Science of the Total Environment 649 (2019) 544–553

Contents lists available at ScienceDirect

Science of the Total Environment

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

Leaching behavior of major and trace elements from sludge deposits of a French vertical flow constructed wetland

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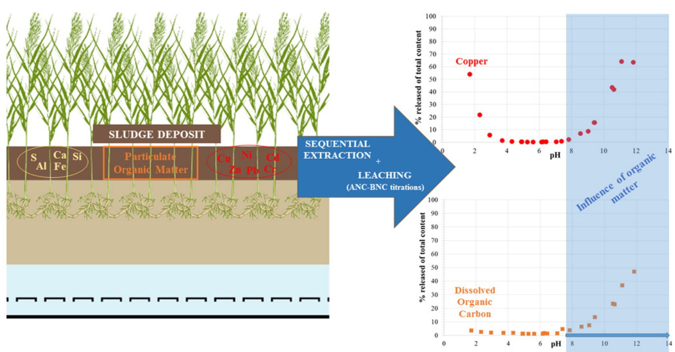
HIGHLIGHTS

- Leaching of inorganic elements into aqueous solution was very low at neutral pHs.
- The high organic content of the sample influenced the leaching of several trace metals.
- Copper was the trace metal most associated to organic matter in the sample.
- Copper pH-dependent leaching followed the leaching pattern of organic components.
- Leaching of organic compounds and associated trace metals was increased at alkaline pHs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 April 2018
Received in revised form 25 July 2018
Accepted 25 August 2018
Available online 27 August 2018

Keywords:
French constructed wetlands
Sludge deposit
Trace elements release
Acid and basic neutralization capacity
Organic matter
Sequential extraction

ABSTRACT

Surface sludge deposits were collected from a French Vertical Flow Constructed Wetland (French VFCW) sewage treatment plant. The objectives were to characterize the retention of major elements and trace metals within the sludge deposits particles under regular operating conditions, and the influence of extreme pH conditions on their potential release which may occur in situations when the plant malfunctions or after land application of the dredged sludge. A sequential extraction protocol was first used to assess the distribution of the elements within the sludge deposits. Results showed that most of Cu and Pb were associated to organic matter within the oxidizable fraction. Zn, Ni and Cd were distributed in several fractions, notably bound to Fe-Mn oxides and associated to organic matter. Cr was analyzed mostly in the residual fraction. Aliquot fractions of sludge deposits were also submitted to Acid and Base Neutralization Capacity tests (ANC-BNC) where the samples were suspended into acidic or alkaline aqueous solutions, and the solutions analyzed after 48 h contact time. Results showed a pH-dependent leaching profile for all monitored elements. The role of organic matter was observed for almost all metals. It was particularly dominant for Cu which was leached more extensively under alkaline than acidic conditions. Since Cu is not an amphoteric element, this leaching pattern was attributed to the leaching of organic matter which followed a similar pH-dependent profile than Cu. Spectrometric indices were used to characterize soluble organic compounds. Results showed that complex and humified dissolved organic compounds were mostly released under alkaline conditions.

1. Introduction

Constructed wetlands are considered among the technologies best adapted to domestic wastewater or storm water treatment from small communities. In France, the development of Vertical Flow Constructed

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https://doi.org/10.1016/j.scitotenv.2018.08.364
0048-9697/

Wetlands (VFCWs) has been considerable since the end of the 90s. French VFCWs have proved to be efficient for the treatment of carbon and nitrogen (Kim et al., 2014; Molle et al., 2005; Morvannou et al., 2015). For phosphorus removal, additional treatment stages are necessary to guarantee low level release (Molle et al., 2004; Kim et al., 2014). One of the solutions is to precipitate dissolved phosphates by injecting $FeCl_3$ before the percolation of the influent through the filter stages. The precipitates thus formed, mixed with the suspended solids from the influent, progressively accumulate at the surface of the French VFCW in the form of a sludge layer (Chazarenc and Merlin, 2005; Molle et al., 2004). Several studies have already been published on sludge characteristics and their evolutions in reed bed treatment systems (Caicedo et al., 2015; Matamoros et al., 2012; Nielsen, 2005; Nielsen and Bruun, 2015). However, there is still a lack of specific studies focused on surface sludge deposits from French VFCWs.

Besides phosphorous and nitrogen issues, a diversity of metallic pollutants are transported in wastewater streams (Vriens et al., 2017) and may accumulate in this layer via (co)-precipitation, complexation or adsorption mechanisms onto particulate organic matter (OM) and/or mineral phases such as clays, Fe-, Mn- or Al-oxides and oxy-hydroxides. These retention mechanisms have positive effects when considering the treatment performance of a French VFCW (Gill et al., 2017). However over the years of operation of the French VFCW, the sludge layer may undergo various biophysicochemical changes (pH; Eh), which may influence the fate of trace metals and/or organic matter (Grybos et al., 2009), leading to potential environmental risks. For example, acidification of the sludge layer may arise from (i) exposure to acidic rainfalls, with pH reported to range from 4.4 to 5.7 in eastern France (Sanusi et al., 1996) or 2.89 in some parts of China (Du et al., 2014), (ii) temporary or seasonal contribution of acidic wastewater, or (iii) malfunctioning of the system leading to flooding of the filters and acidogenic biodegradation of organic matter (Kim et al., 2016).

