Int. J. Environ. Sci. Technol. (2015) 12:2263–2272
DOI 10.1007/s13762-014-0622-z

ORIGINAL PAPER

Crude oil and bioproducts of castor bean (*Ricinus communis* L.) plants established naturally on metal mine tailings

M. C. A. González-Chávez · A. Ruíz Olivares · R. Carrillo-González · E. Ríos Leal

Received: 7 December 2013 / Revised: 20 March 2014 / Accepted: 11 May 2014 / Published online: 4 June 2014

Abstract Previous research suggested that *Ricinus communis* may be used for soil remediation and oil production. However, the quality of the oil and bioproducts under polluted conditions need to be tested to be assured of their potential use in biofuel production with environmentally friendly bioproducts (cake, seed coats and biomass). Oil characteristics and metal concentrations in oil, cake (de-oiled seeds) and seed coats, as well as the shoot carbon content were analyzed. The oil contents of palmitic and oleic acids from plants growing in polluted mine tailings were comparable to those for plants grown under non-polluted conditions. Linoleic acid content was significantly higher in oil of plants from mine tailings, which enriches the fuel properties. Cadmium and lead were mainly concentrated in the seed coat, whereas copper in the cake. Castor bean oil had low concentrations of cadmium, lead, zinc, nickel, manganese and copper-free. Cake and seed coats can be useful for soil fertilization applications since the metal concentrations are below safety regulations. The biomass carbon was around 43 %, which suggests it may be used for biogas production. These properties make castor bean valuable for its oil and bioproducts even when growing at metal-polluted sites. However, agronomic optimization is needed in order to produce higher plant productivity.

Keywords Bioenergy crop · Castor bean · Energy plantations · Heavy metals · Polluted soils revalue

Introduction

Vegetable oils are the most acceptable alternative to solve the declining global supply of fossil fuels. They are considered as first generation biofuels and have been used as primary raw materials. In comparison with conventional diesel, biodiesel combustion reduces emission of greenhouse gases as follows: 100 % sulfur dioxide, 48 % carbon monoxide and 47 % particles (Caye et al. 2008). However, biofuels may face some constraints: They are required in refined forms to obtain diesel of quality, and some are also foodstuffs. Biofuels have been produced from crops such as rapeseed, soybean, sunflower, coconut and palm oil (Okullo et al. 2012). *Jatropha* and *Ricinus communis* (*R. communis*) both producing non-edible plant oil provide a better economical alternative (Deligiannis et al. 2009), and using pressing and extraction may offer vegetal oils. These can also be used as bio-oil (fuel without transesterification) which can then being completely biodegradable (Boza and Saucedo 2011). Castor bean is a naturally occurring plant, inexpensive and an environmental-friendly resource (Jumat et al. 2010).

Another limitation for biofuel production is the overall global need for suitable soils and water to increase food supplies (Benavidez and Cadena 2011). Marginal soils not suitable for food crops and use of appropriate plants

Electronic supplementary material The online version of this article (doi:10.1007/s13762-014-0622-z) contains supplementary material, which is available to authorized users.

M. C. A. González-Chávez (✉) · A. Ruíz Olivares · R. Carrillo-González
Environmental Microbiology Lab and Environmental Chemistry Lab, Programa de Edafología, Colegio de Postgraduados, Carr. Mexico-Texcoco km 36.5, Montecillo, 56230 Texcoco, Estado de Mexico, Mexico
e-mail: carmeng@colpos.mx

E. Ríos Leal
Dpto. de Biotecnología y Bioingeniería, CINVESTAV-IPN, Av. Instituto Politécnico Nacional No 2508, 07360 México, D. F., Mexico

adapted to poor edapho-climatic conditions give opportunities for biofuel. Castor bean is able to grow under very harsh soil and environmental conditions such as those in metal-polluted sites (Rajkumar and Freitas 2008; Prasad and Freitas 2003). Further, it is one of the plants with the highest oil yield potential (Kitani 1999). Oil content in commercial *Ricinus* plants is around 46 % or wild *Ricinus* plants growing in semiarid areas (in the range of 10–65 %), both in non-metal-polluted conditions (Martínez Pérez et al. 2009; Goytia-Jiménez et al. 2011). The content of oil in seeds from other plants, belonging to the same *Ricinus* family Euphorphiaceae, such as *Jatropha curcas* L (JC) or *J. gossypiifolia* (JC), has been calculated between 24 and 32 % (DeOliveira et al. 2009). Oil content in other oleaginous plants such as soya, cotton or sunflower may be 18, 15 and 44 %, respectively (de Parente 2003).

The high content of ricinoleic acid (12-hydroxy-cis octadec-9-enoic acid) is the reason for the versatile value of castor oil in industry and technology, including the production of coatings, plastics and cosmetics (Suarez et al. 2007). The variety of uses of the oil makes castor bean a strong candidate plant for increased production to provide as a vital raw material for the chemical industries (Ogunniyi 2006).

In Brazil and India, castor bean seed oil has been suggested as a good biofuel alternative, because this plant is able to grow in arid and semiarid areas and appears to be well adapted to the poorest environmental conditions and is thus suitable to promote a sustainable agriculture. In Brazil, 100 % of the reduction on the federal taxes is given to families who produce castor seeds in the semiarid northeast area. Castor bean is a suitable crop for small-scale farming and can help to improve the living conditions of village farmers as well as supply environmentally friendly energy for multiple purposes (Scholz and Nogueira da Silva 2008).

Previous results of Ruiz-Olivares et al. (2013) showed that the natural establishment of castor bean plants in heavily metal-polluted mine tailings produces high oil yields (between 40 and 64 %). Their results consistently showed that *R. communis* had low metal shoot concentrations, high root metal concentrations, low metal translocation factors. However, these authors did not show the quality of the crude oil and bioproducts obtained under these conditions, which is necessary for their safe use. It is expected that chemical or physical oil *Ricinus* characteristics do not change when produced under polluted conditions and therefore use it with biotechnological advantage of both remediation and production of a bioenergy raw material.

