Does the use of arsenic (As) contaminated, dredged harbour sediments, as an agricultural soil improver in Hayle, Cornwall pose serious implications to human health?

Introduction

The long history of metalliferous mining and processing activities in Cornwall is well known. Hayle was at the forefront of these activities and has World Mining Heritage Status. As a result of this industry, large parts of Cornwall, (and in particular Hayle), has high levels of heavy metal contamination. As levels are especially high in this area. Soil As values of over 110 mg kg^{-1} are found on 722 km^2 of land in the Cornish region (Warren et al. 2003). Poor waste management after the mining industry ceased, has led to the As contamination of land and it's continual build up in estuarine deposits via fluvial sediment transport.

In recent history, dredging of Hayle Harbour and areas of the estuary has been undertaken and the sand obtained has been sold for a number of purposes. The largest of these was the sale of sand for agricultural purposes, as animal bedding with the subsequent use as a soil improver, (Buro Happold, 2010).

This review examines the As contamination of the soil in the Hayle area, and discusses the As levels in the dredged sediments along with additional As that could be added whilst being used as animal bedding. A number of additional factors are taken into consideration to evaluate whether the hypothesis that human health is at serious risk from a diet of crops grown in soils where As contaminated dredged harbour deposits are used as a soil improver, is correct. Factors, such as the mobility, the bioavailability and the differing species of As are all taken into consideration with reference to the specified area. This study also examines the uptake of soil As into differing crop plants, the ability of a plant to transfer the As into the edible parts, and the dilution within the food chain.

There has been no published information on whether the use of As contaminated dredged sand on already heavily contaminated land has serious implications for human health. This review attempts to address the fact.

Arsenic contamination of the Hayle area

Cornwall has a long history of metalliferous mining and the subsequent metal processing activities, (such as smelting), dating back as far as the Bronze Age. The mining industry has long since ceased to operate, however the mining waste and heavy metals, (including As), released during these activities, still persist and contaminate the soils surrounding these areas.

Background values for soil As from uncontaminated sites in Cornwall tend to fall within a range of between 26-67 mg kg^{-1}. In comparison background values for soil As around Hayle are typically 125 mg kg^{-1}, but can range up to 750 mg kg^{-1} at contaminated sites around Hayle (Camm et al. 2004). At the New Mill site in Roseworthy (approximately 2 miles from Hayle), levels of soil As reach up to 4466 mg kg^{-1} (Camm et al. 2004).

Hayle is located on an estuary which forms the fluvial catchment zone for numerous areas of previously intense mining activity. The heavy metal contaminants continue to be deposited and stored within the estuarine sediments.

Estuarine samples have been analysed for As at various points within the Hayle Estuary. These samples show very high levels of As contamination, (see table 1).

Table 1. As contamination levels at three sites within Hayle Estuary.

Sample Site	Min. value mg kg^{-1}	Max. Value mg kg^{-1}
Copperhouse Pool	45	3830
Lelant Water	56	550
Mouth of Hayle Estuary	119	1130

Data taken from Smith (1988).

Dredged harbour sediments have also been tested for their heavy metal content. Samples were taken from dredged products on numerous occasions. The mean averages of As contamination levels and pH are shown in table 2.

Fate of dredged sand

The dredged sand has in recent history been used for agricultural purposes as an animal bedding material with the subsequent use as a soil improver on local farms. Animal bedding will inherently contain urine and faeces before it is removed and subsequently used for a soil improvement.

As with all livestock most heavy metals (including As), that are ingested in food and drink will be excreted in the urine and faeces. Livestock manure is one of the most significant sources of metals, (Nicholson et al. 2003). This source of As contamination will then be added to the As present in the bedding material, which is subsequently applied to agricultural land.

At the site at New Mill, Roseworthy, (which was studied by Camm et al. 2004), some arable and pasture land had been identified in analysis to contain relatively low values of As, (100 mg kg^{-1}), but pasture land at site 9E9N contained up to 3029 mg kg^{-1} As.

