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Pollution due to Tobacco Use: Is E-cigarette an Answer?**Dr Rukma Parthvi****Tobacco Cigarettes and Environmental Pollution**

'Soldiers Smoke' or 'Mild May' is a fancy way of glorifying tobacco smoke amongst men and women. It has left us with a world of pollution. Among more than 4000 chemicals present in cigarettes, more than 50 are known carcinogens. Other poisonous chemicals found in cigarettes include benzene, formaldehyde, ammonia, acetone, arsenic and hydrogen cyanide. Smoke directly from cigarette or lungs of the smoker moves up in the atmosphere as it is less dense than air, and stays making air more toxic and carcinogenic (Siegel, 2011). Besides severe respiratory diseases it is also associated with cardiovascular events. Secondhand smoke can increase atherosclerosis, a condition in which fatty material collects along artery walls, hardens and blocks arteries. When a smoker tosses his cigarette onto the street or out of the window of his car, the butt and remaining part of the cigarette becomes a toxic litter. Although it takes about 12 years for a cigarette butt to break down, microscopically speaking, the remnants and toxic chemicals remain for far longer over 25 years to decompose. When it rains, this toxic litter moves into drains and eventually reaches water bodies affecting the entire ecosystem (Polosa et al., 2013).

The pollutants we are talking about here instigate more harm than just the smoky haze seen over large cities, but are known poisonous compounds—ammonia, acetone, arsenic, formaldehyde, tar, and carbon monoxide, to name a few. These toxic chemicals released by cigarettes not only threaten the environment, but human health through secondhand smoke (Dawkins et al., 2012; Glynn, 2014).

Approximately 5.5 trillion tobacco cigarettes are produced globally every year. Every person on the planet could smoke over 785 cigarettes every year. So a significant amount of cigarette butts are discarded in the environment. The US alone spends an estimated \$11.5 billion per year on cleaning up litter, and cigarette butts make up 38% of the litter worldwide, making it the single most littered item in the world, according to Earth911.com.

Keeping in mind that it takes nearly 2000 cigarette butts to equal 1 pound, over 2 billion pounds of butts are discarded annually, and a large percentage of those are ending up in the wrong places.

When a cigarette butt is improperly discarded, it most often ends up being washed or blown into the water supply, where the saturation releases toxic chemicals held within the filter. This harmful process has been scientifically proven to have devastating consequences on aquatic and avian life which by mistake considers the cigarette butts for food and are poisoned by the chemicals.

E-cigarette, E-cig or Electronic Cigarette

An **e-cigarette** (e-cig or e-cig), **personal vaporizer (PV)** or **electronic nicotine delivery system (ENDS)** is a device used by smokers to replace their conventional cigarettes (Bertholon et al., 2013; Grana, 2014). It is a healthier way of smoking and the manufacturers

claim that it can really help people in stopping and reducing addiction (Caponnetto et al., 2011a; Caponnetto et al., 2011b). **The person inhales the vaporized nicotine produced by this device.** This nicotine is dissolved in propylene glycol. This nicotine solution gets vaporized once the sensors that are present in the device detect air flow from the mouth piece when the user tries to smoke. The flavor experienced by the smoker is almost the same when they inhaled a tobacco.

E-cig is a an electronic atomization or vaporization cigarette and a [cigarette substitute](#) for quitting smoking (Caponnetto et al., 2013). It atomizes or vaporizes a nicotinated propylene glycol solution, known as e-liquid, that may be doctored with additional additives such as flavourings and colourings or variable nicotine concentrations. It gives small amounts of the chemical [nicotine](#) without [tobacco](#) or other chemicals from real cigarettes. It is a [battery-powered vaporizer](#) which simulates [tobacco smoking](#) by producing an [aerosol](#) that resembles [smoke](#). It can also be modified to vaporise cannabis derived products. It is typically battery-operated devices designed to deliver nicotine through a heated solution to its user. To distinguish, **an ordinary cigarette is called traditional, regular, normal, real, analog, combustible, combusted, burned or tobacco cigarette, or simply a cigarette.**

E-cigs were first invented in 2002 by a Chinese pharmacist as smoking cessation devices, and China remains the primary manufacturer of e-cigs globally today. Despite the current controversy and novelty associated with e-cigs, the concept of water vapor as a vehicle for nicotine delivery to the lungs is not new. Use of a hookah (also known as a *water pipe*) is a practice that has been embraced for hundreds of years and has also seen a dramatic increase in popularity, with a surge in hookah bars and cafes, often located near colleges and universities (Chan and Murin, 2014). E-cigs were first produced and patented in China in 2004 by a Beijing based company, Ruyan Group (Holdings) Ltd, and were introduced to the US market in 2007. There are approximately 250 types of e-cigs for sale in the US and they vary considerably in their ingredients, quality control, and ability to deliver nicotine. Some contain only propylene glycol (used to create the vapor that they emit), water, flavoring agents, and nicotine. Others, however, as tested by the US Food and Drug Administration (FDA), have been found to contain a variety of contaminants, including some that are carcinogenic.

E-cigs generally use a [heating element](#) known as an [atomizer](#) that [vaporizes](#) a [liquid solution](#) of nicotin in propylene glycol. This solution is called **e-liquid, e-juice** or simply **juice**. E-liquids usually contain a mixture of [propylene glycol](#), [vegetable glycerin](#), [nicotine](#), [flavorings](#), and colorings, while others release a flavored vapor without nicotine. Sometimes it contains with differing levels of [alcohol](#) mixed with concentrated or extracted flavorings. A The main substances making up in the liquid of e-cigs are 1-5% nicotine, 80-90% [propylene glycol](#), 2-5% [glycerin](#) and some 1-4% [flavors](#) or [smells](#). Propylene glycol and [glycerin](#) are heated to make a [vapour](#) which looks like the [smoke](#) from real cigarettes. This carries the [nicotine](#) to the lungs where it is absorbed.

Most e-cigs consist of a rechargeable, battery-operated heating element; a replaceable or refillable nicotine-containing cartridge; and an atomizer that uses heat to convert the contents of the cartridge into a nicotine-containing vapor that is then inhaled by the user (Greg, 2014). Some e-cigs can be reused and others are for single use. In addition, some are designed to look

very much like a cigarette, while others have unique shapes and profiles that do not conjure a cigarette at all. Table 1 describes other vocabulary and terminology associated with e-cigs (McQueen et al., 2011).

Table 1. Vocabulary associated with e-cigs

Term	Explanation
E-cig	Electronic cigarette (e-cigarette): a mechanical nicotine-delivery device that includes a reservoir of nicotine solution, a heating element, a battery, and an automatic or manual switch
Vaping	Inhalation of the vaporized solution from an e-cig
E-liquid or juice	The liquid solution vaporized by e-cigs; usually contains water, propylene glycol, and/or glycerin, nicotine, and flavorings
Atomizers ("attys")	Heating element. Heat from the atomizer is used to vaporize the liquid. Lasts weeks or months
Cartomizers ("carts")	A combination of an e-liquid cartridge and an atomizer. May not last as long as an atomizer
Blanks	Refillable e-liquid cartridges
Priming and switches	Activation of the atomizer to heat the e-liquid. E-cig models vary and may have manual or automatic switches that require "priming puffs" prior to inhalation
Dripping	The act of adding extra e-liquid onto the atomizer
PVs and mods	Personal vaporizers and modified e-cigs that may resemble packs or large cylinders
Volts	Starter e-cig kits that usually come with a 3.7-volt battery that may be modified to a 5- or 10-volt battery. The higher-voltage batteries can vaporize a larger quantity of e-liquid
Low-resistance atomizers	When used in combination with lower-voltage batteries, these produce effects comparable to those of standard atomizers with higher-voltage batteries
Pass throughs	Devices used to provide continuous power to e-cigs by means of a USB connection to a computer
Goose neck	E-cig that extends the mouthpiece with a flexible metal tube

Environmental Benefits of Electronic Cigarettes

E- cigarettes have come a long way from their initial version. The current e-cigs look more realistic and are comparatively more user friendly as compared to the earlier ones. The user gets almost the same satisfaction as the conventional cigarette. However, the major advantage is that they offer 'the experience' of smoking but do not produce smoke. Unlike traditional cigarettes which release a cloud of smoke after a puff, there is no visual residue while using e-cigs. Hence, people around are not affected due to passive smoking. The usual effects of smoking like development of yellow fingers and teeth are completely prevented (Hajek et al., 2014).

E-cigs can help prevent air pollution caused by tobacco smoking which accounts for 3000 lung cancer and 37,000 heart disease deaths in nonsmokers and over 10,000 hospitalizations in infants and children under age 18 every year in the United States. Though FDA approved pharmacological methods of tobacco cessation should be tried first, e-cigs needs encouraging studies as it seems to be a solution to environmental threat caused by tobacco smoking (FDA, 2009).

E-cigs do not release secondhand smoke chemicals into the atmosphere. Through the vaporizing of liquid nicotine, they release nicotine gas, water, and propylene glycol (PG). Water and nicotine, obviously, are naturally occurring gases in the atmosphere, and PG is an organic compound naturally found biological materials.

Absence of tobacco cigarettes means absence of cigarette butts, a highly littered item in the world. As an added benefit, e-cigs allow the user to “reduce, reuse, recycle”, as the motto from the EPA suggests to promote environmental conscientiousness. Since one e-cig cartomizer is equal to about 40 tobacco cigarettes (depending on the type and brand), users can reduce the amount of waste produced. Most e-cigs can also be cleaned and reused by simply replacing the vapor before each use, and when it is ready to be disposed off, e-cigs can be recycled, along with batteries, phones, and other e-waste.

