METHODS USED FOR HEAVY METAL DETERMINATION IN AGRICULTURAL INPUTS

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Abstract. *Lately, organic farming has become a big part of the economy, and its importance is constantly growing. Since the organic farming is subject to a number of restrictions, not all agricultural inputs used in conventional agriculture can be used. Focusing on environment and human health protection, a number of inputs have been studied for acceptance in organic farming. Some of the most used inputs are ashes, composts, certain mineral fertilizers and manure. In order to be used as soil amendments, these inputs should meet a series of standards regarding the content on different elements or substances, to be sure that they are not harmful to health or to environment. Besides pesticides, antibiotics, dioxins and other substances, heavy metals are one of the most common contaminants in these inputs. Their quantitative analysis and correlation with current legislation should be one of the key factors in approving their use. These inputs are obtained from materials used in various industries and subject to different treatments such: combustion at 700-1000ºC in the case of ashes, slow fermentation in the case of compost and manure or chemical synthesis for some fertilizers accepted in organic farming. This diversity leads to different methods of analysis, depending on the type of sample. Thus, analysis of certain inputs may require additional steps in the analysis protocol. For some heavy metals, there may be differences from the standard procedure, also. It should be mentioned that each method has its own limitations, and each class of instrumentation had a specific precision that depends of manufacturers. The accuracy of obtained result is strongly related to chemist's decision in choosing proper and most suitable analysis method. This paper presents a list of methods used for heavy metals analysis in different matrices, found in recent studies. For the analytical metods of these elements, the sample preparation is an important step, which consists in sample conversion into a liquid form by various means. The methods for dissolving samples are also presented as they are described by the studies.*

Keywords*: heavy metals, inputs, organic agriculture*

INTRODUCTION

Different analytical methods can be used for determination of heavy metals, each with its advantages and disadvantages. Before the actual analysis, some common steps are required for a succesfull determination. Among them, sampling, sample handling and sample preparation play a significant role (Baltic Marine Environment Protection Commission, 2018).

Given that the amounts of heavy metals in inputs can be divided into 'total' and 'available'(which is the fraction that can be absorbed by plants), the sample may suffer some extraction procedures.

Although the total concentrations of heavy metals offer incomplete information about potentially plant-available fractions, they provide a helpful indicator that shows if a sample has high or low concentrations. This provide information if the analyzed sample is contaminated and had a possible risk of toxicity (Alloway, 2013).

As the last stage before analysis, the sample preparation differs depending on the used method. Usually, the most of analytical methods require the samples as aqueous solution which ensures complete availability of the analytes. Acid digestion is often used to bring the sample to the desired form. Microwave-assisted digestion offers a less-time consuming procedure, with a lot of advantages (Zeiner et al., 2007).

Regarding the analytical methods, there are different methods that can be applied. The most used are Atomic Absorption Spectroscopy (AAS), Flame Emission Spectroscopy (FES), UV/VIS Spectroscopy, Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), X-ray Fluorescence Spectrometry (XRF). Each method has its advantages, and can be successfully applied in determining heavy metals concentrations. Because of this, the found studies used a varied methodology,even combining more technologies.

MATERIAL AND METHODS

This paper aims to review the methods applied for determination of heavy metals for some of the most used inputs in both organic and conventional agriculture: ashes, composts, fertilizers and manure. Since there are no regulations regarding both the sample preparation and heavy metal determination for this type of samples, each study uses its own version derived from standard methodology of different matrixes (soil, wood, organic matter, etc.). An overview of these methods is presented below.

Heavy metals analysis of ashes

Ash is the result of combustions, most often produced by the wood and coal fired power plants. Ash has been used in many applications as cement industry, concrete or agriculture. Still, the utilization rate of ash in agriculture is very low (Phan et al., 2018).

These combustions produce many solid wastes such as fly ash, bottom ash, boiler slag and flue gas (Prem Kishor et al., 2010). Both fly ash and bottom ash were studied as soil amendments. It has been observed an increase of mineral elements in the upper horizon of soil, both for useful elements (Mandre et al., 2006), but also for contaminants (Kishor et al., 2010, Okmanis et al., 2015).