Agricultural soil As guideline limits are 50 mg kg^{-1} where fresh produce is to be grown. This figure is given by the UK's Code of Good Agricultural Practice for the Protection of Soil, (MAFF, 1998). The levels of contamination around the Hayle area are usually at least double these guideline limits. Despite this it is generally considered that concentrations of up to 250 mg kg^{-1} are unlikely to affect animals grazing. Concentrations above 500 mg kg^{-1} can result in animals eating sufficient soil whilst grazing to increase As in their liver and kidneys (MAFF 1998). Soil generally contributes between 50-80% of the total intake of As by cattle, (Thornton. 1996). Pasture land at site 11E3N, (Camm et al. 2004), seriously exceeds this level, (>1000 mg $^{kg-1}$), so As contamination does pose a health risk to the grazing animals in this area. Any manure obtained from this livestock would contain high levels of As and other heavy metals.

Table 2. As contamination and pH levels of dredged sediments obtained from dredging operations in Hayle Harbour.

Date of sample	Average As level mg kg^{-1}	Average pH level
27th Jan. 2007	29.5	8.38
28th Aug. 2008	25.6	8.43
27th Oct. 2008	32.2	8.53
17th Dec. 2008	39.4	8.57
13th Jan. 2009	26.1	8.62
19th Jan. 2009	31.6	8.67
18th Mar. 2009	30.4	8.60
1st May 2009	31.4	8.69
8th Sept. 2009	32.1	9.06
18th Jan. 2010	32.2	9.50
22nd Mar. 2010	23.4	9.51
30th Apr. 2010	28.2	9.24

Data obtained from Hayle Harbour Authority Limited.

Uptake of As in local crop plants

The most significant form of exposure to As in humans is by the oral intake of food and drink, (Huang et al. 2006). To reduce the risk of As exposure, guideline limits are set for both the soil that the crops were grown in, and in the actual produce for sale. Food for sale in the UK must contain less than 1 mg kg^{-1} As, fresh weight, as per the Arsenic in food regulations, 1959, (MAFF. 1998). Arable land at site 9E9N in Camm et al. (2004) study identified As levels as high as 3029 mg kg^{-1}.

The actual transfer of As from the contaminated soil to the crop plants edible parts, forms the main pathway of As into the food chain, (Huang et al. 2006). The amount of As that is taken up by the crop plant depends on the availability of the soil As, (bioavailability). This is determined by numerous factors, including soil pH, organic matter content, type of soil, and the source of As contamination.

Plant uptake of As is usually high in sands and sandy loams, and relatively low on clays and silts. This is due to the mineral assemblages of the clays and silts. Clays and silts contain clay minerals and iron (Fe), which As is strongly adsorbed on to, (Warren et al. 2003). As(III) adsorbs to these minerals and is altered to As(V), becoming less bioavailable as it does so. This factor results in levels of inorganic As being up to 5 times more toxic in sands and loams than in other soil types, (Warren et al. 2003).

Inorganic As tends to be found in 2 species within soil-arsenate, As(v) or arsenite, As(III). Arsenite is the more toxic and mobile species of As (Bhattacharya et al. 2007). Arsenite predominates where pH is higher and soils are waterlogged, (typical of Cornish soils). As contamination resulting from mining tends to be the less mobile species of arsenic, (arsenate). In Cornwall mining sites, such as Hayle, the more mobile species (arsenite) only forms 0.3-1.7% of the total soil As, (Huang et al. 2006). This fact is supported by the water samples taken in Camm et al. (2004), study of the New Mill site. The relatively low water sample As concentrations obtained from the site (less than 50 µg L^{-1}, which is the WHO standard), indicate the low mobility of As in the contaminated soils.

A plants As transfer efficiency also varies with differing plant drop type. Warren et al. (2003) undertook a study into varying vegetable crops and their efficiency in transferring As into the edible parts of the plant. Warren et al. (2003) used typical crops grown in Cornwall and compared the results in 3 differing sites, (one of which was Cornwall). The mean average soil As contamination at this site was 748 mg kg^{-1} and 6 differing vegetable crops were grown. Table 3 shows that the largest uptake of As was in Radish (considering the normal edible parts of the plant).

Table 3 showing the order of greatest uptake of As into the edible parts of the plant.

