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POTENTIAL ENVIRONMENTAL EFFECTS LINKED TO ELEMENTAL TOXICITY OF NEEM BIODIESEL AND ALTERNATIVE FUELS (B20/B100)

*AE Pillay, M Elkadi, S Stephen, J Manuel and MZ Khan
Department of Chemistry, The Petroleum Institute, PO Box 2533, Abu Dhabi, UAE

ABSTRACT

Neem biodiesel is being developed as a future biofuel. Accompanying the growing global production of biofuels is the looming threat of environmental pollution. Such pollution can originate in two ways: firstly, combustion of biofuels containing elevated levels of toxic elements could contribute to atmospheric pollution; and secondly, poor quality biofuel (and waste products) that is returned to the environment could contaminate soil and aquatic resources. In this study the potential environmental toxicity of neem biodiesel was examined and compared with alternative fuels (B20/B100) using high performance ICP-MS. The neem biodiesel was prepared in our laboratory from neem feedstock (kernels and fruit) harvested in 2012. A dual acid-base catalyzed esterification process was employed to produce the biodiesel fraction. Prior to high resolution instrumental analysis all samples were digested in mild acidic media. The basic physical properties of the neem biodiesel were in agreement with those of regular petroleum diesel. Twelve elements (ranging from beryllium to uranium) considered to be environmentally toxic were detected in the neem biofuel and their levels displayed lower profiles of elemental toxicity compared to the B100 samples. B20, on the other hand, displayed reduced levels of toxicity in general. The study is of particular interest to environmental toxicology and sustainable development.

Keywords: ICP-MS, B20, B100, neem biodiesel, trace/toxic metals.

INTRODUCTION

Neem biodiesel is emerging as an alternative fuel (Pillay *et al*., 2012; Sekhar *et al*., 2009) and its characteristic toxic properties are relatively unexplored. In view of this, its elemental toxicity was studied instrumentally and compared with standard biofuels (B20 & B100). The rationale behind studying the toxicity of biofuels is their rising potential impact on the environment. A survey of the relevant literature revealed that, in general, toxic metal studies of biofuels have not been widely considered, and our research focused on this area of interest with particular emphasis on the comparative environmental effects of neem biodiesel. Recent media reports (Gonzales, 2013; Rubens, 2008) proclaim that dumping of poor quality biofuel could contaminate water supplies and create serious environmental pollution. With the growing production of biofuels, potential pollution of the environment by such alternative fuels has also grown and could lead to widespread organic and inorganic (toxic metal) pollution. Poor quality biodiesel from aborted biofuel processes and the accompanying waste products are often replete with noxious trace elements originating mainly from the soil and water used to cultivate the original biomass. These waste products include the wash water, organic material and catalysts. How are these unwanted substances disposed of? In some cases they are poured down the drain. In other cases they are returned to the environment, into landfills and other dumping sites. This creates a potential threat to the environment simply because their toxic elemental content could be transmitted to the soil and ultimately to the water table. It is well known that biodiesel can be derived from a variety of animal and vegetable oils (Sekhar *et al*., 2009). The biodiesels derived from different plant oils will have slightly different toxic metal contents due to the variation of cultivation methods, soil conditions, weather, plant parts used and processing technologies. A common method to generate biodiesel involves the transesterification of the triglycerides with the help of a catalyst to produce alkyl monoesters of chained fatty acids that have comparable properties to that of conventional diesel (Lin *et al*., 2009; Kalam, 2002; Muthu *et al*., 2010; Goering *et al*., 1982). Glycerol becomes a by-product of this chemical reaction that must be removed by separation processes (Schuchardta *et al*., 1998; Singh, 2010). Toxic and heavy elements are present in the biofuel, wash water and by-product. We found in an earlier study that retention of trace elements in the biodiesel fraction is appreciable (Pillay *et al*., 2012). Therefore, elemental analysis of the biodiesel component distinctly reflects the significant toxic metal content of the process.

