



POLLUTANT AND HEAVY METAL RETENTION IN ASPHALTENES: ENVIRONMENTAL IMPLICATIONS?

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ABSTRACT

Environmental sustainability depends on various factors, one of them being the suppression of potential metal contaminants from fossil fuel sources. According to the documented literature, research associated with the retention of toxic and heavy metals in the asphaltene residuum is limited. The aim of this study, therefore, was to explore the phenomena that govern metal retention in asphaltenes and examine the potential environmental outcomes. Asphaltene fractions were isolated from virgin crude oil, purified, digested and analysed for metal and toxic components using ICP-MS. The instrument was standardised with certified materials and adjusted for background and matrix effects according to standard protocol. A range of selected toxic elements were determined, including: Be, Al, Se, Ag, Cd, Sb, Pb and Bi. The elemental levels ranged between 2-1500 ppm in the asphaltene phase; and 1-100 ppm in crude oil. These concentrations are elevated and clearly represent a potential environmental hazard. Wide differences existed in metal levels between asphaltene and crude oil samples and suggested metal transfer to the asphaltene phase at the point of precipitation. The experimental data are discussed in terms of environmental impact and the prospect of remediation. Our work contributes to environmental sustainability and fuels research.

Keywords: ICP-MS, asphaltenes, crude oil, heavy metals.

INTRODUCTION

Pollutants and heavy metals in fuel and fuel fractions affect environmental sustainability and create undesirable ecological problems (Shearman, 1990; Robinson, 1993; Pillay *et al.*, 2014). Metals, in general, tend to poison catalytic treatment of fossil fuels and also affect refining processes (Pillay *et al.*, 2012). Our investigation focused on the level of dispersion of toxic and heavy metals in asphaltenes and their potential environmental ramifications. This work represents an underexplored area of study and would be of considerable practical use in monitoring sustainability and in the refinement and treatment of asphaltenes. Asphaltenes represent the heavy hydrocarbon phase of crude oil (Speight, 2004; Nalwaya *et al.*, 1999). It is used for multiple purposes including widespread application in the construction of roads and thoroughfares. Elevated pollutant and metal levels in asphaltenes (in the form of asphalt) could thus constitute a potential environmental threat, especially from rain-water percolation to the water table (Pillay *et al.*, 2009). Continuous leaching of metals from asphalt could leak through to groundwater reservoirs and thus endanger aquatic resources. This could represent a serious hazard in arid countries where water is scarce.

Crude oil itself is often used on land farms in the form of oily sludge to enrich soil and fertiliser (Elhameed *et al.*, 2015). Trace metal levels in crude oil have been previously reported, although it must be stressed that such levels vary from country to country depending on source-rock and other environmental factors (Speight, 2004). Little or no documentation exists on the accumulation and study of toxic and heavy metals in the asphaltene fraction of crude oil. From this perspective our paper makes an original contribution. Measurement of metals and toxic components in both crude oil and asphaltene fractions was achieved using high performance ICP-MS (inductively coupled plasma mass spectrometry). The technique is known to attain ultra-low detection limits (ng/L) and has multiple advantages over other modern analytical systems (Peisach *et al.*, 1994; Abbu *et al.*, 2000). Some of these advantages include high sample throughput; low sample volume (~200-300 μ L); short analysis time; high sensitivity. Our work provides practical information for application in environmental studies and fuels research.

MATERIALS AND METHODS

Sample treatment / ICP-MS

Crude oil samples were treated with n-heptane and allowed to 'mature' for a period of about three days.