Depending on the combustion temperature, the concentration of heavy metals in ashes may differ. In high capacity furnaces, the temperature is higher, on the one hand, which can volatilize some elements like Hg, Cd and Pb (Ibrahim et al. 2018; Pasanen et al., 2001) , but on the other, at the temperatures over 700°C begin the fusion of small particles, which forms coarse ash fraction that should not be used as soil fertilizer (Okmanis et al. 2015).

Depending on analysis method, ash samples may undergo a digestion (solubilization) procedure, to enhance the availability of mineral elements. This step is usually accomplished using aqua regia (HNO_3:HCl = 1:3, v/v) and sometimes, HF is added to improve digestions. After digestion procedure, the samples can be analyzed using ICP-MS, ICP-OES or FAAS (Flame Atomic Absorption Spectrometry) methods.

Alternatively, HDXRF (High Definition XRF) method can be used without digestion. The methods, the analyzed elements and other particularities of the methods used in recent studies for ashes samples are presented below (Table 1).

Table 1

Methods used for heavy metal analysis of ashes

Ash sample type	Method	Analyzed elements	Sample preparation/Digestion (As described in study methodology)	Source
Briquettes from paper and cardboard waste	ICP-MS	As, Cd, Hg, Pb, Mn	ISO 16968	Ibrahim et al., 2018
Wood-based ashes	FAAS (LVS ISO 11047)	Cd, Cr, Cu, Ni, Pb, Zn	N/A	Okmanis et al., 2015
Wood-burning generated ashes	ICP-OES	Cu, Ni, Zn, Pb, Mn	HF and $HClO_4$ acid digestion	Sinaj et al., 2015
Wood combustion in home fireplaces	ICP-OES	Cd, Pb, Zn, Cu, Mn, Ni, Cr	N/A	Symanowicz et al., 2018
Agricultural residues ashes	ICP-MS	Mn, Zn, Cu, Ni, Cr, As, Pb, Cd, Co, Mo	$H_2O_2/HNO_3/HF$ mixture (ISO EN 15297)	Wang et al., 2011
Bottom and fly ashes from municipal solid waste	ICP-MS	Pb, Cd, Zn, Cu, Mn	65% HNO_3, 35% HCl, 40% HF	Yu et al., 2013
Agricultural residues, forestry, and agri-food processing plants, energy crops	HDXRF	Cr, Mn, Fe, Ni, Cu, Zn, As, Pb	EN ISO 14780	Zajac et al., 2018
Forestry biomass, energy, agricultural residues	XRF	Cd, Cr, Cu, Ni, Cu, Pb, Zn, Fe	N/A	Zajac et al., 2019

Heavy metals analysis of composts

Compost is defined as an organic fertilizer obtained by decomposition of crop residues, animal manure and other organic matters found around the farm. It represents one of the main organic matter inputs in agriculture (FAO, 2010).

Using compost as soil treatment can be beneficial from several points of view: to improve physical properties (erosion resistance, water infiltration), to increase soil fertility and soil biodiversity, to fix carbon in the soil. The importance of these properties was pointed out by European Commission its Communication “Towards a Thematic Strategy for Soil Protection” (COM (2002) 179).

The most important benefit of using compost is the increase in soil organic matter (Erhart et al, 2010). The dynamics of heavy metal soil pollution is influenced by both soil properties and by the type of the compost. Thereby, a positive correlation was established between soil organic matter and total concentration of heavy metal, and also a negative correlation between soil organic matter and available heavy metals (Federal Ministry of Agriculture, Forestry, Environment and Water Management, Austria and European Communities, 2003).