Our biofuel was derived from indigenous non-edible terrestrial feedstock available in the region. The neem tree is prolific in the UAE and its fruit and seeds compared to most non-edible plant species have a higher concentration of oil (30% oil content), which is a major source of neem oil generally used as insecticides, lubricants and in

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*Corresponding author email: apillay@pi.ac.ae

medicines to treat various disorders. In this study toxic elements in neem biodiesel were measured by ICP-MS (inductively coupled plasma mass spectrometry) and compared with some commercial biofuels. ICP-MS has overtaken most modern analytical techniques for attaining ultra-low limits of detection (Ammann, 2007) especially for heavy metals, including the lanthanides and actinides. The multi-elemental capability of this hyphenated method to determine elemental levels in the ppm (mg/L), ppb (µg/L) and ppt range (ng/L) has certainly proved to be superior to contemporary methods such as neutron activation and ICP-OES.

The aim of this paper, therefore, was threefold: (i) to employ a high-performance instrument to characterize selected toxic elements in neem biodiesel (prepared in our laboratory); (ii) to compare our results with standard biofuels: B20; B100C [consumer grade]; and B100R [refinery grade]; and (iii) to evaluate the potential impact on the environment.

MATERIALS AND METHODS

Neem biodiesel preparation

Samples of neem fruit and seeds were harvested (in 2012) locally from surrounding areas and stored in a cool dry place. The vegetable oil was extracted in a blender with normal hexane. To prepare the biodiesel the transesterification process was applied with the help of a catalyst to generate a product with comparable properties to that of conventional diesel (Pillay *et al*., 2012). This transesterification process generally requires the use of methanol in a basic solution such as potassium or sodium hydroxide to produce the monoester and glycerol (by-product). However, the neem biofuel cannot be directly obtained in a one-step process because of the high content of free fatty acids (FFA) in the vegetable oil (Sekhar *et al*., 2009). Under basic conditions soap is produced and this reduces the yield of the reaction and also consumes excessive alkali. This also leads to a slower reaction time and the risk of incomplete conversion. Therefore, pre-treatment with methanol under acidic conditions is necessary to reduce the amount of FFA by converting them to fatty acid methyl esters (FAME). A dual process: acid-catalysed pre-treatment and base-catalysed transesterfication was thus necessary (Sekhar *et al*., 2009). The deprotonation step and catalyst restoration mechanism in the final stage are shown in figure 1.

Hyphenated ICP mass spectrometry

Samples (200µL) were digested in HNO_3/HF, 4:1 v/v in an industrial grade microwave oven and subsequently diluted and submitted for analysis using a Perkin Elmer SCIEX DRC-e ICP-MS (Fig. 2). The nebuliser gas flow in the instrument was 0.80 L/min. The analyte solution was aspirated into the instrument, converted by the nebuliser into a fine spray and mobilised to a plasma source where it was atomized and converted to ions, which were characteristic of the elements of the sample. These ions were subsequently transported to a mass spectrometer for detection. The technique is ultra-sensitive and can achieve limits of detection in the region of ng/L for most elements. The neem biodiesel and three standard biofuels (B20; biodiesel 100 consumer grade [B100C]; and biodiesel 100 refinery grade [B100R]) were prepared under identical conditions. The instrument was standardised with certified standards and a suitable internal standard was used to compensate for the possible drift in instrument measurements (Ammann, 2007). B20 biodiesel is a blend of 20% biodiesel and 80% petroleum diesel; and B100 is biodiesel in the neat form.

Instrumental performance

Prior to each run, the instrument was conditioned for linear calibration and background correction. An aqueous certified standard (Fluka 70007; 10.00µg/L per element) was employed to evaluate the performance of the instrument on homogeneous aqueous solutions. The sensitivity of the Perkin Elmer ICP-MS is linear over several orders of magnitude for aqueous samples, and can cover a wide range of concentrations in a single measurement. A measure of the repeatability in terms of the relative standard deviation (RSD) was computed and, in general, values less than 5% were attained demonstrating that the precision of the system for aqueous samples was satisfactory (Table 1).