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Following ‘maturation’ the asphaltene phase was isolated using a soxhlet distillation system. Purification was achieved by refluxing with n-heptane (Carrier *et al.*, 2000). To authenticate the asphaltene product solubility properties and density guidelines (~1.13 – 1.20 g/mL) were applied. Crude oil and asphaltene samples were dissolved in acidic media under conditions of microwave digestion, and subsequently analysed by a Perkin Elmer SCIEX DRC-e ICP-MS. Care was taken to maintain steady experimental conditions to prevent sample losses. Fluid samples were aspirated into a hot plasma or torch (~6000K), atomised, ionised and conveyed via a quadrupole selector system to a mass detector. The system is kept cool by the continuous flow of argon gas around the periphery of the plasma. The technique is known to be highly capable for trace elemental determination (Peisach *et al.*, 1994a) and can attain limits of detection in the ng/L range (sub-ppb) for metals and certain non-metals. An automated sampler facilitated analysis and turnover times. Slight perturbations in instrumental performance were monitored and adjusted by use of an internal standard. The software was particularly efficient in masking interferences and eliminating unwanted matrix effects. The instrument was programmed to aspirate three successive sample aliquots, and underwent standard calibration and correction for background. Certified standards were used to evaluate the repeatability of measurements, which yielded relative standard deviations <5% indicating that the system was primed for use. The argon gas flow for plasma and sample atomisation was maintained at 0.80 L/min; and sample volumes of about 200µL were diluted for representative analysis.

RESULTS AND DISCUSSION

Metal Retention

Asphaltenes display porphyrin geometries, endowed with “cage-like” structures to entrap metal species within a cavity (Speight, 2004). Porphyrins are strongly conjugated complexes with delocalised electrons, thus metals are drawn into an “alcove” and tightly bound within heavy hydrocarbon macromolecules. Retention of metals in the asphaltene phase is, therefore, not unexpected. However, judging from figures 1 and 2, the level of retention is particularly high implying that a significant fraction of the metals in the bulk material is transferred to the asphaltene phase. The wide gap between asphaltene concentration in crude oil (<1wt%) and metal levels between fuel and fuel fraction suggest metal migration to the asphaltene phase at the point of extraction. It is, however, hard to establish the degree of accumulation of metals in the asphaltene derivative at the onset of extraction from crude oil. It is important to remember that crude oil is made up also of resins and aromatics (Nalwaya *et al.*, 1999) and the extent to which metals are dispersed in these particular components has not been documented. On examination of figures 1 and 2 we can make two comparisons: (i) differences between

metal levels in asphaltene samples themselves; and (ii) differences between metal levels between asphaltene and crude oil samples. Close inspection of figures 1 and 2 reveals typically that all the metals of interest are highly concentrated in the asphaltene fraction. Some of these levels vary widely within the asphaltene suite itself. For example, beryllium (Be) is particularly noticeable and displays a concentration range from about 2 - 42 ppm – a difference by more than a factor of 20. The difference in the ranges of the other listed elements is not as wide, but yields discrepancies of up to a factor of 10, in some cases. The fact that the most pronounced difference in levels is observed with Be suggests that the capture of metals could occur as a function of their size (ionic radius). Metals with lower ionic radii could possibly be smoothly “ensconced” in other hydrocarbon complexes (Li *et al.*, 2015) and, on isolation of asphaltenes, could thus be deficient in the residuum – hence wide differences are encountered. Of interest, is that a few of the asphaltene samples (#5, 6, and 7) originate from wells in the same location and certain elemental levels (for example, those of Pb and Se) are consistent, which could suggest the feasibility of using these metals in mapping or “fingerprinting” studies.

When it comes to differences between metal levels in crude and asphaltenes, there is no ambiguity. Figures 1 and 2 clearly indicate that these differences are highly pronounced – by more than a factor of 20 in some cases. As mentioned earlier, the asphaltene macrocycle displays greater affinity for metal species (Spiecker *et al.*, 2003) on the whole and there is clear indication from the experimental data that they tend to agglomerate in the asphaltene phase. However, the data in figures 1 and 2 do not provide sufficient information on the degree of metal migration into the asphaltene derivative at the point of abstraction from crude oil. This information is important because it may be possible to institute a de-metallisation process at the extraction stage, if it is known what proportion of metals from the bulk migrate at this stage. If the fraction of migrating metals is not significant, there is little point in establishing interim costly de-metallisation treatment. A point to bear in mind is that the crude is accompanied by produced water, which provides a hydrophilic environment for detaching metals from the bulk crude oil. Source-rock and the changes in the composition of source-rock over time could also affect the levels of toxic metals in petroleum. We note therefore, that several factors govern elemental concentrations in crude oil and asphaltenes, and these factors have to be taken into account when differentiating between elemental levels.