E-cig smoke is very less polluting than tobacco smoke. The amount of metals and organics in **second-hand tobacco smoke is about 10 times greater than the levels found in e-cig vapor.**

The traces of metal particulates found in e-cig vapour do not come directly from the e-liquid itself. Rather, from metal parts inside the electronic device. This issue could be addressed through varying manufacturing techniques to prevent metal particles from being released.

E-cigs are non-polluting, non-flammable and non-carcinogenic. The smoker can inhale nicotine vapor and is not affected by tar and tobacco which are found in the cigarettes. The state-of-the-art micro-electronic technology provides the user a real-time experience of smoking without affecting the environment and the people around. Normal cigarettes release about 4000 harmful chemical substances in addition to nicotine. This is avoided by the e-cigs. The ingredients of the e-cigs are not cancer-causing agents.

Smokers can enjoy and experience the physical and emotional sensations of e-cigs. Though the nicotine side effects are still present, the other more serious problems caused due to the harmful ingredients of cigarettes can be totally eliminated.

An important area of uncertainty regarding the safety of e-cigs is secondhand exposure and the impact on indoor air quality. A series of studies comparing the pollutant concentrations between e-cigs and tobacco smoke samples found that, as expected, tobacco smoke contained pollutants including volatile organic compounds (VOCs), carbonyls, polyaromatic hydrocarbons (PAHs), nicotine, tobacco-specific nitrosamines (TSNA), and glycols at levels considered of harm to human health, but that e-cigs produced very small exposures compared to tobacco cigarettes, indicating no apparent risk to human health.

Lastly, smoking using e-cigs is comparatively cheaper than the traditional smoking.

Environmental Harms of E-cigs: E-cig is not always the Answer for the Environment

A common argument arising from opponents of electric cigarettes is that the factories required to produce e-cigs are more harmful than tobacco cigarette factories. Air pollution emitted by their factories outweighs any potential good that e-cigs do. In response, e-cig proponents point out that, as of now, e-cig companies rent factory space to make their product, so the factory would be manufacturing another product if they weren't making e-cigs, and the amount of pollution emitted would be the same regardless.

Another point raised against e-cigs is that the pollution of improperly disposed cartomizers and batteries would be just as bad, if not worse, for the environment as filters from analog cigarettes (McCauley et al., 2014). E-cig supporters acknowledge this danger, but counter by pointing out that it is illegal to discard lithium ion batteries. After all, a very little amount of all

the batteries in the world would end up as a big litter. Butts of real cigarettes and batteries of e-cigs pollute equally.

E-cig users would not know how much of nicotine vapor they have inhaled which is quite dangerous. This is because when smokers smoke a cigarette, they stop once the whole cigarette is exhausted. But e-cigs would work as long as the battery is charged. Even if the charge gets exhausted, nicotine solution is still present. A fully charged e-cig can work for several hours. Thus, the user should be aware of the amount of vapor he is inhaling. Too much of inhaling can cause side effects of excessive nicotine in the body.

E-cigs are not legal in all the countries around the world. Beginners should be careful enough to inhale mild doses of nicotine vapor. There is a legal age to start using these devices. The effect of the e-cigs is the same as the real cigarettes. However, since the vapor released by the e-cigs is harmless, it can be used in a non-smoking or smoking-prohibited areas like restaurants, parks and public areas.

E-cig performance has been found virtually identical to that of regular cigarettes in terms of exhaled nitric oxide (NO) rates. Nitric oxide causes the smooth muscles in the lungs and heart to relax, which can lead to reduced lung function and increased risk of heart attack. The more NO our body retains, the worse it is for us. There is an entire other issue with harmful additives used by less scrupulous offshore firms that we are not even getting into. What we *do* know is in e-cigs is not reassuring.

Multiple studies have found chemicals like acetaldehyde, formaldehyde, and toluene, as well as heavy metals like cadmium, nickel, and lead, in both [first](#) and [second-hand](#) vapour. Again, these were present in concentrations a magnitude lower than conventional cigarettes but at high enough levels that they could arguably fall under California's Proposition 65 rules for mandatory labelling of their carcinogenic nature. **Ten compounds found in E-cigarette mainstream smoke (MS) or Secondhand Smoke (SS) are** acetaldehyde (MS), benzene (SS), cadmium (MS), formaldehyde (MS, SS), isoprene (SS), lead (MS), nickel (MS), nicotine (MS, SS), N-nitrosonicotine (MS, SS) and toluene (MS, SS).

The atomisation process generates ultrafine particles — which can instigate the same effects seen in tobacco smoke or industrial air pollution. The size and chemical composition of these particles can vary greatly between products. This variability has a big effect on their individual cytotoxicities, but the study did conclude that their presence in the air has a similar effect to tobacco smoke in terms of your pulmonary health. Altogether, between 20 and 27 per cent of e-cigarette vapor's ultrafine particles make their way into the circulatory system, compared to 25 to 35 per cent for regular cigarettes. These nanoparticles can trigger inflammation in the mucus membrane and have been linked to chronic diseases like asthma, stroke, heart disease, and diabetes.

An analysis by the FDA's Center for Drug Evaluation and Research (CDER) sampled two of the leading brands of e-cigs and found that of 18 samples tested, one contained diethylene glycol (an ingredient found in antifreeze) and that half of the samples contained tobacco-specific nitrosamines, a human carcinogen. In addition, the FDA has found that "light" e-cigs (labeled as nicotine-free) may still contain nicotine. Other potentially harmful ingredients in e-cigs may include irritants, genotoxins, and animal carcinogens.

Fine particulate matter (PM) appears to be lower in e-cigs than traditional cigarettes. A study of fine and ultrafine PM emissions found higher particulate counts in traditional cigarette smoke versus e-cig vapors ($PM_{10} = 922$ vs 52 mcg/m^3 and $PM_1 = 80$ vs 14 mcg/m^3).

The aforementioned study by the CDER also found that nicotine per puff ranged from 26.8 to $43.2 \text{ mcg nicotine/100 mL}$, and independent studies have shown that the advertised amount of nicotine content may be inaccurate. The presence or absence of nicotine in these products is important since nicotine is a highly addictive substance associated with accelerated coronary artery disease, acute cardiac ischemic events, and hypertension. Additional adverse health effects associated with nicotine include stroke, poor wound healing, peptic ulcer disease, and esophageal reflux. In addition, nicotine reduces sensitivity to insulin and may worsen diabetes as well as contribute to endothelial dysfunction.

Other safety concerns include explosion of the e-cig and contaminated and/or toxic liquids. One study analyzing the cartomizer (combined atomizer and cartridge) contents and aerosols found the presence of metal and silicate particulates, demonstrating the need for improved quality control in e-cig design and manufacture. Inhalation of propylene glycol is also associated with throat irritation, but animal studies have shown no deleterious effects with long-term vapor exposure. In response to these concerns, some manufacturers have begun using combinations of distilled water and glycerin instead of propylene glycol. It can also be noted that propylene glycol and glycerin are the same chemicals used in fog machines of the entertainment industry, e.g., on movie sets or at concerts.

Children playing with e-cig devices is another safety concern. A child may be exposed to nicotine from the device or refill bottles, which could be ingested or absorbed transdermally, leading to a fatal overdose. E-cigs should be disposed of in the same manner as other products containing lithium ion batteries i.e. at a battery recycling center, and charging batteries should not be left unattended.

E-cig users take in 2- 20 times the amount of vapour in volume, and thus nicotine, than normal smoke. This is because it is very easy to keep inhaling from an e-cigarette. It can keep going for the equivalent of a whole pack of cigarettes, doesn't make our clothing or breath smell, and can be vaped indoors. Thus e-smokers are dramatically increasing their intake of nicotine, and therefore increasing the exposure of their colonising bacteria to this substance.

Both real cigarette smoke and e-cigarette vapor make drug-resistant bacteria more virulent.

It took decades to deal with the industry misinformation and misdirection about cigarette smoke. We now understand the harm it does. Yet all indications are that e-cigs are simply another form of nicotine that carries the same risks to both the user and anyone in their immediate vicinity.

Arguments For and Against E-Cigarettes

The questions about e-cigs are hotly debated in the world of tobacco control and public health. There are concerns about the exact benefits and potential harms of e-cigs, secondhand smoke, and air quality. Proponents see e-cigs as a safer alternative to traditional cigarettes, but skeptics question how safe they really are, both for users and people exposed to them as second-hand smoke. So far, they have been manufactured and distributed without oversight,

data, or proof that they are a bridge to quitting more toxic cigarettes. Also, many experts question the industry line that just water vapor is released when users light up. There are social, psychological, medical, and policy reasons that the introduction of e-cigs may prove to be a net benefit or net harm for public health.

Among the “**pros**” favoring e-cigs are:

- Their ability to deliver nicotine to the user in a much less harmful way than tobacco cigarettes, which contain more than 4000 other chemicals, including more than 50 carcinogens
- Their absence of secondhand cigarette smoke, meaning they release only a vapor with sharply reduced potential for harm compared with combusted cigarettes
- Their resemblance to regular cigarettes to cigarette smokers, which provides the tactile and visual sensations (eg, holding them in a certain way, a glowing tip, blowing smoke, etc) that many cigarette smokers have become used to, or even psychologically dependent upon and
- Their potential for aiding cigarette smokers who wish to quit smoking.