In addition, the thickening of the sludge layer over the years of operation may progressively reduce the permeability of the systems. It is commonly considered that surface sludge layer should be dredged from the filters after 10 to 15 years of operation (Chazarenc and Merlin, 2005). Dredged sludge may be used for land application, provided the associated potential environmental risks are acceptable. European and French regulations have set threshold limits for trace metals contents (Cd, Cr, Cu, Hg, Ni, Pb, Zn) in sludge and in the receiving soil. Total contents are not however the key factor in the potential environmental risk of trace metals release from sludge. Mobility, which is related to their chemical speciation and the physico-chemical local conditions, has a major influence on their potential release to the water phase (Yang et al., 2014). A proper assessment of the potential risks of sludge deposits in land application should therefore include the evaluation of the potential mobility of the contaminants, and the influence of environmental conditions such as acidity or redox potential on their leaching potential (Chatain et al., 2013; Gonzalez et al., 2017). Although a large number of studies have been published on the subject in the field of solid waste or contaminated soils management, to our knowledge, no specific study has yet been released on the speciation and mobility of inorganic contaminants present in French VFCW sludge deposits.

This study was therefore conducted to experimentally assess the release of major inorganic elements (Al, Ca, Fe, Si and K) and a selection of trace metals (Cr, Cu, Ni, Zn, Cd and Pb) from surface sludge deposits sampled from a French VFCW sewage treatment plant. The selected plant was already extensively studied by Kim et al. (2013, 2015), Kania, 2018, and Kania et al. (2018a and b, 2019). In this purpose, a methodology was developed based on waste management protocols (Chatain et al., 2013; Gonzalez et al., 2017). Batch pH-dependent leaching tests were conducted following acid and base neutralization capacity (ANC-BNC) European standard CENTS/TS 14429, in order to investigate the influence of pH conditions on the leaching behavior of the material. This method was complemented by sequential extractions of major and trace elements (Chatain et al., 2005; Tessier et al., 1979) to assess their distribution within the sludge deposits mineralogical phases.

2. Materials and methods

2.1. Origin of the sludge deposits sample

A representative sample of surface deposits was collected from the sludge layer of a full-scale French VFCW sewage treatment plant located in Vercia (France). The plant was being in operation for 8 years at the sampling date. Previous studies described in details the design of the plant and its performance (Kim et al., 2014). The plant was designed and operated according to AZOE-NP® process, which combines an aerobic trickling filter and ferric chloride injection prior to the classical 2 stages of filters. It was designed for 1100 population equivalent and received mostly domestic wastewaters from the Vercia town, and some winery effluents during autumn.

Surface deposits were sampled using a power shovel to extract the entire depth of the sludge layer at 8 spots of the surface of the first filter. The samples were then treated on site to remove gravels and reeds rhizomes manually, mixed and carefully homogenized by quartering with shovels before being transported to the laboratory within no >3 h. There, an aliquote fraction was freeze-dried and then crushed at 1 mm. The powder obtained was carefully homogenized and stored at 4 °C until they were used.

Previous studies (Kania, 2018; Kania et al. 2018a, 2019) conducted on 14 different French VFCW plants, including the one selected here, revealed remarkably similar characteristics of the surface deposits taken from plants of 2–3 years of age and more. This group of samples revealed very strong analogies in terms of organic matter composition and physical properties, and was designated as the “mature deposits” typology. The surface deposits sample selected in the present study was representative of this group.

2.2. Chemical composition

The Organic matter (OM) content was determined by combustion at 550 °C until constant mass of a given precise mass of the surface deposits sample (AFNOR, 2007 NF EN 15169). The results were considered to represent the Particulate Organic Matter (POM) since the soluble organic matter was negligible (Kania et al., 2018b). Elemental analyses were performed by alkaline fusion ($LiBO_2$) followed by acid digestion (HNO_3) and subsequent analyses of the solutions by inductively coupled plasma atomic emission spectrometry (ICP-AES) (IRIS Advantage ERS, Thermo Scientific). The following elements were analyzed: silicon (Si), aluminum (Al), iron (Fe), manganese (Mn), magnesium (Mg), calcium (Ca), sodium (Na), potassium (K), titanium (Ti) and phosphorus (P). Other trace metals (chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), cadmium (Cd) and lead (Pb)) were analyzed using a Sciex Perkin Elmer ELAN 5000a. ICP-mass spectrometer.

Carbon and sulfur contents were determined with a HORIBA EMIA 320 V2 analyzer. 1 g of dry powdered samples was calcined at 1400 °C under a flow of O_2, followed by quantification of carbon and sulfur oxides by infrared absorption.

2.3. Sequential chemical extraction

A sequential chemical extraction protocol adapted from Chatain et al. (2005) and Tessier et al. (1979) was carried out in triplicates to determine the distribution of metals in the sludge, with respect to five fractions, namely: (F1) exchangeable fraction, (F2) extractible fraction bound to carbonates, (F3) reducible fraction (bound to Fe-Mn oxides), (F4) oxidizable fraction (bound to organic matter), (F5) and residual fraction. The so-called “reducible” and “oxidizable” fractions corresponded to phases that can be dissolved respectively by reduction (oxides and oxi-hydroxides) or oxidation (sulfides or organic matter). A