Environmental implications

When considering the levels of the listed elements (Figs. 1 and 2) and their impact on the environment, due consideration must be given to indirect transfer of such toxins to other sources, such as drinking water.

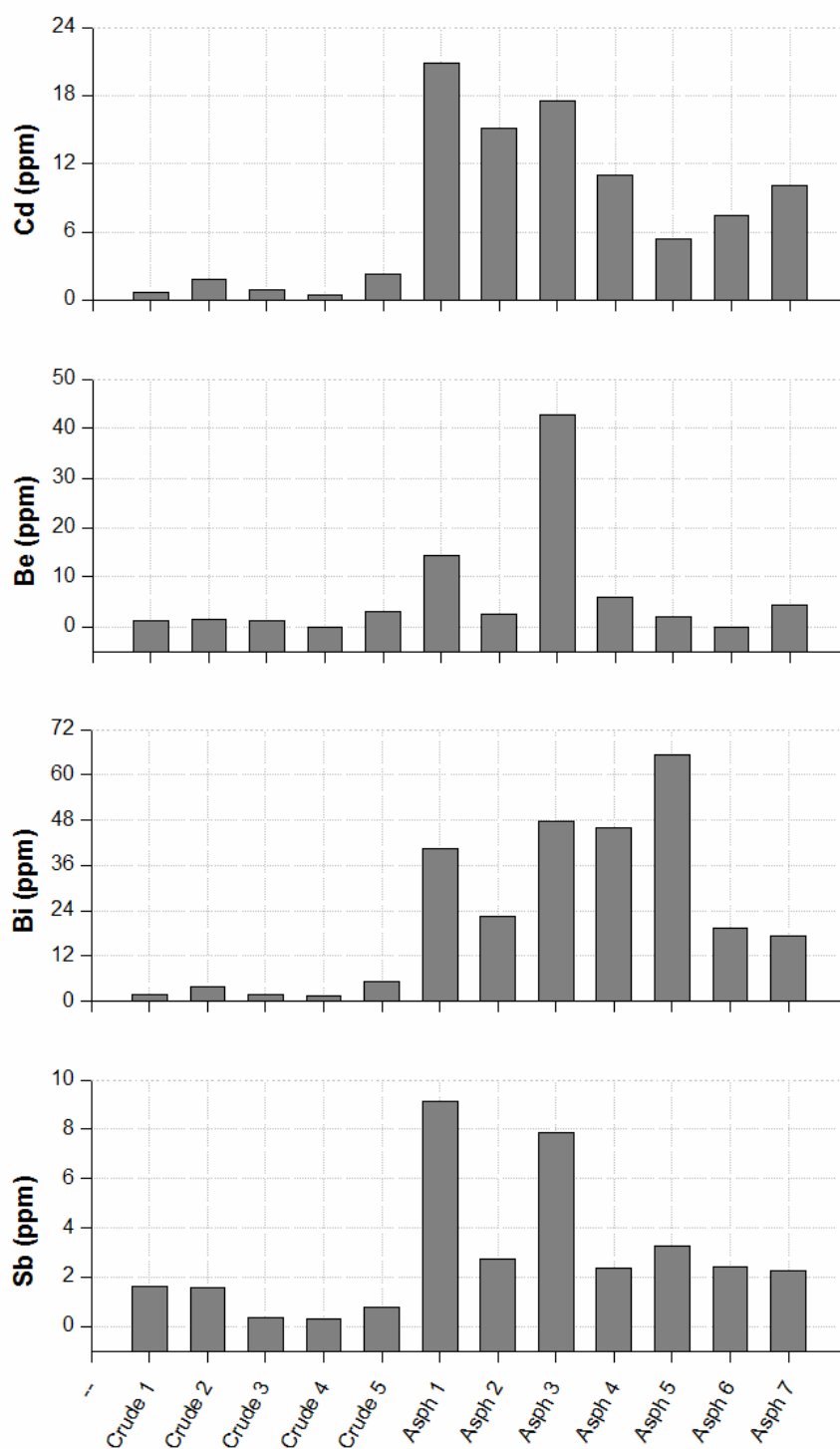


Fig. 1. Elevated levels of Sb, Bi, Be and Cd in asphaltenes.