Among the “**cons**” arguing against e-cigs are:

- The lack of sufficient scientific data about their safety. E-cig users cannot be sure of what they are inhaling, since e-cigs have not been subjected to thorough independent testing and, due to their manufacture by many different companies, quality is not always assured in their production
- Lack of scientific data about their effectiveness as smoking cessation aids
- Lack of scientific data regarding their ability to deliver enough nicotine to satisfy withdrawal effects
- Lack of scientific data regarding the potential for e-cigarette use to reverse the decades-long public health effort to “denormalize” combusted cigarette use
- Lack of scientific data about the effects of secondhand vapor from e-cigs, as well as the desire of most people to avoid being exposed to this vapor in public places such as restaurants, movie theaters, and airplanes, whether proven to be a health hazard or not
- Lack of scientific data about whether the use of e-cigs encourages smokers who might have otherwise quit to continue smoking and only use e-cigs when they are in no-smoking environments (i.e. the “dual use” concern) and
- Lack of scientific data about whether youth may use e-cigs as an introduction to smoking real cigarettes.

Considering these lists of potential benefits and harms, it is easy to see why e-cigs are a source of controversy, even among the most sophisticated and informed scientists, clinicians, advocates, and policymakers.

Not surprisingly, the scientific community also remains split on the e-cig issue regarding e-cig vapor and its effect on indoor air quality. **We need more data and more robust market regulation.** The data do not support either the safety or effectiveness of e-cigs as quitting devices. But e-cigs may have a role in reducing the horrific toll of death and disease from tobacco cigarettes. This lack of scientific consensus has, of course, been a challenge for policymakers as they are faced with immediate questions regarding e-cigs at the state and local

levels, such as how to address e-cig use in public spaces, how to tax e-cigs, how to keep people from using both traditional cigarettes and e-cigs, how to keep e-cigs out of the hands of children, etc.

We should allow science to work: obtain solid, independent data and then make decisions and recommendations based on those data. To do otherwise, to develop public health policy on the basis of opinions and anecdotes, will not serve public health well and will, ultimately, undermine both points of view.

The scientific debate will not end at any point soon. Science as a process is never complete. It is not a foot race with a finish line. People will always be waiting at a particular finish line. As long as we won't commit to knowing everything, the presumption is we know nothing.

Suggestions

The benefits and risks of e-cig use are uncertain. More improvements need to be made to ensure e-cigs will continue to leave a small environmental footprint when demand grows in the future (McQueen et al., 2011; Williams et al., 2013). There are constantly new and exciting advancements being made that have applicable uses in e-cig technology, such as faster-charging, more durable lithium batteries which would of course substantially reduce waste by providing longer-lasting batteries. Scientists should discover how to extend the use of batteries, cartomizers, and mouthpieces, and perhaps even find ecofriendly organic compounds for e-cig production, instead of pure plastic materials.

Ultimately, it will depend on vapers themselves to dispose of their e-cigs responsibly, but it is little debated that e-cigs offer users better opportunities to reduce, reuse, and recycle. This is one step closer to reducing our overall environmental footprint on the planet, or perhaps better said, one footprint erased.

The most immediate action required to address the controversies surrounding e-cigs is assert regulatory authority. The first and most important thing to do is that e-cigs be included in existing clean indoor air laws. There are already 150 to 200 cities in the USA that have already done this including major cities like New York, Los Angeles, Chicago, and San Francisco. E-cig manufacturers must register their products with the FDA, provide a list of their ingredients, establish (or continue) good manufacturing practices, address untested product additions and misbranding issues, and restrict marketing and sales only to those aged 18 years and older.

E-cigs are synthetic chemical cocktails that we know little about (Goniewicz et al., 2014). So we must think twice before absentmindedly puffing away. We do know with certainty that smoking is harmful. There is a great danger that in restricting e-cigs because of *uncertainty*, we will end up with more smoking, which we are *certain* is harmful. So the right way to handle the long term uncertainty is:

- keep studying the physics and chemistry of e-cigs and liquids
- develop and test theories by which harm may be caused
- keep up epidemiological surveys on the user population
- set standards for products that make sure they are reasonably safe and high quality
- be flexible enough to intervene and change policy to introduce restrictions if problems emerge

- recognise that any problems may be confined to narrow circumstances (particular flavours, or devices) so target restrictive regulation on them – not the whole category
- do'nt put restrictions on e-cigs. It may cause more smoking and thereby do more harm than good (Odum et al., 2012).

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HEAVY METAL CONTAMINATION IN MARKET VEGETABLES OF MATHURA CITY

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INTRODUCTION

The effect of heavy metal contamination of fruits and vegetables cannot be underestimated as these foodstuffs are important components of human diet. Fruits and vegetables are rich sources of vitamins, minerals and fibers and also have beneficial antioxidative effects. However, the intake of heavy metal-contaminated fruits and vegetables may pose a risk to human health. Hence the heavy metal contamination of food is one of the most important aspects of food quality assurance ([Elbagermi et al., 2012](#)). Heavy metals, in general, are not biodegradable, have long biological half-lives, and have the potential for accumulation in different body organs, leading to unwanted side effects. Plants take up heavy metals by absorbing them from airborne deposits on the parts of the plants exposed to the air from the polluted environments as well as from contaminated soils through root systems. Also, the heavy metal contamination of fruits and vegetables may occur due to their irrigation with contaminated water.

Dietary intake of metals via vegetables is an important issue owing to food quality and safety. Metals can only change their chemical form. They cannot be degraded or destroyed. Vegetables are exposed to heavy metals either by absorbing them from contaminated soil as well as from deposits on parts of the plants exposed to the polluted air. Excessive and long term intake of metals via vegetables can cause serious health risk to consumers ([Dzomba et al., 2012](#); [Rao et](#)

al., 2011). Heavy metals can cause diseases related to cardiovascular, kidney, bone etc., and are also implicated in causing carcinogenesis, mutagenesis and teratogenesis (Harmanescu et al., 2010; WHO, 1992; Steenland and Boffetta, 2000; Jarup, 2003; Oskarsson et al., 2004). Keeping in view of the potential toxicity, non-degradable nature and cumulative behavior as well as the consumption of vegetables, it is prerequisite to test and analyze these vegetables to ensure that the levels of metals meet the agreed international requirements. In the last two decades, Mathura has expanded a lot in terms of industrialization and urbanization in Uttar Pradesh, India. Thus, food safety issue becomes a matter of concern in rapidly urbanizing region.

OBJECTIVES

The objectives were to:

- (1) determine the level of nine heavy metals (copper, chromium, lead, cadmium, zinc, manganese, nickel, iron and cobalt) in the selected vegetables sold in the local markets of Mathura city, India
- (2) compare the metals concentrations with the recommended limits and
- (3) evaluate the health risk associated with metals contaminations in the vegetables.

MATERIALS AND METHODS

Vegetable samples were collected from the local markets in the Mathura city. They included: spinach (*Spinacea oleraceae* L.), carrot (*Daucas carota* L.), mustard (*Brassica campestris* L.), turnip (*Brassica rapa* L.), radish (*Raphanus sativus* L.), potato (*Solanum tuberosum* L.), cauliflower (*Brassica oleracea* L.) and beet (*Beta vulgaris* L.). They were washed in fresh running water to eliminate dust, dirt, possible parasites or their eggs and then were again washed with deionized water and oven-dried at 90°C for 24 h. They were digested by following the method

described by **Allen et al. (1986)**. In brief, one gram of vegetable samples was digested (wet acid digestion) with 15 ml of concentrated HNO_3 , H_2SO_4 , and HClO_4 in 5:1:1 ratio at 80°C until a transparent solution was obtained (**Derbie and Chandravanshi, 2010; Diacono, 2011; Sinha et al., 2006**). Metals were determined using atomic absorption spectrometry (Perkin Elmer AAnalyst 100). Wavelengths for Cu, Cr, Pb, Cd, Zn, Mn, Fe, Ni and Co were 324.8, 357.9, 217.0, 228.8, 213.9, 279.5, 248.3, 232.0 and 240.7 nm, respectively. The detection limits of Cu, Cr, Pb, Cd, Zn, Mn, Fe, Ni and Co were 0.006, 0.007, 0.0025, 0.005, 0.005, 0.003, 0.005, 0.0025, and 0.006 $\mu\text{g/mL}$, respectively. Recovery test was done by spiking with varied amounts of standard solutions of the metals and recoveries obtained were in the range of 92.5 %–107.6 %. The daily intake of metals (DIM) was determined by the following equation:

$$\text{DIM} = [\text{C}_{\text{metal}}][\text{K}][\text{D}_{\text{intake}}]/\text{B}_{\text{average weight}}$$

where C_{metal} , K, D_{intake} and $\text{B}_{\text{average weight}}$ represent the heavy metal concentration in plant (mg/kg), conversion factor, daily intake of vegetables and average body weight, respectively. The conversion factor used to convert fresh green vegetable weight to dry weight was 0.085, as described by **Rattan et al. (2005)**. The average daily vegetable intakes for adults and children were considered to be 0.345 and 0.232 kg/person/day, respectively, while the average adult and child body weights were considered to be 55.9 and 32.7 kg, respectively, as used in previous studies (**Ge, 1992; Wang et al., 2005**). The health risk index (HRI) was calculated as suggested by **US EPA (2002)**:

$$\text{HRI} = \text{DIM}/\text{RfD}$$

where DIM and RfD represent daily intake of metals and reference oral dose respectively. Oral reference doses used for calculation were 0.04, 0.3, 0.001, 0.004, 0.02, 1.5, 0.06 and 0.14 mg/kg/day for Cu, Zn, Cd, Pb, Ni, Cr, Co and Mn,

respectively (RAIS, 2003). The HRI < 1 indicates the exposed population to be safe.