Field castor bean establishment, such as this observed at Zimapan, Hidalgo State gives the opportunity to study and obtain relevant information related to natural metal attenuation and metal partitioning in bioproducts grown in a multipolluted mine tailing (zinc = Zn, cadmium = Cd, lead = Pb, nickel = Ni, copper = Cu and manganese = Mn). This information cannot be gained through greenhouse experiments using hydroponics or spiked soils which in general are exploring only one metal as contaminant. Pot experiments are also limiting for plant development.

The aims of this research were as follows: (1) to determine accumulation and translocation of heavy metals to oil, cake (de-oiled seeds) and seed coats of castor bean; (2) to compare seed and oil characteristics produced by *R. communis* shrubs naturally growing on metalliferous tailings heaps with these from plants grown in non-polluted sites; and (3) to analyze the carbon content in shoots of castor beans under metal-polluted conditions tested. This was followed in order to guarantee crude oil quality and environmentally friendly bioproducts of *Ricinus* plants obtained from heavily metal-polluted sites. The three main hypotheses were as follows: (1) Metals are not highly translocated to the oil of seeds of castor bean plants grown in metal-polluted mine tailings, (2) fatty acids content is similar in oil of seeds produced in metal-polluted mine tailings than those from non-metal-polluted soil, (3) Besides oil, some other castor bean bioproducts may be obtained under metal-polluted mine tailings without risk of metal transfer.

The sampling of plants and seeds of *R. communis* growing from the natural field study was performed in September 2011 at Zimapan, Hidalgo State, Mexico.

Materials and methods

Study area

The study was undertaken in the arid region of Zimapan, Hidalgo state, Mexico. From 18 castor bean shrubs naturally established in four metal mine tailings heaps, only five shrubs were fruiting on two metal mine tailings heaps San Francisco (SF) and Santa Maria (SM). From these fructifying shrubs, aerial biomass and seeds were collected. The seed collection was made in September 2011. Plants from SM sites had 9,558 and 6,720 seeds, while from SF had between 6,458 and 16,506 seeds, where plant from SF10 had the lowest and SF9 the highest number of seeds per plant. Aerial biomass, seed coats and cake of these plants were dried; ground and three replicates of each one were used for analysis. It means that 18 total samples of each one of these plant bioproducts and oil were used for each variable analyzed. The five plants from San Francisco Mine, the two from Santa Maria and one from Montecillo were analyzed separately because their rhizospheres in relation to physical and chemical characteristics are different. They were tested as single individuals. More detailed sites description and physicochemical mine tailings characteristics can be found in Ruiz-Olivares et al. (2013).

Seeds and oil general characteristics

Castor bean seeds were shelled and the coats weighed, then percentage of shell relative to endosperm was calculated. Moisture content was determined in complete seeds and endosperm from initial and final weights after oven-drying for 12 h at 60 °C. For oil extraction, seeds were manually shelled, crushed in a porcelain mortar and dried for 12 h at 60 °C. Oil was then extracted using a Lab Conco Soxhlet System extraction unit and reagent grade hexane. The samples (three replicates/plant) were extracted for 12 h at 70 °C. A rotatory evaporator Buchi R-114 at 40 °C was used to separate the hexane from the oil. The oil content was expressed on a dry weight basis. Oil density was determined by obtaining the weight of 1 mL on an analytical balance.

Oil fatty acids analysis

The oil seeds were saponified, hydrolyzed and methylated. Sigma fatty acid (FA) standards (stearic, palmitic, oleic, linoleic and ricinoleic acids), Merck analytical grade reagents (ethylic ether and KOH) and analytical grade HPLC solvents (methanol, hexane and ethanol) were used. The resultant methyl esters were analyzed by gas–liquid chromatography, CG-FID (Perkin Elmer Auto System). A HP-INNOWAX 30 m $\times$ 0.32 mm DI, 0.50 μm column was used with a temperature detector at 300 °C, injection temperature of 260 °C and column temperature of 150 °C for 4 min, increasing 5 °C/min until 250 °C for 12 min. The injection volume was 2 μL using nitrogen as the mobile phase (1 mL/min).

Total carbon content in shoots of *R. communis*

Plant shoots were sequentially washed with tap water, 0.01 % EDTA, distilled water and finally with deionized water. They were dried at 65 $\pm$ 2 °C for 48 h and ground in a stainless steel mill. The analysis of total C content was carried out in an automatic analyzer (Shimadzu, TOC-5050).

Metal concentrations in *Ricinus* bioproducts (seed coats, cake and oil)

Concentration of metals was determined in seed coats, cake and oil produced by seeds of *Ricinus* plants naturally established under the two mine tailings (SF and SM). In order to compare these bioproducts obtained under polluted conditions versus those from non-polluted conditions, a control plant from a non-mining site (Montecillo, M, Mexico State) was also included in the study. Seed coats were ground in a stainless steel mill and oven-dried at 65 °C for 48 h. Oil was obtained from seeds extracted with hexane at 70 °C for 12 h. The resultant product from the de-oiled seeds is named cake. Oil and cake were also oven-dried under the same conditions. Representative 0.5 g samples of seed coat or cake, and 0. 5 mL of oil were used for metal analysis. Metal concentrations were analyzed in digested samples with an HNO_3–$HClO_4$$^{-}$$H_2O_2$ (3:1:1) mixture by flame atomic absorption spectrometry (FAAS-Perkin Elmer 3100). All metals were determined in triplicate in seed coats, cakes and oil produced by castor bean plants. For control of the digestion procedure, blanks for digestion and analysis were done in triplicate in each set of samples. Certified standard stock solutions (1,000 mg/L) were used for calibrating the instrument used for sample analyses. The quality of the analytical methods was controlled considering the sensitivity parameters (detection limit) and precision (variation coefficient). The detection limit was calculated using standard deviation (3σ) of the reading of the concentration of the blank (10 analyses) (Wels and Sperling 2007).