RESULTS AND DISCUSSION

Elemental toxicity

Pollution of the environment by toxic elements in one form or the other has been the subject of extensive research. The properties of the biodiesel produced relies on the biomass used (Singh, 2010). The properties of the vegetable oil generated from the same plant species may fluctuate depending on fertilizers, soil conditions, weather, plant parts used and processing technologies. As

Table 1. Instrumental precision (µg/L) using a multielemental aqueous standard (Fluka 70007).

Measurement	Be	Co	In	Pb	Bi
1	10.7	9.66	9.98	10.3	9.62
2	11.6	9.87	9.68	10.2	9.63
3	10.4	9.74	9.94	10.7	10.1
Mean ± RSD	10.9 ± 5.7%	9.76 ± 1.1%	9.87 ± 1.7%	10.4 ± 2.5%	9.8± 2.8%

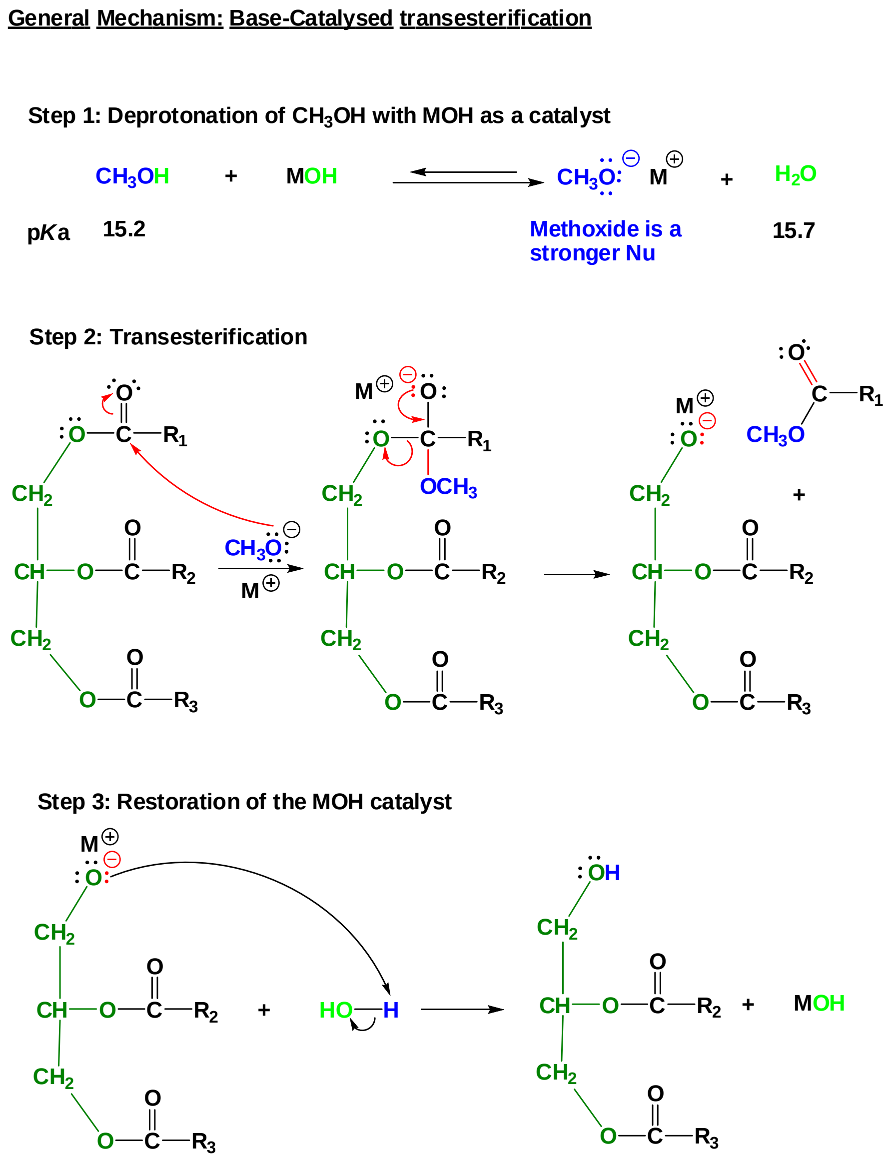

Fig. 1. Base catalysed mechanism showing deprotonation and transesterification steps.