RESULTS AND DISCUSSIONS

The mean concentrations of metals (Cu, Cr, Pb, Cd, Zn, Mn, Fe, Ni, and Co) in vegetables sampled from the local markets in Mathura are shown in Fig. 1. The concentrations of metals were also compared with the safe limits for metals set by FAO/WHO (2001) and Prevention of Food Adulteration (PFA) Act 1954 (Awasthi, 2000). Pb and Cd were above the recommended limit in all the examined vegetables (Fig. 1). The relatively high Pb found in all vegetables could be attributed to deposition from industrial and vehicle fume. Cd may have its origin from contaminated irrigation water and atmospheric deposition. No international standards or guidelines exist for Cr, Fe, Mn, Co or Ni. On comparing Cr levels with Indian standards (Awasthi, 2000), it is observed that except for the Turnip, all vegetables were within safe limits (Fig. 1) while Ni level exceeded the limit in all examined vegetables (Fig. 1). Metals contaminations reported in previous studies have been listed in Table 1. Cr and Ni levels in all the tested vegetables in the present study exceeded those reported in the previous studies (Song et al., 2009; Sharma et al., 2009; Parveen et al., 2003). Zn is essential to neutralize the toxic effects of Cd. In this study, the highest quantity of Zn was found in spinach (65.94 mg/kg). Further, Zn values exceeded the FAO/WHO (2001) safe limit in spinach and Indian safe limit in radish (Fig. 1). To appraise the health risk associated with heavy metal contamination of market vegetables in the vicinity of Mathura industrial area, DIM and HRI were calculated. The DIM for Cu, Cr, Pb, Cd, Zn, Mn, Fe, Ni and Co ranged from 0.0003 to 0.0051, 0.0004 to 0.011, 0.001 to 0.024, 0.001 to 0.003, 0.015 to 0.035, 0.003 to 0.039, 0.004 to

0.084, 0.012 to 0.019 and 0.002 to 0.013 respectively for adults, and from 0.0003 to 0.006, 0.0004 to 0.0013, 0.001 to 0.028, 0.002 to 0.003, 0.017 to 0.039, 0.004 to 0.045, 0.005 to 0.097, 0.014 to 0.022 and 0.003 to 0.014 respectively for children. HRI values for adult and children are shown in Tables 2 and 3. Overall HRI ranged: 0.007–0.128 (Cu), 0.0002–0.008 (Cr), 0.362–6.115 (Pb), 1.327–2.901 (Cd), 0.05–0.115 (Zn), 0.025–0.277 (Mn), 0.015–0.282 (Fe), 0.62–0.959 (Ni) and 0.041 to 0.2114 (Co) in adults. In children HRI ranged from 0.008 to 0.147 (Cu), 0.0003 to 0.009 (Cr), 0.416–7.03 (Pb), 1.526–3.335 (Cd), 0.058–0.132 (Zn), 0.029–0.319 (Mn), 0.017–0.324 (Fe), 0.707–1.1 (Ni), and 0.047–0.243 (Co). DIM and HRI values indicated that the intake of Pb and Cd contaminated vegetables can pose serious health threat to the local consumers. **Mapanda et al. (2007)** also reported potential health risk due to Cd intake via leafy vegetables, in Harare, Zimbabwe. **Singh et al. (2010)** also reported potential health risk due to Pb, Cd

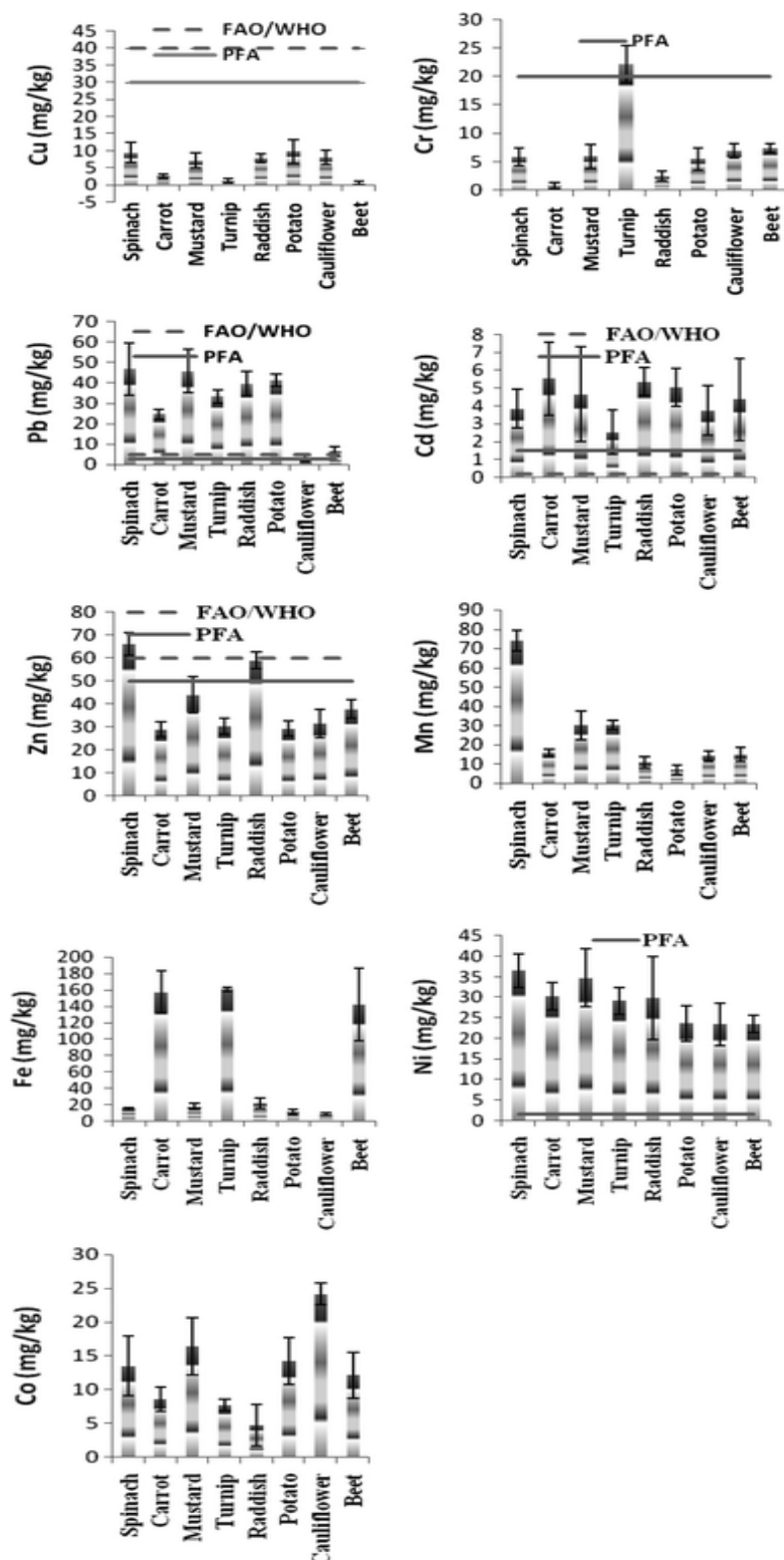


Fig. 1 Mean concentrations of metals (mg/kg dry wt.) in the market vegetables

Table 1 Metals reported in vegetables in literature data of similar studies in the world (mg/kg dry wt.)

Vegetables	Cu	Cr	Pb	Cd	Zn	Ni	References
Spinach, Egypt	4.5	–	0.34	0.11	20.89		Radwan and Salama (2006)
Spinach, India	27.6	–	1.44	1.96	57.56	–	Sharma et al. (2009)
Spinach, China	0.7	0.089	0.031	0.018	2.99	0.07	Song et al. (2009)
Carrot, Egypt	1.5	–	0.18	0.01	8.03	–	Radwan and Salama (2006)
Carrot, China	0.53–0.8	–	0.003–0.004	0.14–0.15	3.229–5.127	–	Zheng et al. (2007)
Radish, China	0.34	0.031	0.074	0.012	2.48	0.07	Song et al. (2009)
Potato, Egypt	0.83	–	0.08	0.02	7.16	–	Radwan and Salama (2006)
Potato, Pakistan	0.10	0.15	0.16	0.08	–	0.8	Parveen et al. (2003)
Potato, China	1.03	0.029	0.067	0.015	3.77	0.054	Song et al. (2009)
Cauliflower, India	35.72	–	1.56	2.57	63.63	–	Sharma et al. (2009)
Cauliflower, China	0.6	0.02	0.03	0.014	5.45	0.68	Song et al. (2009)

Table 2. Estimated HRI for adults via consumption of vegetables

Vegetables	Cu	Cr	Pb	Cd	Zn	Mn	Fe	Ni	Co
Spinach	0.124	0.002	6.115	2.019	0.115	0.277	0.026	0.959	0.118
Carrot	0.033	0.0002	3.235	2.901	0.050	0.059	0.275	0.794	0.075
Mustard	0.093	0.0021	5.997	2.439	0.0768	0.113	0.031	0.912	0.144
Turnip	0.015	0.008	4.358	1.327	0.053	0.114	0.282	0.763	0.0676
Radish	0.102	0.0008	5.169	2.817	0.103	0.0413	0.037	0.783	0.041
Potato	0.128	0.0019	5.403	2.633	0.0511	0.025	0.020	0.62	0.125
Cauliflower	0.106	0.0024	0.362	1.962	0.0551	0.053	0.015	0.615	0.2114
Beet	0.007	0.0026	0.8433	2.292	0.066	0.056	0.248	0.618	0.1064