Obviously, excessively high levels of toxins in asphaltenes could indirectly and naturally pollute aquatic resources (Pillay *et al.*, 2010). In our discussion in this section, we shall also touch briefly on some of the biological effects of the listed metals to underscore the

environmental connotation. A point to note is that toxicity of arsenic and chromium has been reported elsewhere (Elhameed *et al.*, 2015) and will not be discussed here. Also, vanadium/nickel is a subject of a separate study and has been excluded.

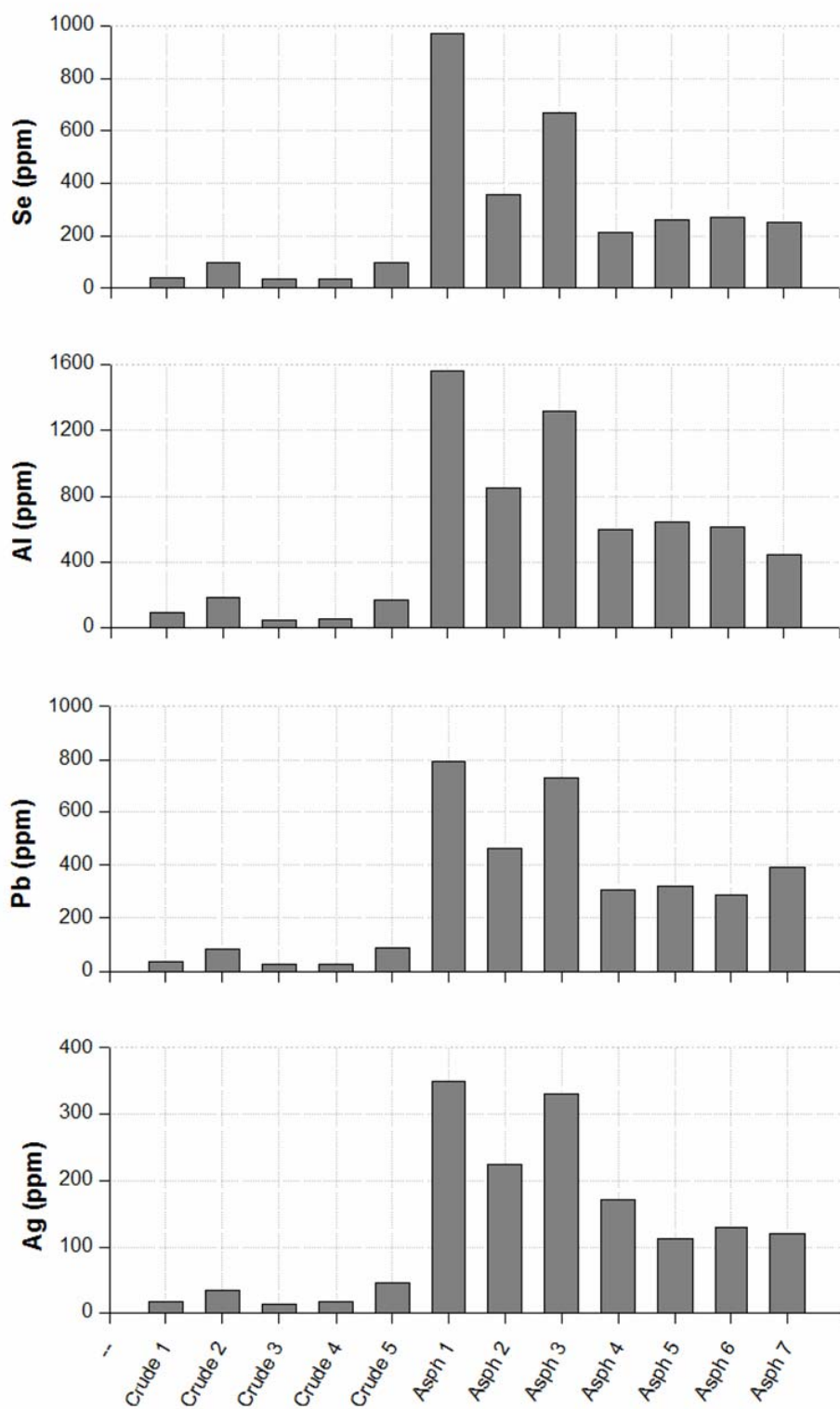


Fig. 2. Elevated levels of Ag, Pb, Al and Se in asphaltenes.