aforementioned, the trace elements detected in neem biodiesel were studied against B20/B100 standard biofuels to compare levels of toxicity. The concentrations of neem biodiesel were also compared with drinking water standards to highlight the potential threat to the environment especially if discarded quantities of biodiesel find their way to drinking water supplies. The toxic elements investigated in this work have a maximum admissible drinking water level in the sub-ppm range, and many of them possess limits between 1-10µg/L (Kumar, 1994). Permissible atmospheric limits are within 10ng/m^3 (Kumar, 1994). Figures 3-5 display elemental trends (in the form of bar graphs) for the samples of interest. For convenience these elements are classified into three separate groups. The capability of ICP-MS for detecting ‘exotic’ toxic elements such as Be, Tl, Bi, Th and U is superior to other modern instrumental techniques. It is quite evident from the profiles shown in figures 3-5 (depicted in 3-D) that the range of elemental concentrations is fairly wide clearly depicting the comparative levels of toxicity, which are discussed below.

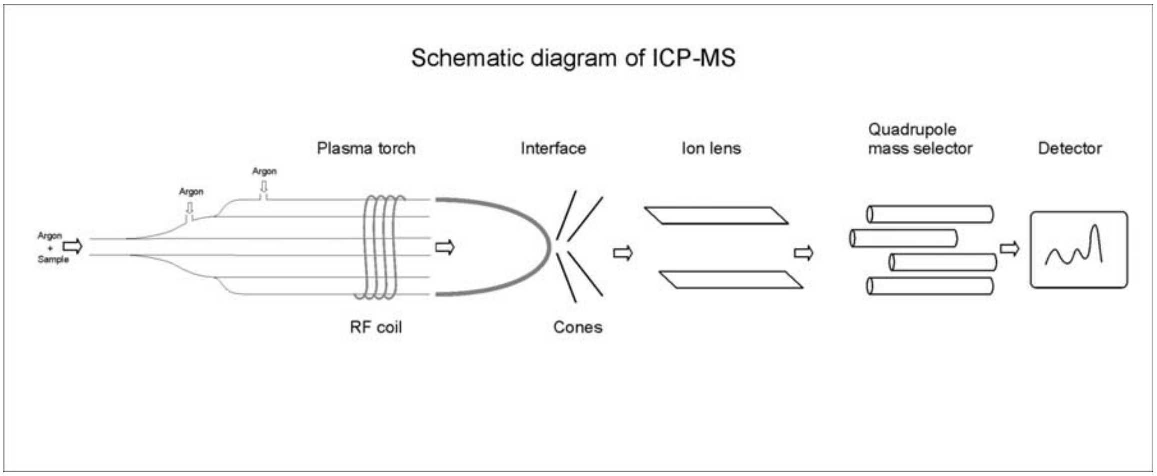

Fig. 2. A schematic of the ICP-MS instrument.

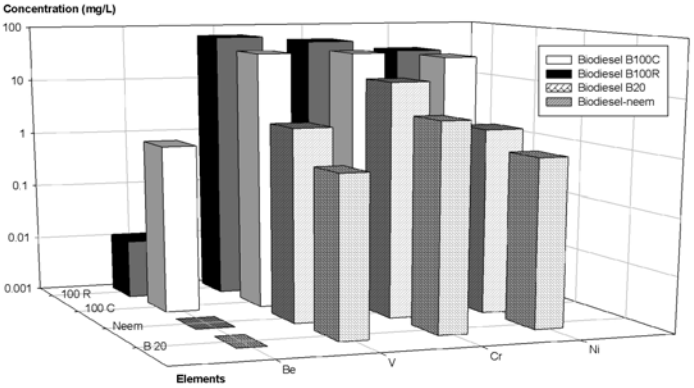

Fig. 3. Profiles for first group of elements in B20/B100C/B100R and neem biodiesel.