Table 3 Estimated HRI for children via consumption of vegetables

Vegetables	Cu	Cr	Pb	Cd	Zn	Mn	Fe	Ni	Co
Spinach	0.142	0.0023	7.03	2.322	0.132	0.319	0.0304	1.10	0.136

Vegetables	Cu	Cr	Pb	Cd	Zn	Mn	Fe	Ni	Co
Carrot	0.038	0.0003	3.72	3.335	0.058	0.067	0.316	0.913	0.086
Mustard	0.106	0.0024	6.89	2.804	0.0883	0.129	0.0358	1.05	0.1651
Turnip	0.017	0.009	5.009	1.526	0.0609	0.131	0.3238	0.877	0.077
Radish	0.117	0.0009	5.94	3.238	0.1184	0.047	0.0432	0.90	0.047
Potato	0.147	0.0022	6.211	3.027	0.0588	0.029	0.0234	0.713	0.143
Cauliflower	0.1223	0.0028	0.416	2.255	0.0634	0.061	0.0169	0.707	0.243
Beet	0.008	0.0029	0.969	2.635	0.0758	0.064	0.2856	0.710	0.122

and Ni contamination in locally produced vegetables in Varanasi, India. Regular monitoring of metals in vegetables and other food items should be performed and appropriate safety measures should be taken at the time of transportation, storage and marketing of vegetables. In addition, the source of vegetables should also be monitored and suitable measures should be taken to deal with the contamination.

CONCLUSIONS

Concentrations of metals were determined in market vegetables of Mathura City in India. The average concentrations of metals (mg/kg dry wt.) in vegetables ranged from 0.57 to 9.77, 0.72 to 22.17, 2.76 to 46.63, 2.53 to 5.53, 28.87 to 65.94, 6.77 to 74.1, 8.43 to 161.1, 23.46 to 36.55 and 4.74 to 24.18 for Cu, Cr, Pb, Cd, Zn, Mn, Fe, Ni and Co, respectively. Pb, Cd and Ni were above the recommended limit in all the examined vegetables.

The daily intake of metals (DIM) was determined by the following equation:

$$\text{DIM} = [\text{C}_{\text{metal}}][\text{K}][\text{D}_{\text{intake}}]/\text{B}_{\text{average weight}}$$

where C_{metal} , K, D_{intake} and $\text{B}_{\text{average weight}}$ represent the heavy metal concentration in plant (mg/kg), conversion factor, daily intake of vegetables and average body weight respectively. The conversion factor used to convert fresh green vegetable weight to dry weight was 0.085. The average daily vegetable intakes for adults and children were

considered to be 0.345 and 0.232 kg/person/day respectively, while the average adult and child body weights were considered to be 55.9 and 32.7 kg respectively. The health risk index (HRI) was calculated as:

$$\text{HRI} = \text{DIM}/\text{R}_\text{f}\text{D}$$

where DIM and $\text{R}_\text{f}\text{D}$ represent daily intake of metals and reference oral dose respectively. Oral reference doses used for calculation were 0.04, 0.3, 0.001, 0.004, 0.02, 1.5, 0.06 and 0.14 mg/kg/day for Cu, Zn, Cd, Pb, Ni, Cr, Co and Mn, respectively. The $\text{HRI} < 1$ indicates the exposed population to be safe.

DIM and HRI values indicated that the intake of Pb and Cd contaminated vegetables can pose serious health threat to the local consumers. Based on HRI values the health threat of individual vegetables for Pb was of the order: **Spinach > Mustard > Potato > Radish > Turnip > Carrot > Beet > Cauliflower** and for Cd it was: **Carrot > Radish > Potato > Mustard > Beet > Spinach > Cauliflower > Turnip**. Regular monitoring of metals in vegetables and other food items should be performed and appropriate safety measures should be taken at the time of transportation, storage and marketing of vegetables. In addition, the source of vegetables should also be monitored and suitable measures should be taken to deal with the contamination.

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HEAVY METAL CONTAMINATION OF DIFFERENT NONALCOHOLIC DRINKS

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INTRODUCTION

The industrial processes of extraction and distribution of mineral resources which undergo synthetic changes yield chemicals such as heavy metals that have an atomic weight and density almost five times that of water. The pollution of soil, atmosphere, underground and surface water with effluents of such industrial activities inevitably results in chemicals finding their way into our food chain and consequently into our foods and beverages. The presence of heavy metals in beverages or soft drinks has been documented in a number of worldwide studies. A recent study of beverages produced in Poland detected increased heavy metal content in fruit juice samples (**Krejpcio et al., 2005**). This study highlighted the fact that beverages are rarely free from heavy metal contamination regardless of the environment they are produced. In particular, foodstuffs produced in regions suffering from high levels of pollution and environmental problems such as Nigeria, are thought to be more prone to violating guideline values of the permissible amounts of heavy metals in locally produced products. The recent proliferation of a number of different brands of Nigerian beverages has also necessitated the study of the extent of heavy metal contamination of these products.

Heavy metals such as mercury (Hg), antimony (Sb) and tin (Sn) are known to have toxic effects when administered acutely and chronically to laboratory animals. Although studies of heavy metal contamination in beverages have shown that concentrations are generally too low to cause any immediate toxic effects, chronic exposure has the potential to cause severe adverse effects to human health.

Antimony a suspected carcinogen with unknown biological function and effects on long term exposure is used as a catalyst in the production of polyethylene terephthalate (PET) plastics, with many applications including its use in the packaging of beverages and foodstuffs (**Hansen et al., 2010**). Low doses of antimony is known to cause headaches, dizziness and depression, but in larger doses can cause violent and frequent vomiting.

Food and water are the main sources of mercury in non-occupationally exposed populations. According to **Galal-Gorchev (1991)**, the average daily intake of mercury from food and water ranges from 2-20 µg. Acute administration of mercury was found to induce severe vacuolation of the renal tubular epithelium and nephropathy in the kidneys (**Carmignani et al., 1989**) and caused a decrease in seminiferous tubule diameter, spermatogenic cell counts and leydig's cell nuclear diameter in the male reproductive structure (**Lamperti and Printz, 1973**). A study carried out by the **WHO (1990)**, found mercury to be a neurotoxin particularly affecting the developing brain and causing mental retardation to the unborn foetus due to its ability to cross the placenta.

Tin was found to cause testicular degeneration in rats at a dose of 10 mg/kg daily for 13 weeks (**de Groot et al., 1973**) and was carcinogenic at doses of about 0.2000 mg in B6C3F1 mice with increased incidence of hepatocellular adenomas (**ATSDR, 2003**). Higher concentrations of tin are typically found in canned foodstuffs as a result of dissolution of the tin coating or tin plate, the levels depending largely on the type and acidity of the food, the presence of oxidants, the duration and temperature of storage and the presence of air in the can headspace (**Vannoort et al., 2000**).

Several studies of Nigerian soft drinks and juice drinks (**Orisakwe et al., 2009; Maduabuchi et al., 2008**), dairy drinks and drinking water (**Orisakwe et al., 2006**) have detected the presence of trace quantities of heavy metals that have exceeded the maximum contaminant levels (MCL) recommended by the United States Environmental Protection Agency (USEPA), European Union (EU) and World Health Organization (WHO).

A recent renowned study of the concentration of antimony in commercial juices (**Hansen et al., 2010**), found eight of the products to have antimony concentrations that were up by a factor of 2.7 above the EU limit for drinking water. Studies

of mercury and tin in various foodstuffs have also indicated the presence of these heavy metals in excess of safety limits.

Many studies to date have described environmental exposure of humans to heavy metals in African populations, but little is known about the exposure to heavy metal toxins from processed or unprocessed foods consumed in Africa. No data currently exists on the concentrations of antimony, tin and mercury in Nigerian beverages and findings from studies conducted worldwide are varied.

This study determined the concentrations of antimony, tin and mercury in a number of commonly sold and consumed beverages in Nigeria and assessed the extent of the violation of recommended limits set by the USEPA, EU and WHO guidelines.

MATERIALS AND METHODS

50 different samples of beverages or soft drinks were utilized in the study including dairy drinks, soft drinks, water and various types of juice drinks such as fresh juice, juice concentrates and mixed fruit juices, which were purchased in May 2010 in Mathura City. The samples chosen were considered to be a fair representation of the beverages available in the Mathura market, with the minor exception of a few products that were newly introduced to the market such as energy drinks.

The samples were prepared for analysis by hydrolysing 20 ml of the beverage with 10 ml of hydrochloric acid (HCl) and 20 ml water (H₂O). The hydrolyzed samples were well shaken and transferred to a centrifuge tube for centrifugation at the rate of 3000 rpm to remove solid particles. The resulting homogenised samples were thoroughly mixed before sub-samples were taken for analysis to ensure homogeneity of the mixture. The presence of antimony and tin were analysed in samples using the Perkin Elmer Atomic Absorption Spectrophotometer (AAS) Model AAnalyst 100, employing an air-acetylene oxidizing (lean, blue) flame at the recommended wavelength of 217 nm and a nitrous-oxide-acetylene reducing (rich red) flame of wavelength 286.3 nm for antimony and tin respectively. Determining the presence of tin and antimony in dairy drinks involved precipitation of the milk proteins including casein by adding trichloroacetic acid (TCA) to the samples. All other determinations were carried out in malt drinks, soft drinks, energy drinks and the table waters by the direct aspiration method.