Regarding environmental issues related to heavy metals in composts, only the soluble forms are relevant. European Commission emphasised the risk of analysis based only on total heavy metals. Yet, there is no commonly agreed methodology at the moment. Considering this aspect, almost all studies regarding heavy metal content of compost were focused by total amount of these contaminants. Consequently, specific methods were used for this type of determination: ICP-MS, ICP-OES, CV-AAS (Cold Vapour - AAS) (for Hg determination) or FAAS. The table below (Table 2) shows a series of studies on heavy metal determinations in compost and the used methods.

Table 2

Methods used for heavy metal analysis of composts

Sample type	Method	Analyzed elements	Sample preparation/Digestion (As described in study methodology)	Source
Mature compost from organic fraction of municipal waste	ICP-OES	Ni, Pb, Cd, Cr	Mineralization in aqua regia	Becher et al., 2018
Composted sewage sludge with the addition of straw and wood chips	FAAS	Cd, Pb, Cu, Zn, Cr, Ni, Mo, Co, Fe, Mn	Aqua regia (36% HCl and 65% HNO_3)	Bożym et al., 2015
Compost from Solid Waste Recycling and Composting Plant	ICP-MS	Cu, Ni, Zn, Pb, Zn, Cd	**Step 1**: 1:1 water and HNO_3 **Step 2**: 5 mL H_2O_2, 5 mL HCl, 5 mL water	Elmaslar-Özbaş et al., 2012
compost from sewage sludge from municipal sewage treatment plant	ICP-OES	Cu, Cr, Cd, Ni, Pb	N/A	IGNATOWICZ and BREÑKO, 2011
	CV-AAS	Hg	N/A	
Compost from organic residues	ICP-OES	Cd, Co, Cr, Cu, Ni, Pb, Zn	5 mL HCl	Kupper et al., 2014
Compost from fish waste, seaweed and pine bark, 1:1:3	ICP-OES	Pb, Cd, Cu, Ni, Cr	Digestion with HNO_3	López-Mosquera et al., 2011
Compost from fish waste 80% and pine bark 20%	FAAS	Cr, Ni, Cu, Zn, Pb, Cd	Microwave digestion with HNO_3 (MARS-5 microwave oven Operation Manual)	Radziemska et al., 2018
Compost originating from organic waste	FAAS	Zn, Pb	Microwave digestion with HNO_3	Zennaro et al., 2005

Heavy metals analysis of various fertilizers

Conventional agriculture uses large amounts of fertilizers to grow crops. Among them, a high proportion consists of synthetic fertilizers. Unfortunately, almost all of them cannot be used in organic farming (IFOAM, 2019). As an alternative for them, a series of natural minerals are used as soil amendments or fertilizers, like biochar (Glaser et al., 2015), magnesium minerals (Jasinskas et al., 2017), rock phosphate (Ditta et al., 2018), apatite minerals and others. Since the composition of these natural fertilizers consists on similar substances as mineral fertilizers, the same method for heavy metal analysis can be used. As example, rock phosphate is one of essential source for the production of chemical fertilizers and although it is a natural resource, it contains high values of heavy metals (Faridullah et al., 2017), even uranium and thorium (Azzi et al., 2017). Accordingly, it is widely known that cadmium occurs naturally in phosphate rocks and its concentration can vary widely between countries and more than that within deposits in the same country. It has been reported cadmium levels that ranges between 1 and 150 mg/kg for sedimentary deposits (Roberts, 2014).

As well as other agricultural inputs, the same methods for heavy metal determination are used, with some variations: ICP-MS, ICP-OES, XRF or FAAS. Since there are no specific method for digestion of each type of fertilizer, each study uses a different way to perform this step. Many of them apply the protocols for soils, sludge or sediment samples, as presented in the Table 3.