Metal bioaccumulation and translocation factors

Bioaccumulation factor (BAF) is an index of metal accumulation by plants. In general, two types of BAF are calculated: one regarding metal concentration in roots and another considering its concentration in the aerial parts, both of them in relation to soil metal concentration (Mattina et al. 2003). In this research, in order to know the distribution of metals in the bioproducts obtained from the castor bean plants grown in the mine tailings, BAFs were calculated regarding seed coat, cake and oil. Therefore, three BAFs were calculated as quotients between: (a) concentration of metals in seed coat/extractable soil metal concentrations; (b) cake metal concentrations/extractable soil metal concentrations; and (c) oil metal concentrations/extractable soil metal concentrations.

Because total metal concentration is a poor indicator of metal soil risk (mobility and toxicity) and plant metal accumulation has a stronger relationship with metal soil bioavailability than with total soil metal concentration (Nolan et al. 2003; Allen 2001; Temminghoff et al. 1998), in this research we used soil metal concentrations extracted by DTPA to obtain this ratio in accordance to some authors (González and González-Chávez 2006; Cortés-Jiménez et al. 2013). The total and DTPA-$CaCl_2$-TEA-extractable metal concentrations in the castor bean rhizosphere of mine tailings were determined (EPA 1992; Lindsay and Norvell

1978). An estimation of plant availability (PA) was calculated according to the so-called bioavailability index (BI) (Chen et al. 1996) based on the ratio of DTPA-extractable and total metal concentrations in the rhizospheric substrate. The quotients were multiplied by 100 to express the BI in percentage.

Translocation factor (TF) is a quotient used to quantify the metal concentration in shoot tissues in relation to metal concentration in root tissues (Stoltz and Greger 2002). However, in order to similarly quantify TFs in other plant organs such as seed coat, cake and oil, the respective TFs were calculated in these plant tissues using the following quotients: (a) metal concentration in seed coat/metal concentration in root tissue; (b) metal concentration in cake/metal concentration in root tissue; and (c) metal concentration in oil/metal concentration in root tissues. TFs < 0.99 indicate that a metal is accumulated in roots, whereas TFs > 0.99 indicate that a metal is accumulated in seed coats, cake or oil. These TFs were only calculated in plant organs from SF7, SM1 and SM2 castor bean plants as root samples from other plants were impossible to be taken off the mine tailings because of the extremely rocky ground conditions and depth of root development. Similarly, a BAF was not calculated for SF6, as it was not possible to obtain root zone soil due to the rocky ground conditions.

Statistical analysis

Analysis of variance (ANOVA) and Tukey's multiple comparison tests were used to determine significant differences among sample means from different sites ($\alpha = 0.05$). Linear regression ($r \geq 0.85$; $p < 0.01$) was used to examine relationships between metal concentrations in oil, seed coat and cake variables with values from Ruiz-Olivares et al. 2013. These data regarded soil properties (pH, carbonates, available P), metal concentrations in soil (total = T, extractable-DTPA = DTPA-, and water soluble = WS) and metal concentration in castor bean plants (roots and shoots). Principal components analysis (PCA) was conducted by PC-ORD 5 and plotted by Sigma Plot 12 in order to explore the relationships between the variables analyzed.

Results and discussion

Seed and oil general characteristics

There is very scarce information about seeds and oil characterization from *Ricinus* plants commercially produced and much less of plants from metal-polluted soils. Therefore, the basic general seed and oil characteristics in the fructifying *Ricinus* plants from the two metal mine tailings were analyzed. It was observed that the proportion of seed coat varied between the seven different castor bean shrubs; even for individual plants from the same mine tailings site (Table 1). Seeds from SF9 had the highest percent of seed coat and SF7 the lowest. The moisture content of seeds and endosperm was significantly influenced by the sites where plants were grown. Seeds from SF7 had the highest seed moisture content, whereas seeds from site SF9 had the lowest. Seeds from SF8 and SM2 had the greatest and the lowest endosperm moisture contents, respectively. The control seeds from non-metal-polluted site had a lower percent of seed coat content and higher seed and endosperm moisture contents than most of the seeds from plants growing in the metal-polluted sites (Table 1).

Oil fatty acids (FAs)

The FAs composition of oil extracted from *Ricinus* seeds growing on two metal mine tailings was similar to the oil composition of this species reported by several authors for non-polluted sites (Okullo et al. 2012; Jumat et al. 2010; Scholz and Nogueira da Silva 2008; Conceicao et al. 2007). In general, oil from castor bean seeds from non-metal-polluted sites has approximately 80–90 % ricinoleic acid, 3–7.3 % linoleic acid, 2–4 % oleic acid 0.9–5.5 %, palmitic acid 0.7–1.3 % and stearic acid 0.9–1.2 %.

There were statistical differences ($p < 0.05$) in the contents of stearic acids of seeds of *Ricinus* from plants growing in the two mine tailings (Fig. 1). The range for stearic acid in seeds from plants grown in the polluted mine tailings was 0.95–1.43 %; seeds from SF9 and SF6 sites had the highest and the lowest amount of this FA, respectively; while M had 1.76 %. The range for oleic acid was 2.9–3.7 %, and seeds from the SM1 shrub had the highest amount of oil and those from SF6 the lowest. Palmitic acid content ranged from 0.47 to 0.91 %; there were no differences in content between the several plants growing at the tailing contaminated sites neither from this at M site. Linoleic content in seed from tailing sites was between 3.6 and 4.6 %, but in seeds from the control site was 1.7 %. The most abundant acid was ricinoleic acid with 85–90.5 %, but no differences were observed between the plants grown at our sites.