Plant name	Order of As contamination. 1 being the highest
Radish	1
Beetroot	2
Lettuce	3
Cauliflower	4
Spinach	5
Potato	6

Data from Warren et al. (2003)

Only radish exceeded limits for fresh produce making them unsaleable.

Studies such as Warren et al. (2003) and Huang et al. (2006), into the availability and transfer of soil As to crops, illustrate how As uptake varies between plants and plant organs. The transfer factor (TF) is used to determine the ability of a plant to transfer available As into the plant system. Warren et al. (2003) used TF_{total} based upon the total amount of As in the soil. Huang et al. (2006) used both TF_{total} and a TF for available As (TF_{avail}), content of the soil. TF_{avail} examines how a plant takes up bioavailable As.

Health risks

In Cornwall the risks of exposure to As, due to its association with historic mining activity, are well known. However, soil As in Hayle tends to be the less mobile species-arsenate. The arsenite only forms approximately 0.3-1.7% of the total As. This means that despite the high levels of As in the soil, only a small fraction of this is bioavailable. This means that plant uptake is generally low and can be variable. A typical varied human diet does not usually consist entirely of local grown vegetables, so there would also be a substantial dilution within the food chain. Plants do tend to act as a geochemical barrier against contamination, and so should only make a small contribution to human As exposure, (Thornton. 1996). However, as this study has shown, there may still be cases where a combination of factors may lead to harmful intakes of As. The addition of As contaminated dredged sand to agricultural land, from its prior use as animal bedding, could be one of these factors.

Adding As contaminated sand to the soil will improve the solubility of As and make it more bioavailable. The soil in Warren et al. (2003), study was clay loam- 40.8% sand, 37.5% silt and 21.7% clay. Adding As contaminated sand will gradually alter the soil make-up and type from a clay loam to a sandy loam. As discussed previously, inorganic As is 5 times more toxic in sandy loams than in clay soils. Another factor is the pH of the dredged sand. Table 2 shows that the pH is relatively high in the dredged sediments, (typically 8.38 - 9.51). Agricultural soils are usually maintained at a pH of 6.0 – 7.5 (MAFF. 1998). The pH of the soil in Camm et al. (2004) study site at New Mill falls within this range. Although it has to be noted that the natural soils here are slightly acidic and have been enriched with calcareous beach sand, (Camm et al. 2004). The use of dredged contaminated sand has been used for a number of years in this area, and not beach sand as published in Camm et al. (2004) study. The regular addition of sand with a higher pH will alter the soils pH over time. Soils with higher a pH have increasingly higher arsenite mobility, thus increasing As bioavailability. Increasing the pH at the New Mill site could liberate large amounts of mobile As into the nearby Rees River as well as into the soil and crop plants. The Rees River drains into St. Ives Bay at Gwithian, which is a well known tourist destination.

Conclusion

Historic mining activity in and around Hayle has left behind a legacy of high levels of As contamination in the environment. As is present in poorly managed mine waste and surrounding soils, as well as in estuarine sediments via fluvial sediment transport. These sediments have in recent history been dredged and sold for agricultural purposes as animal bedding and as a subsequent soil improvement treatment.

Ordinarily, even though As levels are high in the soils in Hayle, the As is found as arsenate, which is the least mobile species of arsenic. As a result, crop plant uptake is limited as the As is not in a bioavailable form. This means that the plants are acting as geochemical barriers against contaminants to a certain degree, reducing the contribution to human exposure.

The addition of As contaminated dredged harbour sand to agricultural land, after the prior use as animal bedding will alter the mobility of As in the soil. This combination of additional As sources integrated into an already high As contaminated soil, could cause harmful intakes of As in humans from the consumption of crops grown in this soil.

In conclusion, the addition of dredged harbour sediments to already contaminated soil does pose a significant risk to human health, and should be investigated further. Studies would need to be undertaken to ensure that the permissible daily intake of inorganic As is not exceeded as a result of a normal healthy diet that included crops grown in the Hayle area. As intake from other foods should also be accounted for as part of a normal diet. Foods such as, meat, fish, eggs, milk and water must be accounted for as part of the daily intake as the inorganic As levels may be significantly greater in combination.

(1893 words)

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