the surface to volume ratio (from $0.39 \, dm^{-1}$ to $0.45 \, dm^{-1}$ after 30 days of aeration) that controlled the rate of aeration of the digestate during the experiment. Therefore, design of digestate storage tank would be an important parameter to limit the increase of trace element mobility during storage. In this context, digestate storage tank with low surface to volume ratio (*i.e.* important height) should be favored. Forced aeration resulted in an important dissolution of all the quantified elements, except for As. Therefore, it is assumed that TEs' mobility could be strongly increased during digestate handling for land spreading. A "safety factor" which counts for TEs' oxidation during digestate handling should be considered for environmental risk assessment.

Alongside particulate/soluble fractions, DGT-labile elements were measured during this study. DGT-labile species (*i.e.* free + weak complexes) are the most reactive species and would represent the most readily bio-accessible fraction of TEs (Zhang and Davison, 2015). During passive aeration, although soluble elements' concentration increased, no correlated increase of DGT-labile concentrations was found for Al, As, Co, Fe, Mn, and Se. Only DGT-labile Ni showed a small delayed increase (≥ 60 days, within a factor 2). Therefore, storage of digestate in an open tank could have no impact on the labile fraction of most of the studied TEs.

During forced aeration, except for Fe and Mn, all quantified labile elements rapidly increased. Moreover, the bio-accessibility of labile elements could increase after land application depending on the soils' sorption capacity (Dragicevic et al., 2018b; Kabata-Pendias, 2004) and plants uptake mechanisms (Lehto et al., 2006; Tack, 2010). Such hypothesis should be further studied for risk assessment. It was also observed that labile Al, As, Co, Ni, Sb and Se decreased after one week of forced aeration, therefore, it is not excluded that their bio-accessibility could remain unaltered during digestate land application.

4. Conclusions

In this work, the influence of aeration of sewage sludge digestate on the fractionation of fourteen TEs (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se and W) was studied with a laboratory-scale tank. Aeration promoted dissolution of all the quantified elements (*i.e.* Al, As, Co, Cr, Cu, Fe, Mn, Mo and Pb), which was certainly due to oxidation of metal sulfide precipitates. Therefore, it was assumed that the observed increase of TEs mobility due to aeration may likely occur during storage in open tank or digestate handling before land application. However, this dissolution did not promote an increase of DGT-labile concentrations during passive aeration. Conversely, forced aeration promoted an increase of the labile Al, As, Co, Mo, Ni, Sb and Se. Therefore, it can be assumed that passive aeration of digestate like in open storage tank would not increase TEs bio-accessibility unless significant aeration such as during digestate handling for land spreading takes place.

Conflict of interest

The authors declare no conflict of interest.

References

Arai, Y., 2010. Arsenic and antimony. In: Trace Elements in Soils. Wiley-Blackwell, pp. 381–407. https://doi.org/10.1002/9781444319477.ch16.

Boulamanti, A.K., Donida Maglio, S., Giuntoli, J., Agostini, A., 2013. Influence of different practices on biogas sustainability. Biomass Bioenergy 53, 149–161. https://doi.org/10.1016/j.biombioe.2013.02.020.

Cao, W., Wang, M., Liu, M., Zhang, Z., Sun, Z., Miao, Y., Sun, C., Hu, C., 2018. The chemical and dynamic distribution characteristics of iron, cobalt and nickel in three different anaerobic digestates: effect of pH and trace elements dosage. Bioresour. Technol. 269, 363–374. https://doi.org/10.1016/j.biortech.2018.08.094.

Carbonell-Barrachina, A.A., Jugsujinda, A., Burlo, F., Delaune, R.D., Patrick Jr., W.H., 1999. Arsenic chemistry in municipal sewage sludge as affected by redox potential and pH. Water Res. 34, 216–224.

Charter, R.A., Tabatabai, M.A., Schafer, J.W., 1995. Arsenic, molybdenum, selenium, and tungsten contents of distinct fertilizers and phosphate rocks1. Commun. Soil Sci. Plant Anal. 26, 3051–3062. https://doi.org/10.1080/00103629509369508.

Devillers, D., Buzier, R., Simon, S., Charriau, A., Guibaud, G., 2016. Simultaneous measurement of Cr(III) and Cr(VI) in freshwaters with a single diffusive gradients in thin films device. Talanta 154, 533–538. https://doi.org/10.1016/j.talanta.2016.04.009.

Dragicevic, I., Eich-Greatorex, S., Sogn, T.A., Horn, S.J., Krogstad, T., 2018a. Use of high metal-containing biogas digestates in cereal production – Mobility of chromium and aluminium. J. Environ. Manag. 217, 12–22. https://doi.org/10.1016/j.jenvman.2018.03.090.