The composition of FAs influences the quality of the plant biofuel. The presence of low levels of saturated and polyunsaturated FAs and the occurrence of high levels of monounsaturated FAs in a biodiesel sample are properties of high-quality biodiesel. Oil from seeds of the control plant (M) had a slightly greater content of stearic acid (1.76 %) than the range reported for castor bean oil, and almost half of the linoleic acid than oil of plants from metal mine tailings (Fig. 1). Oleic and linoleic, among the other

Table 1 Characteristics of seeds and oil of *R. communis* growing on mine tailings of Zimapan, state of Hidalgo

IC[a]	Seed coat[b] (%)	Moisture (%)		Oil content in endosperm (%)	Oil density (g/mL)
		Seeds	Endosperm		
SF6	24.0 ± 0.1 e	6.23 ± 0.20 ab	8.20 ± 0.28 b	64.5 ± 7.0 a	0.75 ± 0.07 b
SF7	17.7 ± 0.4 f	6.89 ± 0.02 a	8.37 ± 0.06 ab	40.6 ± 0.4 bc	0.94 ± 0.03 a
SF8	24.9 ± 0.2 e	5.54 ± 0.14 bc	7.38 ± 0.20 b	59.9 ± 4.1 a	0.67 ± 0.01 b
SF9	44.8 ± 0.4 a	4.20 ± 0.28 d	7.60 ± 0.57 b	52.7 ± 3.6 ab	0.94 ± 0.00 a
SF10	37.7 ± 0.1 c	5.16 ± 0.13 c	8.28 ± 0.21 b	56.3 ± 1.5 ab	0.50 ± 0.07 c
SM1	24.6 ± 0.9 e	5.66 ± 0.23 bc	7.50 ± 0.39 b	55.7 ± 10.2 a	0.81 ± 0.01 ab
SM2	41.2 ± 1.0 b	4.99 ± 0.35 cd	8.49 ± 0.75 ab	59.9 ± 1.5 a	0.76 ± 0.03 b
M	29.8 ± 0.8 d	7.13 ± 0.12 a	10.2 ± 0.00 a	37.4 ± 0.0 c	0.42 ± 0.02 c
LSD	2.37	0.9563	1.8017	–	0.1441

Different letters indicate difference between mine tailings within each variable ($\alpha = 0.05$)

[a]Identification code (IC), SF = San Francisco, SM = Santa Maria; both from metal-polluted mine tailings, M = Montecillo from non-polluted site

[b] Means and standard deviations are presented, $n = 3$

LSD least significant difference, $p = <0.05$

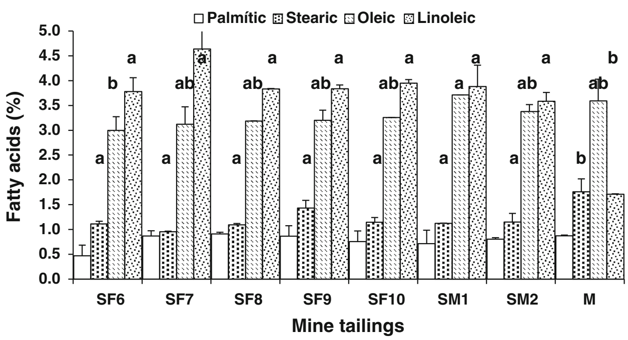

Fig. 1 FA contents in crude oil castor bean from plants naturally growing in metal mine tailings at Zimapan, Hgo., Mexico. SF6–SF10 plants located at San Francisco mine, SM1–2 at Santa Maria mine and M at Montecillo from a non-polluted soil. Values are means with standard deviations, $n = 3$. *Different letters* indicate difference in FA contents ($\alpha = 0.05$). Where no letters are indicated, no significant differences were observed

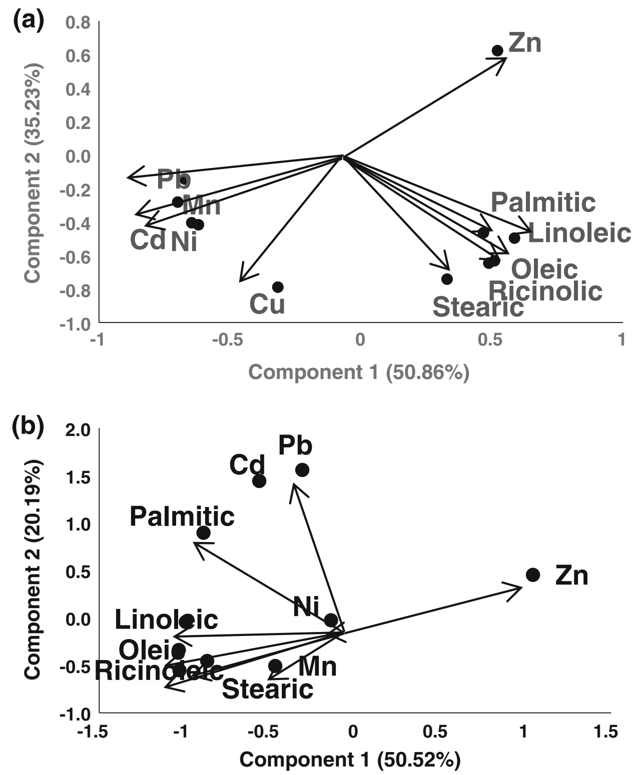

Fig. 2 PCA for fatty acids (*FAs*) content in oil of castor bean trees in metal mine tailings at Zimapan, Hgo. **a** Relationship of shoot metal concentrations and FAs, and **b** relationship of oil metal concentrations and FAs

common FAs, are the most abundant and very desirable FAs, respectively. These two FAs enrich the fuel properties (ignition quality, cloudy point and calorific value) of the biodiesel produced (Knothe 2008; Koria and Nithya 2012). Maintenance of oleic acid content in castor bean is an important fact to make viable its cultivation when growing in marginal soils (Boza and Saucedo 2011).

The principal component analysis representing shoot metal concentration and FAs content (FAs) explained the highest percentage of variance (Fig. 2). This analysis indicated that shoot metal concentrations and FAs content in oil are related (Table S1). Component 1 had a negative relationship with Mn, Ni, Pb and Cu in shoots, but positive relationship with Zn, linoleic, ricinoleic, oleic, palmitic and stearic acids. FAs have similar the large possible variance affected by Zn concentration (a essential nutrient) in shoot. It is likely that increasing Cu, Ni, Cd, Mn and Pb in shoots of castor bean the quality of oil production would be affected. Zinc is the highest concentrated element in these tailing, apparently rules the response of FAs in the oil of castor bean. Component 2 showed a strong and negative relationship with stearic, oleic and ricinoleic acids, and a positive relationship with Zn concentration in oil. In the loading plot (Fig. 2a), it can be clearly noted that FAs form a well-defined distanced cluster from the group of concentrations of metals in shoots. Only oil Zn concentration was isolated from the groups; this variable explains oil variability. The loading plot shows a negative influence of metals in oil in relation to FAs content; but Cu have the strongest negative effect of oil contents.