Mercury was determined by the cold vapour technique after reduction with stannous chloride (SnCl_2) in order to release the mercury in the sample solution. Precaution was taken at all times due to the toxic nature of mercury. A stock standard solution was prepared by dissolving 1.08 g of mercury(II) oxide, in a minimum volume of 1:1 HCl and diluted to 1 litre with de-ionised water. This solution was then analysed by the AAS using an air-acetylene, oxidizing (lean, blue) flame at a wavelength of 253.7 nm.

The concentration of the contaminant was calculated using the arithmetic mean according to **Parkhurst (1998)**, by multiplying the amount of the chemical element/volume of the sample beverage. The volume of one and a half litres was assumed in the calculations of the concentration of antimony, tin and mercury, as it was considered the average intake volume for adults.

Appropriate quality procedures and precautions were carried out to assure the reliability of the results. Reagents used to calibrate the instrumentation were of analytical grades. A spike-and-recovery analysis was performed to assess the accuracy of the analytical techniques used. Post-analysed samples were spiked and homogenized with varying amounts of the standard solutions of the different metals. The spiked samples were then processed for the analysis by the dry ashing method.

RESULTS

The results of the analysed samples were grouped into three subgroups: fruit juices and soft drinks, dairy drinks and bottled waters as shown in Table 1. The group with the highest and broadest concentration ranges of the heavy metals studied were of the fruit juices and soft drinks group.

The results of the analyses of mercury, tin and antimony in 20 fruit juice and soft drink samples are shown in Table 1. Tin had the highest concentration recorded amongst all the heavy metals analysed. The concentration range of tin within the fruit juices and soft drinks such as Coca-cola, Pepsi, Fanta orange, Tango, Sprite, Dew, Seven up etc. was in the range 0.97 - 6.33 $\mu\text{g/L}$ which represented a mean concentration of $3.70 \pm 0.22 \mu\text{g/L}$. Both mercury and antimony were also of the highest concentrations recorded within the fruit juice and soft drinks group. Mercury ranged from 0.61- 6.04 $\mu\text{g/L}$, giving a mean concentration of 2.35

$\pm 0.25 \mu\text{g/L}$ and antimony ranged between $0.21 - 1.86 \mu\text{g/L}$ with a mean concentration of $0.49 \pm 0.05 \mu\text{g/L}$.

Table 1. Metal concentrations in different types of drinks

Drinks analysed	No. of samples	Mercury concentration ($\mu\text{g/g}$)		Tin concentration ($\mu\text{g/g}$)		Antimony concentration ($\mu\text{g/g}$)	
Type	n	Range	Mean	Range	Mean	Range	Mean
Fruit juice and soft drinks	20	0.61 -6.04	2.35	0.97 -6.33	3.88	0.22 -1.86	0.50
Dairy drinks	20	1.44 -4.88	2.93	1.69 -6.17	3.60	0.28 -1.35	0.49
Bottled water	20	0.91 -0.94	0.94	3.66 -5.25	4.34	0.37 -0.55	0.48

Table 1 shows the levels of mercury, tin and antimony detected in 20 dairy drinks. Amongst all the beverage samples, mercury was calculated as having the highest mean concentration of $2.93 \pm 0.34 \mu\text{g/L}$, owing to the lesser variation of concentrations detected, $1.44 - 4.88 \mu\text{g/L}$. The mean concentration of tin was the lowest detected within this group and levels of antimony recorded were similar to that of the fruit juices and soft drinks group.

In the bottled water sample group tin had a narrower range of concentrations recorded, however the mean concentration calculated for tin was the highest of all the beverage samples. The mean concentration of $4.34 \mu\text{g/L}$ was detected for tin, while conversely the mean values of mercury and antimony were the lowest recorded amongst all the samples, as shown in Table 1.

On comparison of the levels of the three heavy metals in the fruit juices and soft drinks, dairy drinks and bottled water samples with standards set by the WHO, USEPA and EU, the dairy drinks group were found in most violation of mercury 100%, 100% and 80% violating the EU, WHO and USEPA guidelines respectively. Fruit juices and soft drinks were found 89.2%, 43.2% and 89.2% in violation of WHO, USEPA and EU permissible levels of mercury respectively.

Tin however was in most violation in the bottled water group with 100% of samples violating the WHO permissible levels and 90% and 86.5% estimated violations within the dairy drink and fruit juices and soft drink groups respectively. Antimony on the other hand was found to be generally low in comparison to the other heavy metals detected, with none of the samples violating the guideline values.

The 'worst case scenario' estimation of the intake of the heavy metals as a result of consumption of beverages from each sample group, on an average weekly basis volume of 4.5 L (1.5 L of the three most contaminated beverage products) was 26.63 µg/L, 5.64 µg/L and 17.79 µg/L respectively, as

DISCUSSION

On analysis of the levels of antimony, tin and mercury detected in the beverage samples, it was found that the concentration of heavy metals varied considerably between each sample group. Some samples were below the recommended safety limits, others within this and some exceeding the threshold limits established by the European Union, World Health Organization and the US Environmental Protection Agency guidelines.

The levels of antimony recorded in this study were found to be within the limits stipulated by the WHO (20 µg/L), EU (5 µg/L) and USEPA (2 µg/L) for antimony in drinking water (**WHO, 2003; USEPA, 2011**). These levels reported however, were much lower than the antimony levels recorded in the study by **Hansen et al. (2010)**, despite the beverage samples similarly having been packed in PET containers. The different instrumentation techniques may have accounted in part for the difference in antimony levels detected.

The intake estimates for antimony calculated using the arithmetic mean for a Nigerian consuming one and half litres of beverages per week was 5.64 µg/L, which was found to be in line with the World Health Organization recommended daily tolerable intake of antimony at 6.0 µg/kgbw/day (**Egan et al, 2002**).

Alarming the mercury levels analysed in 100% of dairy drinks and 89.2% fruit juices and soft drinks were found to violate both the WHO (1 µg/L), EU (1 µg/L) and USEPA (2 µg/L) regulations (**WHO, 2003; USEPA, 2011**). These results are contrary to findings by **Cheung et al. (2008)**, who reported extremely low mercury concentrations in Nigerian

beverages. Considering the daily intake of these beverages in particular dairy drinks by children, young adults and pregnant women, it is feared that long-term exposure may pose significant health risks.

Although fish and other seafood products have been documented as being the main source of mercury in the diet (**WHO, 1990**), this has been disproved by our findings due to the high levels of total mercury that were detected in both the dairy drinks group and fruit juices and soft drink samples.

Although previous authors have recorded detectable concentrations of tin in beverages such as tea, carbonates, fruit drinks, bottled water, herbal drinks and iced tea (MAFF UK 1998) these levels were all below 1 mg/kg and lower than the regulatory limit set by the WHO The Tin in Food Regulations (1992) of 200 mg/kg. In this study however, the levels of tin were found to violate 100%, 88.9% and 90% of bottled water samples, fruit juices and soft drinks and dairy products respectively, exceeding the WHO (2 µg/L) regulation.

The present study has confirmed that contrary to common belief, beverages sold and consumed in Nigeria are not free of contamination of the toxic heavy metals tin and mercury. The values of tin and mercury detected were both found in severe violation of WHO, USEPA and EU safety standards.

Possible routes that are believed to result in the contamination of beverages during the production process include the use of contaminated water, poor assaying of raw materials, poor hygiene, low quality packaging materials and inadequate storage conditions.

Imported beverages were also found to contain high levels of the contaminants, which implies that heavy metals are yet to be regulated and consequently Nigeria has become a dumping ground for beverages untested for these toxic heavy metals.

CONCLUSION

There is currently little information on the concentration of heavy metals in different drinks sold in Mathura markets. The study quantitatively determined the concentrations of antimony (Sb), tin (Sn) and mercury (Hg) in 60 different beverage samples and evaluated the extent of violation of guideline values. Analysis of the beverage samples for the presence of Sb, Sn and Hg was carried out using an atomic absorption spectrophotometer (AAS). The mean values detected for mercury, tin and antimony were 2.35, 3.88 and 0.50 µg/l in fruit juices and soft drinks; 2.93, 3.60 and 0.49 µg/l in dairy drinks; 0.94, 4.34 and 0.48 µg/l in bottled water samples respectively. While antimony detected in all products was below guideline values, mercury and tin were above the acceptable levels established by the World Health Organization, United States Environmental Protection Agency and European Union in most samples tested.

As the heavy metal content in beverages constitutes a significant source of exposure to the general population, increased consumption of beverages unregulated for such contaminants represents a worrying problem. Limited studies of the chronic effects of some of these heavy metals warrants further investigation to determine blood concentrations of highly susceptible population groups such as in children and pregnant women.

This study also calls for mandatory testing of heavy metals in beverages and food as a way of monitoring the extent of violation of guideline values. Tighter regulation on the composition of beverages locally produced and imported into India would help to greatly reduce the extent of this problem.

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HEAVY METAL CONTAMINATION OF SPICES

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SPICES AND CONDIMENTS

Sattvic spices are mild spices including basil, cardamom, cinnamon, coriander, cumin, fennel, fenugreek, fresh ginger and turmeric. Rajasic spices like black pepper and red pepper are normally excluded, but are sometimes used in small amounts, both to clear channels blocked by mucus and to counter tamas.