The present day ideology of sustainability is linked to safety and protection of the environment from everyday hazards originating from sources such as fossil fuel (Robinson, 1993; Shearman, 1990). The role of fossil fuel is entrenched in the fundamental principles of sustainable living and the suppression of noxious pollutants is one of

its key objectives. The standard admissible levels of the elements of interest (Figs. 1 and 2) in drinking water are <0.1 ppm (Li *et al.*, 2015), thus denoting from this perspective that they are all unusually high. Needless to say that when asphaltenes eventually find their way to the environment they come into contact with rain water, drain

water and miscellaneous sources of domestic and industrial water and as a result toxins tend to be leached out and from chronic percolation eventually penetrate the water table (Al Taie *et al.*, 1999). The list of elements in Figures 1 and 2 show that Ag and Bi are somewhat exotic and from the epidemiology point of view no established drastic human disorder has been linked to the two elements (De, 2014), although research into their biological function and side-effects is ongoing. Bismuth (Bi) is known to be beneficial and used in treatment of certain afflictions. However, in high doses it is suspected of producing encephalopathy. Silver (Ag), on the other hand, causes argyria, a dermal condition; but in high doses can be fatal. The health effects of lead (Pb) and cadmium (Cd) are well known (Shukla and Singhal, 1984), leading to neuro and renal disorders, respectively. The biological effects of selenium (Se) and antimony (Sb) are also the subject of much study (Feng *et al.*, 2011; De, 2014). Elevated levels of Se are carcinogenic; while high doses of Sb cause hair loss and liver disease. High levels of aluminium (Al) lead to Alzheimer's disorder; and last, but not least, beryllium (Be) is particularly deleterious and is linked to cancer and chronic beryllium disease (CBD) (De, 2014). Of note is that all the toxins listed in this study are at highly elevated levels and will decidedly form a potent threat to the ecosystem when dispersed in the environment.

Impact of the study / Remediation

The study reveals two key points. First, it is not clear from the experimental data whether metal retention in asphaltenes takes place largely at the point of extraction; or whether asphaltene-metal complexes tend to predominate in the bulk material. Metal transfer at the point of precipitation is an interesting theory and could be the subject of further study. It must be underscored, though, that no clear method presently exists to test this theory. Part of the experimental data denotes consistency in levels of some metals in the asphaltene samples (#5, 6 and 7) gleaned from oil wells in a common location and could suggest grouping on the basis of their concentrations and deploying in mapping studies - for example, Pb: 317/288/399 ppm; and Se: 260/270/250 ppm (Punyadeera *et al.*, 1997).

Second, all metal pollutants studied here are abnormally high. This has serious indirect environmental consequences. Gradual attrition of asphalt by running water could lead to ultimate pollution of groundwater resources through chronic percolation. Remediation of the problem lies in one of two strategies. The asphaltene, in the form of asphalt, could be adulterated by sand and aggregate for road building. Sand (from deserts) is usually abundant in most oil-producing countries, especially in the Arabian Gulf. Adulteration of this nature is cost-effective and would minimise the undesirable impact on the environment. The second remediation strategy evidently lies in de-metallisation. This process, however, entails chemical treatment and is costly and could lead to

the introduction of other unwanted chemicals in the asphaltene bulk.

CONCLUSION

Based on the elevated levels of metal ratios between crude oil and asphaltene samples, the experimental data suggest migration of toxic metals to the asphaltene phase at the point of abstraction from crude oil. This theory could be tested as the subject of future study, to establish the degree of migration. However, as it stands, the experimental data provide evidence of prospective metal migration, and this information could be significant to plan interim de-metallisation treatment when isolating asphaltenes from the host crude oil. Of equal significance is the potential environmental impact of the elevated profile of metal pollutants in the asphaltene residuum. Some form of remediation is recommended and one possible strategy to mitigate the impact is to dilute the asphaltene with sand/aggregate mixture when putting it to practical use such as road building. Our research has important practical implications and could play a role in monitoring environmental sustainability, and advancing fuels research.

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