For metal accumulated in oil and FAs (Table S1), component 1 had negative relationship with FAs and Cd, and a positive one with Zn. Other metals do not show any significant relationship with component 1. Component 2 indicates a negative relationship with ricinoleic acid and positive with palmitic acid, Cd and Pb. The loading plot (Fig. 2b) illustrates that FAs form a defined cluster. Only palmitic acid was distanced from this group and was close to Cd and Pb. Zn in oil was negatively related to FAs; on the contrary, Mn was positively related with these acids. Ni in oil had no detectable relationship with the other metals or FAs.

Apparently, no research has been published before regarding content of FAs in oil influenced by metals from neither mine tailings nor other contamination source. Similarly, there is not available information for this or other plants, but single relationship between some metals and FAs in leaves of two plants has been investigated by some authors. Chromium and Ni accumulated in leaves of *Lactuca serriola* negatively affected FAs content in leaves (Le Guédard et al. 2012). A negative influence of Cu and Cd in membrane lipids of tomato (*Lycopersicum esculentum*) was observed (Ouariti et al. 1997).

It is important to clarify that PCA is only an exploratory procedure useful for data analysis and suggests possible relationship. To determine with high confidence, the effect of plant metal concentrations on FAs content in oil of *R. communis* seeds, it will be necessary to probe this effect experimentally using a range of metal concentrations and different metals with especial emphasis Zn and Cu.

Total carbon content in shoots of *R. communis*

Soil carbon sequestration by terrestrial vegetation is one main approach for greenhouse gas mitigation (Watson et al. 2000). Some authors have found a linear relationship between the amount of carbon sequestered in the soil and carbon input as biomass or residues of different plants (Rasmussen and Parton 1994; Sainju et al. 2007). Apparently, there is not information about the carbon input as biomass in metal-polluted sites, hence total carbon content in shoots of castor bean plants was quantified. Shoot carbon content varied little between the castor bean plants from different sites and was between 40.3 and 43.3 %. No significant difference was observed between castor bean plants from polluted mine tailings and those from the non-polluted soil (M). Lal (1999) mentioned the high potential of carbon sequestration through plants grown in degraded soils may be 0.3–0.8 Pg C/year, which can be similar for biofuel production on severely degraded soils of 0.3–0.7 Pg C/year. Therefore, studies should be followed in order to know the probable use of *Ricinus* biomass as energy source and quantify carbon sequestration under metal-polluted conditions. The resultant information can be used for carbon crediting and may give more attributes to this plant related with ecosystem services and multipurpose phytoremediation.

Metal concentrations in seed coats, cake and oil

Concentrations of metals in oil, seed coats and cake were different between the castor bean seeds from the plants grown at the metal-polluted sites (Fig. 3). Oil contained the lowest concentrations of metals than seed coats and cake in all castor bean shrubs. None of the oil samples had detectable amounts of Cu, which shows that there is no translocation of Cu at all.

Although high total, DTPA-extractable metal concentrations and very high BI in SF9 and SF10 were observed in the rhizosphere of castor bean plants grown in metal mine tailings (Fig. S1), remarkably their oil had low metal concentrations (Fig. 3). The range of metal concentrations for oil from plants collected from mine tailings was Cd: 0–1.26 mg/L, Pb: 0–2.2 mg/L, Zn: 13.7–87.7 mg/L, Ni: 0.87–5.1 mg/L. Oil metal concentrations were similar between plants from metal-polluted sites and this from the non-polluted site (M). Among the factors influencing the oxidation process of biodiesel, besides light intensity and elevated temperature, high metal concentrations in oil may be a restrictive property for its use as biofuel (Knothe 2008). Therefore, the oil produced by these *Ricinus* shrubs growing in these metal-polluted sites does not have this restriction and may be used as raw material.

The range of concentrations of metals in the seeds coats was as follows: Cd: 2.5–3.8 mg/kg, Pb: 3.1–27.4 mg/kg, Zn: 13.8–156.3 mg/kg, Ni: 1.3–6.6 mg/kg and Cu: 6.2–19 mg/kg. While in cake, it was similar for Cd: 0.7–2.7 mg/kg and Ni: 1.3–17.9 mg/kg, lower for Pb: 2.6–8.8 mg/kg and higher for Zn: 167.9–397 mg/kg and Cu: 23.7–103.8 mg/kg. Comparable metal concentrations in seed coats between plants from polluted sites and this from M site were observable; however, the last one had the highest Ni concentration and the lowest Zn and Cu concentrations in cake. Due to this research appears to be the first one presenting metal concentrations in different bioproducts of *Ricinus* plants growing in metal-polluted sites, it is not possible to make suitable comparisons of any other