Characterisation study

Representative/transition metals: Figure 3 shows that a distinct pattern exists for B100C/B100R but similar trends are not apparent for B20 and neem biodiesel. In the case of Be, no detectable levels were observed for the B20, B100R and neem samples. The toxic effects of Be are still under considerable clinical research and it is known that elevated levels of Be in humans could lead to beryllosis and pulmonary disorders, including lung cancer (Kumar, 1994). The Be concentration in B100C was ~1mg/L, which was considered to be unusual and attributed to possible extraneous sources during the production of B100C. Vanadium, on the other hand, appeared in all samples. It is generally present in humans at ultra-trace levels (ng/L) and higher levels tend to affect the respiratory, circulatory and digestive organs. The levels in B100C/B100R were ~ 40 and ~ 66mg/L, respectively. Neem biodiesel and B20 displayed much lower levels: ~3 and ~1 mg/L, respectively. The elevated levels in B100C/B100R cannot be readily explained and could clearly create atmospheric pollution from combustion of these biofuels. Although the level of V in neem biodiesel is more than ten times lower than in B100C/B100R it is probably high enough to necessitate demetallisation procedures. Permissible drinking water levels of V are in the region of 15 µg/L so contamination from dumped biodiesel could have an impact on the environment. As regards chromium, the B100C/B100R levels were ~39 and ~53mg/L, respectively. B20 produced a level of ~5mg/L; and neem biodiesel ~15 mg/L. Here again the lowest levels were observed with B20. Compared to B100C/B100R the neem concentration was a factor of 2-3 lower, which could be explained by considering the differing factors associated with growth, cultivation and production of the feedstock related to these products. Chromium toxicity is usually linked to its oxidation states Cr^{3+} and Cr^{6+}, of which Cr^{6+} is considered to be more hazardous to human health. Speciation in neem biodiesel and commercial biofuels is a subject of future study but knowledge of the total levels of Cr gives an overall picture of the extent of its toxicity. In drinking water Cr permissible levels are <0.10mg/L. The detected levels reflected in figure 3 are much higher than this indicating that if these alternative fuels found a pathway to drinking water sources a hazardous situation would undoubtedly be created. The threshold level of atmospheric Cr is

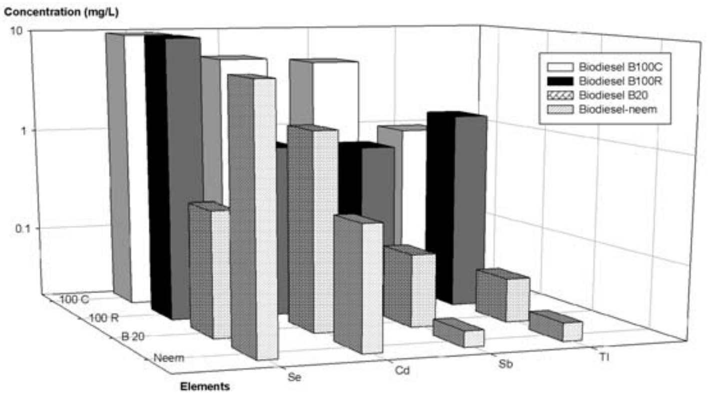

Fig. 4. Profiles for second group of elements in B20/B100C /B100R and neem biodiesel.

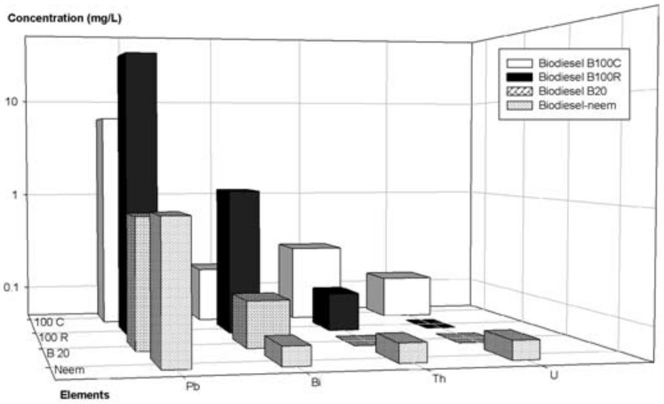

Fig. 5. Profiles for third group of elements in B20/B100C/B100R and neem biodiesel.