Dragicevic, I., Sogn, T.A., Eich-Greatorex, S., 2018b. Recycling of biogas digestates in crop production—soil and plant trace metal content and variability. Front. Sustain. Food Syst. 2, 1–14. https://doi.org/10.3389/fsufs.2018.00045.

European Commission, 2016. Sewage Sludge [WWW Document]. URL. http://ec.europa.eu/environment/waste/sludge/index.htm, Accessed date: 10 February 2018.

Fermoso, F.G., van Hullebusch, E.D., Guibaud, G., Collins, G., Svensson, B.H., Carliell-Marquet, C., Vink, J.P.M., Esposito, G., Frunzo, L., 2015. Fate of trace metals in anaerobic digestion. In: Guebitz, G.M., Bauer, A., Bochmann, G., Gronauer, A., Weiss, S. (Eds.), Biogas Science and Technology. Springer International Publishing, Switzerland, pp. 171–195. https://doi.org/10.1007/978-3-319-21993-6_7.

Fu, M.H., Tabatabai, M.A., 1988. Tungsten content of soils, plants, and sewage sludges in Iowa. J. Environ. Qual. 17, 146–148. https://doi.org/10.2134/jeq1988.00472425001700010024x.

Hamnér, K., Kirchmann, H., 2015. Trace element concentrations in cereal grain of long-term field trials with organic fertilizer in Sweden. Nutrient Cycl. Agroecosyst. 103, 347–358. https://doi.org/10.1007/s10705-015-9749-7.

Healy, M.G., Fenton, O., Forrestal, P.J., Danaher, M., Brennan, R.B., Morrison, L., 2016. Metal concentrations in lime stabilised, thermally dried and anaerobically digested sewage sludges. Waste Manag. 48, 404–408. https://doi.org/10.1016/j.wasman.2015.11.028.

Hooda, P.S., 2010. Assessing bioavailability of soil trace elements. In: Trace Elements in Soils, pp. 227–265. https://doi.org/10.1002/9781444319477.ch11.

Jain, D.K., Tyagi, R.D., 1992. Leaching of heavy metals from anaerobic sewage sludge by sulfur-oxidizing bacteria. Enzym. Microb. Technol. 14, 376–383. https://doi.org/10.1016/0141-0229(92)90006-A.

Kabata-Pendias, A., 2004. Soil-plant transfer of trace elements - An environmental issue. Geoderma 122, 143–149. https://doi.org/10.1016/j.geoderma.2004.01.004.

Kupper, T., Bürge, D., Bachmann, H.J., Güsewell, S., Mayer, J., 2014. Heavy metals in source-separated compost and digestates. Waste Manag. 34, 867–874. https://doi.org/10.1016/j.wasman.2014.02.007.

Laera, A., Buzier, R., Guibaud, G., Esposito, G., van Hullebusch, E.D., 2019. Assessment of the DGT technique in digestate to fraction twelve trace elements. Talanta 192, 204–211. https://doi.org/10.1016/j.talanta.2018.09.033.

Lehto, N.J., Davison, W., Zhang, H., Tych, W., 2006. Analysis of micro-nutrient behaviour in the rhizosphere using a DGT parameterised dynamic plant uptake model. Plant Soil 282, 227–238. https://doi.org/10.1007/s11104-005-5848-6.

Liebetrau, J., Clemens, J., Cuhls, C., Hafermann, C., Friehe, J., Weiland, P., Daniel-Gromke, J., 2010. Methane emissions from biogas-producing facilities within the agricultural sector. Eng. Life Sci. 10, 595–599. https://doi.org/10.1002/elsc.201000070.

Maharaj, B.C., Mattei, M.R., Frunzo, L., van Hullebusch, E.D., Esposito, G., 2018. ADM1 based mathematical model of trace element precipitation/dissolution in anaerobic digestion processes. Bioresour. Technol. 267, 666–676. https://doi.org/10.1016/j.biortech.2018.06.099.

McBride, M.B., 2003. Toxic metals in sewage sludge-amended soils: has promotion of beneficial use discounted the risks? Adv. Environ. Res. 8, 5–19. https://doi.org/10.1016/S1093-0191(02)00141-7.

Möller, K., Müller, T., 2012. Effects of anaerobic digestion on digestate nutrient availability and crop growth: a review. Eng. Life Sci. 12, 242–257. https://doi.org/10.1002/elsc.201100085.

Ortner, M., Rachbauer, L., Somitsch, W., Fuchs, W., 2014. Can bioavailability of trace nutrients be measured in anaerobic digestion? Appl. Energy 126, 190–198. https://doi.org/10.1016/j.apenergy.2014.03.070.