Table 3

Methods used for heavy metal analysis of fertilizers

Sample type	Method	Analyzed elements	Sample preparation/Digestion (As described in study methodology)	Source
Commercial phosphate fertilizers	XRF	Sb, Pd, Ag, Mo, Nb, Zr, Bi, Mn	N/A	Azzi et al., 2017
	AAS	Cd, Zn, Pb, Fe, Cu	HCl:HNO_3 = 3:1 (v/v) Microwave digestion	
Fertilizers marketed in northeastern Brazil	ICP-OES	Cd, Ni, Pb, Cr	MAPA (Brasil, 2006)	da Silva et al., 2014
		Cd, Ni, Pb, Cr	USEPA 3051A	
		Cd, Ni, Pb, Cr	USEPA 3052	
Two types of fertilizer, marine sediment	ICP-OES	Cd, Cr, Co, Cu, Pb, Mn, Ni, V, Zn	HCl + HNO_3	Brigden et al., 2002
	CVG ICP-AES	Hg, As	N/A	
Mineral fertilizers from different enterprises	ICP-OES	Cd, Pb, Ni, Cu, Cr, Zn	HNO_3 + redistilled hot water, 1:1	Gambus & Wieczorek, 2011
	AAS	Hg	N/A	
Urea, calcium superphosphate, iron sulphate, copper sulphate	AAS	Cu, Ni, Pb, Zn, Fe , Mn	HNO_3 + $HClO_4$	Gimeno-Garcia et al., 1996
	GF-AAS	Cd, Co	HNO_3 + $HClO_4$	
Phosphate ore, manufactured phosphate products, N-P-K blends, organic fertilizers, and micronutrient materials	ICP-OES	As, Pb, Cd, Co, Ni, Cr, Mo, Se	digestion with HNO_3	Kane & Hall, 2006
NPK fertilizers	FAAS	Pb, Cd, Cu, Mn	N/A	Milinović et al., 2008
Marketed fertilizers	AAS	Pb, Cd, Ni, Co, Cr	AoAc digestion	Modaihsh et al., 1999
Granules of Zn fertilizer from fertilizer companies	FAAS	Cd, Pb, Cr	N/A	Nacke et al., 2013
Commercial fertilizers	AAS	Mn, Cu, Zn, Pb, Ni, Co, Cr	HCl + HNO_3, 1:1 Microwave digestion	Ogabiela et al., 2009
P-containing fertilizers	ICP-OES	Cd, Cr, Pb	HNO_3 + HCl, 3:1 Microwave digestion	Vieira da Silva et al., 2017
	HG-AAS	As, Hg	N/A	

Heavy metals analysis of manure

Animal manure represents a natural source of nutrients needed for plant growth, especially N, K, P. They are a suitable alternative of commercial fertilizer and also can be succesfully used in organic farming (Adesoye et al., 2017).

Animal manure is used for a long time in agriculture, as his benefits improving the soil fertility and organic matter content is known. However, this actions leads in serious environmental problems (nitrate and phosphate contamination of waters) or metal contamination of soils, as manure is rich of heavy metals (Zhang et al., 2012).

For instance, when animal manure is used, Cu and Zn tend to reach excessive values in soils. Therefore, high quality manure should match quality standards established by any country (European Union, 2004).

The concentration of heavy metals in manure can vary considerably depending on multiple factors such as the age of the animal, type of ration, housing type and waste management practices.

Usually, the high concentration of metals in animal feed have often resulted in higher concentration in the manure (Bolan et al., 2004). After composting the manure, the metals seems to be in more stable forms and can consequently be considered unavailable for plant uptake. A much lower percentage of heavy metals was found in bioavailable fractions, after fermentation (Ahmed et al., 2007). Yet, a study revealed that after the anaerobic digestion of pig manure the bioavailability of Zn was increased (Fard et al. 2011).

Generally, the majority of heavy metals cations react with organic molecules to form chelates, that are not soluble, the metals being tightly bound. These metals are not available to plants, but they could be slowly released through decomposition process (Urunmatsoma et al., 2010) and finally, endanger environment. Therefore, the analysis of the total content of heavy metals is a good practice.

Regarding the methods used for total heavy metal content in manure, the reported studies revealed that the AAS method is widely used, together with ICP-OES or ICP-MS. For Hg determination, Atomic Fluorescence Spectrometry (AFS) was used, as well. Table 4 contain the methods used for heavy metal determinations in some recent studies.