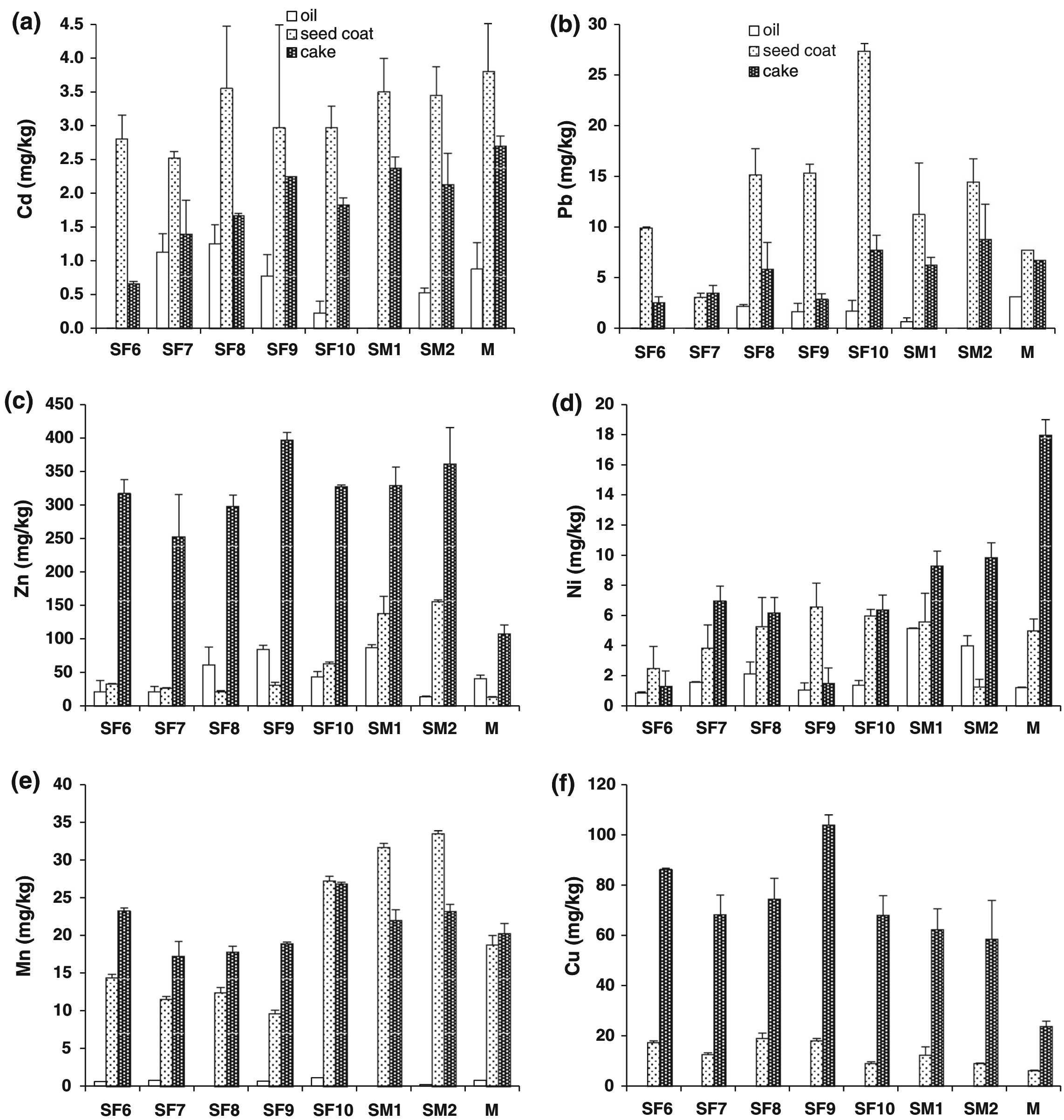

Fig. 3 Concentrations of metals in crude oil, cake (de-oiled seeds) and seed coats from castor bean plants in metal mine tailings at Zimapan, Hgo., Mexico. **a** Cd, **b** Pb, **c** Zn, **d** Ni, **e** Mn and **f** Cu. Values are means with standard deviations, $n = 3$. SF6–SF10 plants located at San Francisco mine, SM1–2 at Santa Maria mine and M at Montecillo from a non-polluted soil

works in relation to metal concentrations in oil, cake or seed coats. However, in order to have a general idea about metal concentrations, a comparison with the maximum normal concentrations of metals in plants given in Alloway (1995) is useful: 2.1 mg/kg Cd, 20 mg/kg Pb, 400 mg/kg Zn, 5 mg/kg Ni and 20 mg/kg Cu. Similarly, according to concentrations of metals in organic fertilizers for cakes (EPA 1999), the maximum allowed concentrations are as follows: Cd (6 mg/kg), Pb (77 mg/kg), Ni (32 mg/kg), Mn (no reported), Cu (508 mg/kg) and Zn (697 mg/kg). In general, metal concentrations in oil, seed coats and cake were not in excess of these values, which suggest their use as safe bioproducts. These may be used as metal adsorbent too and considered new green materials (Zamani et al. 2013; Dubey and Shiwani 2012). Research is followed in our laboratory regarding the use different *Ricinus* plant parts to adsorb metals from polluted waters.

Bioaccumulation and translocation factors

Bioaccumulation factors and TFs for the different metals are presented in Figs. S2 and S3. In general, BAFs in oil are <0.99 for Zn, Mn or Pb suggesting that these metals were not accumulated in oil. In the case of Cd, BAFs are unity and hence no concentration of this metal is occurring (Fig. S2). BAFs > 0.99 show that Pb was mainly accumulated in seed coats of plants growing in SF9 and SF10 sites, and Cd in plants from SF7 and SF8 sites. BAFs > 1 in cake indicate that endosperm of plants established in SF7 site accumulated the highest concentrations of Ni, Zn and Cu. From the BAFs, Ni was partitioned in the rank order: cake > seed coat > oil, but overall concentrations are quite low to be considered toxic. Cu was distributed as follows: cake > seed coat, but again concentrations cannot be classified as toxic or high. Cu was not detected in oil. Zn was mainly accumulated in cake > seed coat = oil. Mn was similarly accumulated in cake and seed coat but not in oil. A BAF for Pb > 1 was only observed for the seed coat from the SF10 plant. Cake had high concentrations, but no toxic of Cu; hence it can be useful as a soil amendment to improve soil fertility for soils deficient in this micronutrient. Castor bean cake, also named castor oil pomace, can be useful as a high-nitrogen fertilizer (Saribiyik et al. 2010). Future research should quantify essential elements in order to find more uses for this castor bean bioproduct when obtained from metal-polluted sites. Toxicity of the ricinoleic acid may limit the use of this cake for animal food. In Mexico, there are presently three large national projects underway researching the management of cake toxicity in order to use it as innocuous bioproduct. Moreover, some alternatives to ameliorate ricinoleic acid toxicity are available (Friedman and Rasooly 2013).

All the TFs are <1 (Fig. S3) indicating that poor metal translocation occurs from the root to different organs of castor bean plants. In the case of the more toxic metals (Pb and Cd), there is a clear trend of decreasing TFs from seed coat to cake and to oil. Low concentrations of metals in the different bioproducts analyzed, and low BAF and TFs are according with previous report taking in account concentration of metals in shoots; castor bean is not a metal accumulator plant. Moreover, this plant behaves as metal stabilizer; this is useful for phytostabilization, immobilization in plant roots (Mani and Kumar 2013).