Øygard, J.K., Gjengedal, E., Røyset, O., 2007. Size charge fractionation of metals in municipal solid waste landfill leachate. Water Res. 41, 47–54. https://doi.org/10.1016/j.watres.2006.09.027.

Panther, J.G., Bennett, W.W., Teasdale, P.R., Welsh, D.T., Zhao, H., 2012. DGT measurement of dissolved aluminum species in waters: comparing chelex-100 and titanium dioxide-based adsorbents. Environ. Sci. Technol. 46, 2267–2275. https://doi.org/10.1021/es203674n.

Plana, P.V., Noche, B., 2016. A review of the current digestate distribution models: storage and transport. In: 8Th International Conference on Waste Management and The Environment, pp. 345–357. https://doi.org/10.2495/WM160311.

Riva, C., Orzi, V., Carozzi, M., Acutis, M., Boccasile, G., Lonati, S., Tambone, F., D'Imporzano, G., Adani, F., 2016. Short-term experiments in using digestate products as substitutes for mineral (N) fertilizer: Agronomic performance, odours, and ammonia emission impacts. Sci. Total Environ. 547, 206–214. https://doi.org/10.1016/j.scitotenv.2015.12.156.

Savage, K.S., Tingle, T.N., O'Day, P.A., Waychunas, G.A., Bird, D.K., 2000. Arsenic speciation in pyrite and secondary weathering phases, Mother lode gold district, Tuolumne County, California. Appl. Geochem. 15, 1219–1244. https://doi.org/10.1016/S0883-2927(99)00115-8.

Scarlat, N., Dallemand, J.F., Fahl, F., 2018. Biogas: developments and perspectives in Europe. Renew. Energy 129, 457–472. https://doi.org/10.1016/j.renene.2018.03.006.

Shakeri Yekta, S., Svensson, B.H., Björn, A., Skyllberg, U., Yekta, S.S., Svensson, B.H., Björn, A., Skyllberg, U., 2014. Thermodynamic modeling of iron and trace metal solubility and speciation under sulfidic and ferruginous conditions in full scale continuous stirred tank biogas reactors. Appl. Geochem. 47, 61–73. https://doi.org/10.1016/j.apgeochem.2014.05.001.

Tack, F.M.G., 2010. Trace elements: general soil chemistry, principles and processes. In: Hooda, P. (Ed.), Trace Elements in Soils. Wiley-Blackwell, pp. 9–37. https://doi.org/10.1002/9781444319477.ch2.

Tampio, E., Salo, T., Rintala, J., 2016. Agronomic characteristics of five different urban waste digestates. J. Environ. Manag. 169, 293–302. https://doi.org/10.1016/j.jenvman.2016.01.001.

van Hullebusch, E.D., Guibaud, G., Simon, S., Lenz, M., Yekta, S.S., Fermoso, F.G., Jain, R., Duester, L., Roussel, J., Guillon, E., Skyllberg, U., Almeida, C.M.R., Pechaud, Y., Garuti, M., Frunzo, L., Esposito, G., Carliell-Marquet, C., Ortner, M., Collins, G., 2016. Methodological approaches for fractionation and speciation to estimate trace element bioavailability in engineered anaerobic digestion ecosystems: an overview. Crit. Rev. Environ. Sci. Technol. 46, 1324–1366. https://doi.org/10.1080/10643389.2016.1235943.

Vrana, B., Allan, I.J., Greenwood, R., Mills, G.A., Dominiak, E., Svensson, K., Knutsson, J., Morrison, G., 2005. Passive sampling techniques for monitoring pollutants in water. TrAC Trends Anal. Chem. (Reference Ed.). https://doi.org/10.1016/j.trac.2005.06.006.

Zhang, H., Davison, W., 2015. Use of diffusive gradients in thin-films for studies of chemical speciation and bioavailability. Environ. Chem. 12, 85–101. https://doi.org/10.1071/EN14105.

Zhang, H., Davison, W., 1999. Diffusional characteristics of hydrogels used in DGT and DET techniques. Anal. Chim. Acta 398, 329–340. https://doi.org/10.1016/S0003-2670(99)00458-4.

Zhang, H., Davison, W., 1995. Performance characteristics of diffusion gradients in thin films for the *in situ* measurement of trace metals in aqueous solution. Anal. Chem. 67, 3391–3400. https://doi.org/10.1021/ac00115a005.

Zhang, H., Davison, W., Knight, B., Mcgrath, S., 1998. In situ measurements of solution concentrations and fluxes of trace metals in sells using DGT. Environ. Sci. Technol. 32, 704–710. https://doi.org/10.1021/es9704388.