Poppy Seeds (Kashkash or Posta Dana)

Poppy is cultivated either for manufacture of opium or for seeds. The white seeds are very small. 1000 seeds weigh only 0.25 to 0.5 g. Besides moisture and organics they contain 1.03-1.45% or 1584 mg/100g Ca, 0.79-0.89% or 432 mg/100g P, 0.79-0.89% Fe, 29 mg/kg Mn, 22.9 mg/kg Cu, 15.6 g/kg Mg and 130 mg/kg Zn. They are used as food and as a source of fatty oil. They are utilized in breads, curries, sweets and confectionery.

Cumin Seeds (Jira, Zira or Safaid Zeera)

Cumin seeds are dried yellowish to greyish brown seeds of a small slender annual herb of the coriander family. Besides moisture and organics they contain 7.7% mineral matter with 0.9% Ca, 0.45% P, 0.48% Fe, 0.16% Na & 2.1% K. Due to aromatic odour and nutritive value they are used in all mixed spices and curry powders for flavouring soups, pickles and for seasoning breads and cakes.

Caraway Seeds (Shia Jira or Siya Zeera)

This jira is better than the above jira but is more expensive. Besides moisture and organics it contains 1.0% Ca, 0.11% P, 0.02% Na, 1.9% K and 0.09% Fe. Caraway has much sharper odour than cumin. It is widely used as a spice for culinary purposes and for flavoring bread, biscuit, cake and cheese.

Clove (Laumg, Lawang)

Clove is an air dried unopened flower bud obtained from an evergreen straight trunked tree that grows in Kerala and TN to height of 10-12 m. Besides moisture and organics it contains 0.7% Ca, 0.11% P, 0.01% Fe, 0.25% Na & 1.2% K. It is very aromatic, has a fine flavour and imparts warming qualities. In all Indian houses it is used as a culinary spice.

Coriander (Dhania)

Coriander seeds contain moisture, many organics, 0.08% Ca, 0.006% Fe, 0.44% P, 0.02% Na and 1.2% K.

Cardamom (Chhoti Elaichi)

It is lesser cardamom, green cardamom or Malabar cardamom. Besides moisture and organics it contains 0.3% Ca, 0.21% P, 0.01% Na, 1.2% K and 0.012% Fe. It is consumed for chewing, flavouring and as a spice.

Fennel (Saurf)

The dried ripe fruit (seed) of fennel herb contains, besides moisture and organics, 1.3% Ca, 0.48% P, 0.01% Fe, 0.09% Na and 1.7% K. It has a fragrant odour and a pleasant aromatic taste. So it is used as a mastiatory or for chewing alone or in pans.

Bishop's Weed or Ajowan

Ajowan is an annual herb bearing greyish brown fruits (seeds) which are used as spice. Besides moisture and organics it contains 1.42% Ca, 0.30% P and 14.6 mg/100 g Fe.

Curry Leaf (Kury Patta or Mitha Neem)

Curry leaf is the leaf of a small tree or shrub found almost throughout India. Besides moisture and organics, it contains 810 mg/100 g Ca & 600 mg/100g P. It is used as food flavourant and indigenous medicine.

Pomegranate Seed (Anardana)

Anardana comprises the dried seeds (dried with flesh) of pomegranate fruit. Besides moisture and organics, it contains 10 mg/100 g Ca, 12 mg/100 g Mg, 70 mg/100 g P, 0.3 mg/100 g Fe, 0.9 mg/100 g Na, 133.0 mg/100 g K, 0.2 mg/100 g Cu and 12.0 mg/100 g S. It is mostly used as a condiment for acidification of chutneys and certain curries as in case of tamarind and amchur.

Mace (Japatri, Jaivetri) and Nutmeg (Jaiphal)

Mace and nutmeg are two distinctly different species produced from a single fruit of an evergreen, aromatic nutmeg tree usually 9-12 metres high, but sometimes reaching a height of 20 metres or more. Mace is the dried reticulated aril of nutmeg. Nutmeg is the black shining shell of the seed of the peach or apricot like fruit. Besides moisture and organics mace contains 0.18% Ca, 0.10% P and 12.6 mg/100g Fe. Nutmeg contains 0.12% Ca, 0.24% P and 4.6 mg/100g Fe. Nutmeg and mace are used as condiment and in medicine. Mace is also chewed for masking foul breadth.

Sesamum (Til)

Sesame or sesamom is a tropical herbaceous plant cultivated esp. in India for its small oval seeds. Besides moisture and organics they contains 1450 mg/100g Ca, 570 mg/100g P and 10.5 mg/g Fe. They are used in flavouring bread and yielding an edible oil.

Neem Leaves

Neem (margosa) is a large tree of India, all parts of which are useful to man. The leaves act as a natural pesticide, the fruit and seeds yield a medicinal oil, the bark is used to make a tonic, and the trunk exudes a gum. The leaves contain 50 mg/100g Ca, 80 mg/100g P and 47.1 mg/100g Fe.

CURRY WORRIES - HIDDEN DANGERS IN INDIAN SPICES

Indian spices with poisonous additives have been in the news lately.

The recent ban on Indian chilli powder imports to the UK sent alarm bells ringing in Indian kitchens across the world. That food adulteration exists is no surprise. From watered milk to tales of wedding parties being poisoned by cooking oil, stories of adulteration have always been

Turmeric and chilli powder, the two staples of every Indian kitchen, are the likely culprits. Chilli powder is always suspect because the consumers' preference for a deep red has led to its being dyed with an extremely carcinogenic dye. Called Sudan 1, it has been linked with health concerns, not least of which is the increased risk of cancer.

Turmeric has an even more deadly secret. Lead chromate adds not only color and weight, but the very real risk of lead poisoning. Even if this most toxic salt of lead is not the additive, it could be metanil yellow which is less lethal but nevertheless harmful and illegal. The list goes on, from Argemone seeds mixed with mustard causing paralysis and even death, to sawdust in the coriander powder.

How then do we enjoy our curry without the harmful effects? We can go back to basics: Get whole spices and grind our own. We get the freshest flavors and aromas, but it takes time.

Another option is to go organic. The regulation imposed on the organic industry translates into stringent packaging and purer products. The market for organic products is growing in India. Organic products taste more authentic, but are costlier.

Thankfully it is not hard to find a decent product at a decent price. The first rule of thumb is not to buy unpackaged or “loose” items. Reliable companies have the FPO, ISI or Agmark seal of approval. These are the most commonly used certifications and do give a third party check and approval of the products. Packaging should also include packing and expiration dates. What we lose in convenience and economy is the unique flavor of individually ground and mixed spices, but at least the safety of our family is not compromised.

[illegible]

Most parents have already cleared their children's toy boxes of playthings containing lead-laden plastics or paint. But according to a new study published in *Pediatrics*, the toxic heavy metal may continue to lurk in other, less expected sources in the home — like in the kitchen pantry (**Park, 2010**).

After several reports of lead poisoning in Indian children in the Boston area were linked to consumption of Indian spices, researchers at Children's Hospital Boston and the Harvard School of Public Health decided to measure the amount of lead in the seasonings as well as in ceremonial powders commonly used to mark newborn Indian infants for religious and cultural purposes.

The team visited 15 Indian specialty stores in the Boston area and purchased 71 cultural powders and 86 spices and food products. About 25% of the food items including spices such as cardamom, fenugreek and chili powder, contained more than 1 microgram of lead per gram of product. About 65% of the ceremonial powders, including sindoor which is used as a symbol of marriage, contained the same amount. Those levels are below the EU's acceptable threshold of 2 to 3 mcg/g of lead, but the study's authors say that regardless of the amount, the presence of lead in these products should be a reason for concern, since they could potentially add to exposure from other sources of the neurotoxin in a child's environment. Three of the food products the team tested exceeded the EU guidelines: two brands of sindav salt and one type of sindaloo powder, or sea salt.

With repeated exposure at high enough levels, lead can cause cognitive damage and behavioral changes in children. In most cases, lead poisoning can be treated by reducing the child's exposure and by making sure he or she eats a balanced diet with sufficient iron, calcium and vitamin C deficiencies in these can increase the body's absorption of lead. In extreme cases of extended lead exposure, doctors use drugs called chelating agents which bind to the lead and pull it out of the body through urine. In severe cases of prolonged poisoning, however, the cognitive and developmental damage may be permanent, says Dr. Cristiane Lin, the study's lead author, who is now at Seton Medical Center in Austin, Texas.

Studies have shown that a blood level of 10 mcg of lead per deciliter of blood is associated with potentially irreversible harm, although recent studies have shown that as little as 5 mcg/dL can also be dangerous. By extrapolating from their data, researchers estimated that if a population of children under age 4 was routinely exposed to Indian spices or ceremonial powders, the additional ingestion of lead would lead to a threefold increase — from 0.8% to 2.8% — in the %age of children with a blood level of lead over 10 mcg/dL. "Our message is to say, Be aware of these products that may contain lead," says Lin. "From a pediatrician's perspective, it's good to push for screening of nonpaint sources of lead."

Although the majority of lead poisoning cases in the U.S., about two-thirds, occur when young children lick or ingest lead-containing paint as it peels or chips off walls, the new study reminds doctors and parents that they need to be aware of less obvious sources. Imported products such as the ones studied by the Boston group are a particular problem, since environmental standards around the world are not the same as they are in the US. In countries like India, for example, leaded gasoline is still commonly used in cars (in the US it was replaced by unleaded fuel in the 1970s), and the lead from car exhaust can seep into the ground, saturating the soil in which food plants, including those that are dried and ground into spices,

are grown. Such environmental exposure is the most likely source of lead in the products they tested, say the authors.