Final comments

To the knowledge of the authors, this is the first study of oil and bioproducts produced by plants grown in metal-polluted mine tailings. The results presented here show that oil production from castor bean plants grown in metal-polluted mine tailings is feasible and offers environmental-friendly crude oil and bioproducts with similar characteristics to those from plants grown in non-metal-polluted sites and without risk to introduce metals to the trophic chain. Castor bean is a plant naturally and widely adapted to very harsh environmental conditions but it requires domestication. Optimization of plant growth under these marginal soil conditions in these metal-polluted sites does need to be improved through agronomical management in order to obtain sustainable crop productivity in the long term. Phytomanagement of metal-polluted areas such employing natural vegetation is a good option to improve the ecological indicators and avoid transport of metals to nearby areas as pointed by Conesa et al. (2013).

Biofuels do have strong production constrains; they should not be produced in fertile soils to neither compete with food production nor destroy natural ecosystems. Although a phytoremediation approach is not the best option to produce raw materials for biofuels, it represents a good option in combination with biofuel production, because it has strong impact on soil sustainability, may offer economical regional opportunities with work generation, biofuel production for local consumption, plant carbon sequestration and environmental services are feasible (Wiebe 2008).

Conclusion

We have previously evaluated plant metal uptake and oil content in seeds from *R. communis* growing naturally in tailings heaps containing high concentrations of heavy metals. Castor bean behaved as a Ni-, Zn- and Cd-stabilizer plant and produced high quantities of oil (41–64 %). However, the crude oil was not evaluated. In the present research, we analyzed some oil characteristics, FAs content and the metal concentrations in oil, de-oiled seeds (cake) and seed coats. The results showed that oil from the metal-polluted mine tailings had similar properties (palmitic and oleic FAs content) to that from plants grown under non-metal-polluted conditions, but has higher content of linoleic acid, which is a very desirable FA in biofuels. Castor bean oil had low concentrations of Cd, Pb, Zn, Ni, Mn and was free of Cu. Results also demonstrated that seed coats concentrated Cd and Pb, while cake does accumulate some Zn and Cu. However, these concentrations cannot be considered toxic.

Cake and seed coats as castor bean bioproduct may be useful to improve soil quality through fertilizer application and this should be tested in future field research. In addition, the high carbon content in the biomass of castor bean can be also of interest for biogas production. This is the first research reporting production and characterization of oil from castor bean shrubs established naturally on metal-polluted mine tailings and suggesting the use of their plant bioproducts. These several properties make castor bean potentially a valuable resource when growing at metal-polluted sites. However, agricultural management practices are highly recommended in order to optimize these yields.

Acknowledgments This research form part of FORDECYT 191357 Project. ARO carried out this work at Colegio de Postgraduados. We sincerely thank Prof. AJM Baker (Universities of Melbourne and Queensland, Australia and University of Sheffield, UK) for improving this manuscript. We acknowledge the help from Dr. Irma Díaz Aguilar to follow PCA analysis.

References

Allen HE (2001) Terrestrial ecosystem: an overview. In: Allen HE (ed) Bioavailability of metals in terrestrial ecosystems: importance of partitioning for availability to invertebrates, microbes and plants. SETAC Press, Pensacola, pp 1–6

Alloway BJ (1995) Heavy metals in soils. Springer, Glasgow

Benavidez J, Cadena A (2011) Políticas y capacidades de investigación y desarrollo e innovación (I&D + I) para el desarrollo de biocombustibles en América Latina y el Caribe. In: Rodríguez A (ed) Investigación y desarrollo e innovación para el desarrollo de los biocombustibles en América Latina y el Caribe, Serie Seminarios y Conferencias No. 68. Naciones Unidas CEPAL, Santiago de Chile, pp 11–48

Boza S, Saucedo A (2011) Análisis comparativo de patentes en la cadena de producción de biocombustibles entre América Latina y el resto del mundo. In: Rodríguez A (ed) Investigación y desarrollo e innovación para el desarrollo de los biocombustibles en América Latina y el Caribe, Serie Seminarios y Conferencias No. 68. Naciones Unidas CEPAL, Santiago de Chile, pp 49–79

Caye MD, Nhuan P, Terry HW (2008) Biofuels engineering process technology. McGraw-Hill, USA

Chen B, Shan XQ, Qian J (1996) Bioavailability index for quantitative evaluation of plant availability of extractable soil trace elements. Plant Soil 186:275–283

Conceicao MM, Candeia RA, Silva FC, Bezerra AF, Fernandes VJ Jr, Souza AG (2007) Thermoanalytical characterization of castor oil biodiesel. Renew Sustain Energy Rev 11:964–975

Conesa HM, María-Cervantes A, Álvarez-Rogel J, González-Alcaraz MN (2013) Role of rhizosphere and soil properties for the phytomanagement of a salt marsh polluted by mining wastes. Int J Environ Sci Technol. doi:10.1007/s13762-013-0323-z

Cortés-Jiménez EV, Mugica-Álvarez V, González-Chávez MC, Carrillo-González R, Martínez Gordillo M, Mier MV (2013) Natural revegetation of alkaline tailing heaps at Taxco, Guerrero, Mexico. Int J Phytoremediation 15:127–141

de Parente EJS (2003) Biodiesel: UMA aventura tecnológica num país engraçado. Tecbio, Fortaleza, p 68

Deligiannis A, Anastopoulos G, Karavalakis G, Mattheou L, Karonis D, Zannikos F, StournasS, Lois E (2009) Castor (*Ricinus communis* L.) seed oil as an alternative feedstock for the production of biodiesel. Proceeding of the 11th international conference on environmental science and technology, Chania, Crete, Greece

DeOliveira JS, Leite PM, de Souza LB, Mello VM, Silva EC, Rubim JC, Meneghetti SMP, Suarez PAZ (2009) Characteristics and composition of *Jatropha gossypiifolia* and *Jatropha curcas* L. oils and application for biodiesel production. Biomass Bioenergy 33:449–453

Dubey A, Shiwani S (2012) Adsorption of lead using a new green material obtained from *Portulaca* plant. Int J Environ Sci Technol 9:15–20