<0.5ng/m^3 purporting that combustion of the biofuels shown here could be a distinct threat to the environment. Nickel is another first-row transition metal that could lead to dermal and respiratory disorders in humans at elevated levels (Kumar, 1994). The threshold level of Ni in ambient air is 10ng/m^3. The admissible level of Ni in potable water is 20µg/L. Again we find that B100C/B100R display relatively elevated concentrations (~31 and ~34mg/L, respectively) compared to B20 (~1mg/L) and neem (~2 mg/L). Clearly the pronounced levels in B100C/B100R reflect the conditions and plant material from which they were derived and blended. As in the case of V, demetallisation processes to deplete Cr and Ni would be expedient prior to extensive use of these biofuels on machinery and in vehicles.

Intermediate/heavy elements: the concentrations of Se, Cd, Sb and Tl are shown in figure 4 for the biofuels of interest. A clear pattern of declining levels is seen for Se (B100C<B100R<neem<B20), but not for the other elements in this batch. The health effects of Se are still under wide clinical consideration. Its ingestion causes renal, cardiovascular and respiratory disorders (Kumar, 1994). The admissible level of Se in potable water is 10 ug/L; and its atmospheric limit is <1g/m^3. The experimentally recorded levels for Se for B100C/B100R were ~10mg/L in both cases. The neem biodiesel sample produced a concentration of ~5mg/L, and the B20 sample, ~ 0.5mg/L. Apart from the B20 sample the rest are considerably elevated when compared to the permissible drinking water level and if biofuels of this nature are returned to the environment it could penetrate the water table and affect aquatic resources. Unlike Se, cadmium is a common toxic metal. Its biological effects are well known. High levels of Cd can cause bone disease and kidney problems. In drinking water the maximum limit is 5ug/L. The levels of Cd detected in our experiments were: B100C/B100R: ~5 and ~1mg/L, respectively; B20: ~2mg/L; and neem: <0.5mg/L. Surprisingly, the B20 level for Cd is within the range of the B100C/B100R levels. It is possible that Cd could have been introduced into these biofuels via the blending and refining processes. Nevertheless, these levels in B20/B100C/B100R are far too elevated to be considered safe and use of these biofuels could result in a potential hazard to the environment from either combustion or disposal. Antimony is known to be carcinogenic and elevated levels in the air and water could pose an environmental threat. The maximum permissible level in drinking water is 6µg/L (Kumar, 1994). The levels detected in our biofuels and neem biodiesel were far higher than this. The reported levels for the B100C/B100R are ~5mg/L and ~1 mg/L, respectively. The B20 and neem biodiesel samples produced results that were much diminished at <0.5mg/L. Thallium pollution is not common, and the fact that it exists at appreciable levels in the biofuels analysed indicates that it could be present in the feedstock itself. Thallium itself is a notable poison, and is seldom detected because of its highly diminished levels. Its maximum permissible dose in drinking water is 2µg/L and health effects associated with elevated Tl levels could be linked to renal and liver disorders. In our study Tl concentrations were ~1mg/L for B100C and B100R (comparatively high); and <0.05 mg/L for B20 and neem.