Table 4

Methods used for heavy metal analysis of manure

Sample type	Method	Analyzed elements	Sample preparation/Digestion (As described in study methodology)	Source
Manure samples from domestic animals	FAAS	Mn, Cd, Zn, Pb, Ni, Cu	aqua regia HNO_3:HCl = 3:1 (v/v)	Adesoye et al., 2014
Manure samples after composting process of 0, 40,80 and 120 days	AAS	Zn, Cu, Cr, Ni , Pb, Cd	Sequential extraction procedure	Gul et al., 2015
Poultry manures, sewage sludge compost	ICP-OES	Cd, Cu	Two-step decomposition; dry ashing/ HNO_3 and HF/ aqua regia	Hanč et al., 2008
Composted cow manure and poultry litter + plant residues	AAS	Pb, Ni, Zn, Cu, Cd	N/A	Haroon et al., 2019
Five types of manures	AAS	Ni, Pb, Cd, Hg	Modified versions of sequential extraction procedure	Irshad et al., 2013
Animal manure collected from a composting facility	AAS	Cu, Zn, Mn, Fe, Cd, Pb	Determination of water-soluble heavy metals	Irshad et al., 2014
Poultry and livestock feeds and manures	ICP-AAS	Zn, Cu, Pb, Cd, Cr, Ni, Ba, Co, Mo, Mn, Sr, Ti	HNO_3 + $HClO_4$	Cang et al., 2004
	HG-AFS	As, Hg	HNO_3 + H_2SO_4 + $HClO_4$	
Animal manures collected from a pig farm	FAAS	Cu, Zn, Cd, Pb	N/A	Lupascu et al., 2009

Chicken manure	ICP-OES	Cr, Cu, Ni, Pb, Zn	HNO_3:HCl = 3:1 (v/v) Microwave digestion	Ravindran et al., 2017
Mature animal manure	FAAS	Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn	EPA-3050B	Sungur et al., 2017
Faeces, urine, and manure slurry from different livestock animals	FAAS GFAAS	Ni, Cu, Zn, Fe, Mn	HNO_3 digestion	Svane & Karring, 2019
Composted animal manure	AAS	Fe, Mn, Zn, Cu	Aqua regia digestion	Vukobratović & Vukobratović, 2017
	ICP-OES	Ni, Mo, Cr, Cd, Co, Pb	Aqua regia digestion	
Swine manure	ICP-MS	Zn, Cu, Cr, Cd, Pb, Ni, As, Se	N/A	Wang et al., 2017
Animal manure compost	ICP-MS	Zn, Cu, As, Cr, Cd, Ni, Pb, Co	HNO_3-$HClO_4$ digestion	Yang et al., 2017
	AFS	Hg	HCl-HNO_3 digestion	
	ICP-MS - HPLC	As	H_3PO_4 treatment	
Animal feeds and manures	AAS	Cu, Zn, As, Cr, Cd, Pb	HNO_3 and H_2O_2 digestion	Zhang et al., 2012
	AFS	Hg		

CONCLUSIONS

Accurate monitoring of metal concentrations in inputs used for ecological agriculture is an important action which aim is to minimize health hazards resulting from consumption of contaminated agricultural food products. Therefore, it is essential to have a general understanding of the main analytical methods which could be properly selected for input characterization.

This paper provides an overview of the most used and sensitive analytical methods used for heavy metal quantification. As agricultural inputs are of various types, from different sources and heavy metal concentration from sample lie within a large range, the selection of the most reliable and accurate method is an important step which is always connected with chemist's knowledge and skills.

Because European legislation do not impose some specific methodology for heavy metal analysis in agricultural inputs, each country uses various protocols for these determinations. Also, there are no specific range for all metal concentrations, leaving everyone to set their own limits for most of them.

The methodology for heavy metal analysis is not so varied, and two methods are most often used for these determinations: AAS and ICP (-MS or -OES), for all types of reviewed inputs. Sample preparation, on the other hand is quite different form one user to another.

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