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II) Wood pellets for home heating can be considered environmentally friendly fuels? Heavy metals determination by inductively coupled plasma-optical emission spectrometry (ICP-OES) in their ashes and the health risk assessment for the operators

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ABSTRACT

The aim of the present study was to determine the concentrations of twelve potentially hazardous elements in wood pellet ashes obtained by the combustion of 13 pellet brands for sale in Italy, the impact of adding the ashes to soils and health risk of operator due to dust exposure. Samples were analysed by Inductively Coupled Plasma Optical Emission Spectrometry. The concentrations of heavy metals in ashes from stoves ranged from 0.41 to 7.2 mg kg^{-1} for As, from 1.3 to 12 mg kg^{-1} for Sb, from 1.8 to 12 mg kg^{-1} for Zn, from 0.23 to 0.8 mg kg^{-1} for Pb, from 0.18 to 2.8 mg kg^{-1} for Ni, from 0.09 to 1.0 mg kg^{-1} for Cd, from 0.46 to 3.4 mg kg^{-1} for Cr, from 0.94 to 2.7 mg kg^{-1} for V, from 2.2 to 11 mg kg^{-1} for Cu, from 60 to 409 mg kg^{-1} for Mn, from 83 to 432 mg kg^{-1} for Fe and from 3484 to 15,484 mg kg^{-1} for Al. The total concentrations for the 12 investigated elements, expressed as the sum of the concentrations ($\sum$me), ranged from 3703 mg kg^{-1} to 15,946 mg kg^{-1} of dry weight with a mean of 8455 mg kg^{-1}. Considering all the metals, the results indicate that there are very low risks for operators regarding non-carcinogenic and carcinogenic elements contained in the wood pellet ashes produced during cleaning of pellet stoves in confined environments.

1. Introduction

At present, there is an increasing interest in the use of biomass for energy production [1], in particular, wood and/or their residues, have been always one source of biomass fuels, cheap in price and abundant in quantity. However, in stoves that use wood or wood pellet as combustible, a problem is due to the high ash and salt production. In biomass, the elements that form the ashes are present as salts that are chemically bonded to the carbon structure (inherent ash), or they can come with biomass as mineral soil particles that have been caught during growth or are swiped during harvest and transport (foreign ash) [1]. The main ash forming elements are: Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si and Cl [2].

For residential applications, about stoves and boilers, there is an increase in the use of wood pellet worldwide as fuel that is due to the fact that, in contrast to standard fossil fuels which produce greenhouse gas emissions, wood combustion is considered as sustainable CO_2 neutral energy resource. Pellets are usually made from compressed sawdust or other waste materials like, working of lumber and manufacture of wood products. Moreover, by mechanical treatment, several raw biomasses can be transformed into a pellet form with improved fuel properties [3,4]. The improved density reduces the storage space and transportation costs while the homogeneous size helps the handling and feeding issues. The aim of indoor combustion of pellet in stoves and fireplaces is to transform combustible into heat, but, unfortunately, they have a higher content of minerals, including sodium, potassium, phosphorous and chloride, and in several cases, high hazardous element content [5–7]. Also, as reported in a previous paper [8], in not optimal combustion conditions, pellets may lead to the production of hazardous organic compounds such as PAHs that are in part emitted into the atmosphere, but, considerable amounts remain in the ashes.

Several authors considered the emission from residential pellet wood combustion as a major contributor to ambient air pollution [5]. Indoor air of the environments in function wood stoves may contain health-damaging pollutants such as carbon monoxide, particulate matter, heavy metals [5] and polycyclic aromatic hydrocarbons [8,9].

The good maintenance of the stoves or fireplaces that burn pellets, requires the removal of the ashes daily, therefore we can assume that operators (generally the owners) are exposed and inevitably assume dusts and compounds released in indoor air from the ashes.

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Only few studies have been conducted on environmental risk assessment regarding the ashes produced by biomass combustion [8–10]. The biomass ashes may pose threat to the environment and humans due to the presence of hazardous substances [11].

The attention on metals, both from the analytical, environmental and toxicological viewpoint, lies with the fact that they are ubiquitous pollutants [12–15]. In the past few years, much work has been carried out to establish the concentrations and identify sources of these contaminants in common matrices and, in particular, in environmental and food ones [14].

Humans, and in particular operators, are exposed to heavy metals via many pathways because several metals are ubiquitous in the ashes of wood. The elements of the ashes can be assimilated in the human body via direct inhalation, ingestion and dermal contact absorption, and pose potentially adverse effects on the health of human beings [16]. In addition, for a sustainable use of wood pellet fuel, both domestically and on industrial scale, it is important to know that the ashes can be added to soils, replacing the extracted nutrients by plants, especially P and K and microelements [17]. An important condition for sustainable use of ashes in agriculture, however, is the evaluation of safety and possible environmental impacts. The ashes containing high concentrations of hazardous substances cannot be recycled or be used for agriculture purposes (as fertilizer and/or to neutralize soil acidification) but could be used in other fields, including, for example, as additives for the production of building materials [17].