Post-transition metals/actinides: in figure 5 Pb is most pronounced and probably originated from the feedstock and processing methods. On the other hand, bismuth, thorium and uranium are rare toxic metals often escaping detection largely because their ultra-low concentrations in typical environmental samples are not within the reach of most contemporary analytical techniques. The clinical effects of these three metals (Bi, Th, U) are relatively underexplored and are the subject of extended research in toxicology. Bismuth poisoning constitutes ingestion of elevated levels of the metal in chemical form and could lead to multiple disorders including cardiovascular and respiratory problems (Kumar, 1994). The admissible level of Bi in potable water is 4µg/L. Figure 5 shows that all samples, B20/B100C/B100R/neem, reflect comparatively higher levels to within 1mg/L. Elevated levels of thorium and uranium levels in the human body are not desirable and could lead to multiple organ failure. B100C showed the highest level of Th and U at ~270 ~130ng/L, respectively. The sources of these elements are probably the soil and water used to cultivate the plants from which the biofuels are derived.

Potential environmental effects

Our research could provide useful information on the potential detrimental impact of these noxious elements on the environment. With the growing need for the development of alternative energy sources the study is of interest to sustainable living. The presence of abnormal levels of toxic elements in biofuels could create unwanted hazards especially if pathways exist for pollution of the biosphere and lithosphere. From this perspective the disposal of appreciable quantities of sub-standard biodiesel and waste products (glycerol) in landfills could lead to significant contamination of the water table. In arid countries this would be highly deleterious to aquatic resources because of the dependence of overhead streams and borehole water for watering livestock and arable areas. Due to the relatively slow movement of groundwater, contaminants from waste products could build-up, and thus pose a looming threat to ecosystems (Pillay *et al*., 2010). Atmospheric pollution is another potential hazard and combustion of biodiesel laden with undesirable trace metals is a daunting prospect. Of significance is that our research highlights the looming threat to the environment, especially if unwanted heavy metals from engine exhaust fumes pervade the atmosphere; and poor quality biofuel is discarded. Hence, the impact on the environment is a distinct cause for concern, and our work could make a useful contribution to continuing sustainability. With reference to the elements detected in this study, the source of Be is a matter of speculation and it can only be surmised that this element was present in the plant material from which the biodiesel was derived. The other toxic elements appearing in figure 3 (V, Cr, Ni) could have either been present in the feedstock or introduced via the relevant chemical processes (or both). All the four metals reflected in figure 3 possess their own particular toxic effects on the human body and could undoubtedly pose a threat if they infiltrated water supplies. Proceeding to figure 4 we find that the trend is not consistent and the highest concentration was observed for Se particularly in B100C/B100R and neem. The remaining metals (in Fig. 4), Cd, Sb and Tl also occur at appreciable levels and, here again, it is of interest to have some knowledge of their origins in biodiesel. Thallium, especially, is an "exotic" element escaping detection with less sensitive instruments and responsible for fatal disorders at elevated levels. It is unlikely to encounter Tl in the blending and refining processes leading to the inference that it could only occur in the original biomass. Lead (Fig. 5) is most pronounced and could commonly arise from numerous natural and technological sources. Bismuth on the other hand is uncommon and is of interest because Bi pollution is rare. It occurs at a maximum level of ~1mg/L and its effect on the environment and the human body is the subject of ongoing research. The actinides Th and U are equally exotic and occur at such low sensitivities in environmental samples that only the most sophisticated instruments can detect them. Largely because of this, their toxicology is not well defined and necessitates more profound clinical and environmental studies to obtain an insight into their roles in the human body and the biosphere.

CONCLUSIONS

Our work is of interest from the perspective of environmental pollution originating from discarded biofuels and accompanying waste products. The study attracts attention because the production of neem biodiesel is expected to increase, and it can be linked to sustainable development. We found that the levels of several toxic elements in the samples investigated were appreciable and could cause serious contamination of drinking water supplies if dumped biodiesel pervaded such resources. In light of this possibility remedial measures to pre-empt such a prospect should be considered. One such measure to reduce trace metals in neem biodiesel is demetallisation. And to safeguard dumped waste biofuel, it would be practical to immobilize the waste biofuel by converting it to sludge (for example) using sand, gravel and waste oily sludge, and subsequently constructing solid blocks for storage in sub-surface caverns. This operation may be relatively inexpensive, because sand and oily sludge are plentiful especially in desert regions and any potential threat to the environment is thwarted.

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