EPA (Environmental Protection Agency) (1992) Acid digestion of sediments, sludge, and soils. Method 3050, Washington, USA

EPA (Environmental Protection Agency) (1999) Background report on fertilizer use, contaminants and regulations. EPA-747-R-98-003. Washington, USA

Friedman M, Rasooly R (2013) Review of the inhibition of biological activities of food-related selected toxins by natural compounds. Toxins 5:743–775

González CR, González-Chávez MC (2006) Metal accumulation in wild plants surrounding mining wastes. Environ Pollut 144:84–92

Goytia-Jiménez MA, Gallegos-Goytia CH, Núñez-Colín CA (2011) Relationship among climatic variables with the morphology and oil content of castor oil plant (*Ricinus communis* L.) seeds from Chiapas. Rev Chapingo serie Ciencias Forestales Amb 17:41–48

Jumat S, Dina AMN, Nazrizawat AT, Mohd Firdaus MY, Noraishah A (2010) Fatty acid composition and physicochemical properties of Malaysian castor bean *Ricinus communis* L. seed oil. Sains Malays 39:761–764

Kitani O (1999) CIGR Handbook of Agricultural Engineering. American Society of Agricultural Engineers, St. Joseph

Knothe G (2008) Designer biodiesel: optimizing fatty ester composition to improve fuel properties. Energy Fuel 22:358–1364

Koria L, Nithya G (2012) Analysis of *Datura stramonium* Linn. biodiesel by gas chromatography-mass spectrometry (GC-MS) and influence of tarry acid composition on the fuel related characteristics. J Phytol 4:6–9

Lal R (1999) Soil management and restoration for C sequestration to mitigate the accelerated greenhouse effect. Prog Environ Sci 1:307–326

Le Guédard M, Faure O, Bessoule JJ (2012) Soundness of in situ lipid biomarker analysis: early effect of heavy metals on leaf fatty acid composition of *Lactuca serriola*. Environ Exp Bot 76:54–59

Lindsay WL, Norvell WA (1978) Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci Soc Am J 42:421–428

Mani D, Kumar C (2013) Biotechnological advances in bioremediation of heavy metals contaminated ecosystems: an overview with special reference to phytoremediation. Int J Environ Sci Tech. doi:10.1007/s13762-013-0299-8

Martínez Pérez D, Partida Sedas JG, Pérez Portilla E (2009) Especies vegetales para biocombustibles en sistemas agrícolas diversificados en Veracruz, México. Rev Bras Agroecol 4:4338–4342

Mattina MJI, Lannucci-Berger W, Musante C, White JC (2003) Concurrent plant uptake of heavy metals and persistent organic pollutants from soil. Environ Pollut 124:375–378

Nolan AL, Mclaughlin MJ, Mason SD (2003) Chemical speciation of Zn, Cd, Cu, and Pb in pore waters of agricultural and contaminated soils using Donnan dialysis. Environ Sci Technol 37:90–98

Ogunniyi DS (2006) Castor oil: a vital industrial raw material. Bioresour Technol 97:1086–1091

Okullo A, Temu A, Ogwok P, Ntalikwa W (2012) Physico-chemical properties of biodiesel from Jatropha and castor oils. Int J Renew Energ Res 1:47–52

Ouariti O, Boussama N, Zarrou M, Cherif A, Ghorbal MH (1997) Cadmium and copper-induced changes in tomato membrane lipids. Phytochemistry 45:1343–1350

Prasad MNV, Freitas HMO (2003) Metal hyperaccumulation in plants and biodiversity prospecting for phytoremediation technology. Electron J Biotechnol 6:284–321

Rajkumar M, Freitas SH (2008) Influence of metal resistant-plant growth promoting bacteria on the growth of *Ricinus communis* soil contaminated with heavy metals. Chemosphere 71:834–842

Rasmussen PE, Parton WJ (1994) Long-term effects of residue management in wheat-fallow: I. Inputs, yield, and soil organic matter. Soil Sci Soc Amer J 58:523–536

Ruiz-Olivares A, Carrillo-González R, González-Chávez MCA, Soto-Hernández RM (2013) Potential of castor bean (*Ricinus communis* L.) for phytoremediation of mine tailings and oil production. J Environ Manage 15:316–323

Sainju UM, Schomberg HH, Singh BP, Whitehead WF, Tillman PG, Lachnicht-Weyers SL (2007) Cover crop effect on soil carbon fractions under conservation tillage cotton. Soil Tillage Res 96:205–218

Saribiyik OY, Özcanli M, Serin H, Serin S, Aydin K (2010) Biodiesel production from *Ricinus communis* oil and its blends with soybean biodiesel. J Mechan Engineer 56:811–816

Scholz V, Nogueira da Silva J (2008) Prospects and risks of the use of castor oil as a fuel. Biomass Bioenergy 32:95–100

Stoltz E, Greger M (2002) Accumulation properties of As, Cd, Cu, Pb and Zn by four wetland plant species growing on submerged mine tailings. Environ Exp Bot 7:271–280

Suarez P, Meneghetti SMP, Meneghetti MRM, Wolf CR (2007) Transformation of triglycerides into fuels, polymers and chemicals: some applications of catalysis in oleochemistry. Quim Nova 30:667–676

Temminghoff EJM, Van der Zee SEATM, Da Haan FAM (1998) Effects of dissolved organic matter on the mobility of copper in a contaminated sandy soil. Eur J Soil Sci 49:617–628

Watson RT, Noble IR, Bolin B, Ravindranath NH, Verardo DJ, Dokken DJ (2000) Land use, land use change and forestry. Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge

Wels B, Sperling M (2007) Atomic absorption spectrometry. Wiley-VCH, New York

Wiebe K (2008) Biofuels: Implications for natural resources and food security in developing countries. Sustainable Biofuels and Human Security Conference, University of Illinois, Urbana-Champaign

Zamani AA, Shokri R, Yaftian MR, Parizanganeh AH (2013) Adsorption of lead, zinc and cadmium ions from contaminated water onto *Peganum harmala* seeds as biosorbent. Int J Environ Sci Technol 10:93–102