The presence of heavy metal and their concentrations in wood pellet ashes are an issue in toxicological and environmental field because their concentrations are highly variable due to the difference in origin of raw materials, manufacturing processes, etc. Concentrations of some hazardous elements in wood ashes can be very high due to the enhanced enrichment of such elements in the combustion residue due to the high contents of organic matter in biomass.

Unfortunately, there is little information regarding the potential risk for heavy metal exposure in these access routes, and their relationship with environmental factors. Whereas said before, this study aims at determining the metal content in the ashes produced from the combustion of several types of pellets in real conditions, representative of typical domestic users and to assess health risk of exposure to metals for operators. To obtain an estimate of the health risk associated with ash manipulation in indoor environment, investigations have been performed on twelve elements (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V, Zn). In the ash samples, all the elements were quantified by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [14,18].

This is the first study reporting heavy metal concentrations of ashes of wood pellet combustion in real conditions from stoves and estimation of health risk due to exposure to heavy metals from ashes. In summary, the main objectives of the current study were a) determining heavy metal concentrations of wood pellet ashes; b) determining metal uptake rates of operators via ingestion, inhalation and dermal contact to ashes; c) estimation of health risk posed by heavy metal exposure through wood pellet ashes; and d) valuing the impact if used in agricultural field.

Table 1
List of analysed samples.

Sample	Country	Calorific kW/h	Ashes %	Moisture	Essence
1	–	5.7	<0.4	5	–
2	–	5.3	<0.7	4	Fir
3	–	5.2	<0.6	8	Fir/beech
4	Austria	4.8–5.3	<0.5	8	Fir
5	USA	4.8	<0.5	<7	Conifers
6	–	5.2	<0.5	<7	–
7	USA	>5.0	<0.5	<7	Conifers
8	Italy	<5.0	<0.7	7	Conifers
9	Italy	4.6	<0.6	<7	Conifers + deciduous
10	Italy	5.4	0.9	<10	Beech
11	Italy	>5.0	<0.5	<8	Beech
12	Canady	5.0	<0.4	<6	Fir
13	Canady	5.7	<0.4	4	Red fir

Table 2
ICP-OES operating conditions.

RF power (W)	1300
Sample uptake flow rate (mL/min)	1.5
Gas flow rates (L/min)	Auxiliary: 0.2 Nebulizer: 0.8 Argon: 15
Viewing mode	Axial

2. Materials and methods

2.1. Pellet samples

Metal analyses were performed on ash of 13 different samples of wood pellet listed in Table 1. For each pellet type, tree species, calorific value, and moisture (if known) are shown in Table 1. These specimens were purchased within a 50-mile radius of Palermo (Italy), from retail outlets including large supermarkets, shops garden articles and retailers of solid fuels. All purchased specimens had a label and none was purchased from occasional vendors. The selected wood pellet types were manufactured in different regions of the world and were representative of the various essences and between the most consumed in Italy.

2.2. Appliance, fuels and experimental procedures

Analysis was carried out on the ashes produced with a top-feed pellet stove, representative of small household heating devices. The burner is a cast iron cup with holes for the introduction of the combustion air that is produced by an electric fan. The combustion is triggered by an electrical resistance. A heat exchanger, placed along the hot flue gases conduit, transfers the heat to a secondary air flow that heats the indoor environment. During tests, the stove was operated at about 4.0 kW h^{-1} in order to imitate a more realistic utilization, since the system is usually not operating at maxim power (11 kW h^{-1}).

All the collected ash samples were stored at 4 °C. Before analysis, the samples were dried at 105 °C in a hot air oven. The colour of the analysed ashes ranged from light grey to anthracite.

2.3. Laboratory equipment and chemicals

Before use, all the vessels and flasks were cleaned by rinsing three times with HNO_3 (3%) and several times with Milli-Q water. All the analyses of metals in wood pellet ashes samples were repeated three times and the relative standard deviation results ranged from 0.2 to 7%. Every five samples, blanks were carried out and the results demonstrate that the treatment used for cleaning vessels and flasks and chemicals ($HNO_3$and Milli Q water) was suitable to obtain the quality

Table 3
Wavelengths used for elemental determinations by ICP-OES.

Element	Wavelength 1 (nm)	Wavelength 2 (nm)
Al	396.153	308.215
As	193.696	188.979
Cd	228.802	214.440
Cr	267.716	205.560
Cu	327.393	324.752
Fe	238.204	239.562
Mn	257.610	259.372
Ni	231.604	221.648
Pb	220.353	217.000
Sb	206.836	217.582
V	292.464	310.230
Zn	206.200	213.857