Currently the Food and Drug Administration which oversees the safety of food products imported into the U.S., does not have specific guidelines for screening lead in dried products like spices. That is because the FDA feels there is no safe level of lead in dried products, since studies have not yet established that lead exposure doesn't lead to adverse health effects.

The agency has different thresholds for acceptable lead levels depending on the product and how it is to be used, says FDA spokesperson Ira Allen. For example, in 2006 the agency lowered its acceptable level of lead in candy which children are likely to eat in large amounts. The FDA also reaffirmed its position that paints used in candy labels should be entirely lead-free, or they would be in violation of the Federal Food, Drug and Cosmetic Act. "We look at imports and we look for lead and other elements," says Allen. "But we do it on a targeted basis, and some of that basis is how the product is intended to be used."

Since last spring, the agency has been reviewing its protocols for spices, to determine whether the risk of contamination or exposure to elements such as lead from dried products imported from overseas warrants more scrutiny. "We have extensive surveying of imported foods at major ports," says Allen. "Obviously we can't look at everything, but we do target inspection based on where the food comes from and what the history of the product is, and we do ban certain products."

The levels of lead found in Indian spices and powders in the current study may not set off the FDA's alarms, but, as Lin and her team note, it should alert pediatricians to diagnosing lead poisoning and getting exposed youngsters into treatment sooner.

After paints, toys and pet food, now Indian spices and ceremonial powders have entered the long list of sources where lead has been found. The recently published study in the journal *Pediatrics* identified Indian spices and cultural powders as a more recent source of lead poisoning. While the study is reported to have been undertaken after several reports of lead poisoning in Indian children in Boston were found, experts and healthcare providers have also seen cases of lead poisoning due to exposure to Indian spices and powders in California.

Julie Kurko, health services manager at Alameda County Lead Poisoning Prevention Program said, "Though it is not a widespread problem we have seen such cases of lead poisoning every few years and I think mostly the problem has been with turmeric."

"CDPH (California Department of Public Health) has identified cases of lead poisoning associated with lead contaminated spices including chili powder and turmeric," said Dr Linda Crebbin, chief of CDPH's Care Management Section, Childhood Lead Poisoning Prevention Branch. "California cases of lead poisoning from turmeric have occurred in adults, children and a pregnant woman." The U.S. Food and Drug Administration (FDA) has set the maximum exposure limit for children at 6 micrograms per day (mcg/day) for children and 75 mcg/day for adults.

Crebbin also pointed out that turmeric associated with all of the California cases was obtained directly from India, Nepal and Bangladesh rather than being sold in local stores. Since they were in unmarked bags, it was not possible to identify a manufacturer or a distributor.

Most experts noted that lead can penetrate into spices if they are grown in lead contaminated soil or can be inadvertently added during the manufacturing or drying process or may be intentionally added to add color or weight to the product. Some health care providers also

observed that many of these products are brought into the United States when people go back to their home countries or when their families come to visit them here.

Lead poisoning in children and adults may be completely asymptomatic, and most people with lead poisoning do not look or act sick. But even lead levels which do not cause noticeable symptoms can cause problems in infants and children such as decreased intelligence quotient (IQ), learning difficulties and behavior problems. It can also cause problems such as kidney disease and high blood pressure.

At higher blood lead levels, lead poisoning may cause symptoms such as abdominal pain, nausea, tiredness, headaches, irritability, and at very high levels it can cause seizures, coma and even death.

The only way to determine if someone has lead poisoning is by a blood lead test. Young children are considered most at risk because of their hand to mouth activity. So, even if parents are not directly applying these powders to children, they can be easily transferred to them.

“Powders with high amounts of lead are particularly hazardous because powders are easily dispersed and transferred from hand to mouth, and they also have the potential to be inhaled,” Crebbin said. “Since young children have increased hand to mouth behavior and they also absorb more lead than adults from their gastrointestinal tract, they are at increased risk of lead poisoning.”

Crebbin also noted that some of the yellow chalk/powders (reported to be made of rice and turmeric) and Sindoor (orange or red colored powder used on forehead, scalps and face for ceremonial purposes) that were tested by the state laboratory contained up to 94 % of lead.

Louis Girling, deputy health officer and medical director for Child Health and Disability Prevention Program (CHDP) at Santa Clara County pointed to a case in which they recently realized that a child was being poisoned with lead through Indian ceremonial powder that the family was applying to his forehead and face. The child who is now three years old was picked up at CHDP’s routine screening when he was under 1. CHDP is a preventive program that delivers periodic health assessments and services to low-income children and youth in California.

Girling explained that once a child is detected with elevated levels of lead the public nurse would offer basic counsel to the family regarding common sources of lead exposure and would also recommend foods rich in iron and calcium that can reduce lead absorption in the blood. CHDP also informs California Children’s Services (CCS) if a child has higher lead levels. According to Girling, the CCS can provide funds for a low-income group child to be treated by the authorized medical specialists.

The State Childhood Lead Poisoning Prevention Branch (CLPPB) also geared at preventing and eliminating lead poisoning notifies and works with the State Food and Drug Branch, the U.S. FDA and the U.S. Consumer Product Safety Commission when it encounters previously unrecognized sources of lead poisoning.

Crebbin said, “The state CLPPB also notifies all of the county Childhood Lead Poisoning Prevention programs throughout the state. The environmental and other investigators in counties throughout the state can then look for the products during investigations of lead poisoning cases and also during inspections of restaurants, stores and flea markets.”

The Childhood Lead Poisoning Prevention Programs in different counties also undertake outreach initiatives to consumers, stores, healthcare providers and merchants in their jurisdictions. While there are many programs that can offer support for prevention or treatment

of lead poisoning particularly for children, the FDA, the agency that oversees the safety of foods imported to the United States, doesn't have an established safe level of lead.

"The FDA will typically evaluate the potential health hazard regarding the lead in the product based on the concentration, nature of consumption, the quantity consumed and the risk to population who consumes the product," Dr. Richard Jacobs a retired chemist who worked with FDA for 47 years explained. "If the product poses a health hazard it can take regulatory action. For some findings, for example where it is known that lead arsenate, a prohibited pesticide, was used on food, the FDA could take action at a much lower level."

FDA spokesperson Michael L. Herndon said that FDA is typically most concerned with products that are consumed in large amount or have the potential to deliver a large accumulation of lead in a short period of time.

Jacobs pointed out that though 1.00 ppm or less of lead in imported spices generally won't pose an excessive exposure and therefore would not be typically actionable, but in case of infants action might be taken at levels far less than one ppm.

Sometimes lead may be found in packaging of spices and ceremonial powders. As part of our investigation for this story, New America Media collected 22 samples of spices and ceremonial powders of varying brands, purchased from three different stores in the Bay Area. The Center for Environmental Health (CEH) tested the spices and Sindoor samples using an X-ray fluorescence spectrometer, and could not find anything in the spices because the device could not detect lead levels lower than three or four ppm. But Caroline Cox, research director at CEH, pointed out that ink on the packets of one of the brands that was tested had a high level of lead content in it.

"The red parts of the Pooja brand package had quite high in lead upto 9,000 parts per million as compared to the 100 ppm required by the Toxics in Packaging Law," said Cox. "Since the ink is on the outside of the package, I think the issue would be transfer to hands rather than transfer to spices inside. I would suggest putting the spices in a container other than the original bag for the Pooja spices and washing hands carefully after handling the bag."

The FDA only regulates lead in packaging if it is contaminating food. Otherwise, says Jacobs, it goes under the jurisdiction of the Consumer Product Safety Commission.

While the findings are not conclusive, experts recommended caution especially when it comes to bulk spices and powders that come in unmarked packages. And if there are doubts, especially where children are concerned, a blood test is not a bad idea.

Desi Products with High Lead Content

Fair is fair. Three years ago we blogged about how researchers discovered something desi households have known for years, turmeric is good for your health. So when a study comes out that turmeric may not necessarily be as good as advertised, we're here to report on that. As it turns out, the turmeric the previous researchers used was probably not bought in some (or, even worse, all???) Indian grocery stores in the US.

Now, a study published today in the journal Pediatrics said young children who regularly ingest some imported Indian spices may be exposed to lead — a dangerous neurotoxin. The study, conducted from 2006 to 2008, followed patients from the Pediatric Environmental Health Center at Children's Hospital in Boston who had ingested or been exposed to Indian spices and powders.

One 12-month-old boy in the case study was found to have lead poisoning after regularly eating spices such as tumeric, black mustard seed and asafetida.

Turmeric, mustard seeds and asafetida are not the only culprits here. Indian women often use “sindoor” or “kumkum”. Whether it bestows their husbands with long lives is debatable. What is scientifically proven is the potential for lead poisoning for women.

But of greater concern to researchers are religious powders like cherry-colored “sindoor” — which is applied cosmetically on the skin and which **Tilak** also uses routinely in her home. **Some of these ritual powders comprise 47 to 64% lead**, according to the study, and can be particularly dangerous when applied on young children.

Bringing these two to a confluence, are the haldi kumkum ceremonies celebrated in multitudes on Indian households across the US. If it turns out these products have that high levels of lead as advertised, these ceremonies ultimately could very well turn to be annual lead poisoning orgies.

Having said that, we have to point out that most of this is conjecture, and this study was conducted in the Boston area. It is unknown if any of the products belonged to stores outside that area or even within that area, for that matter. By law, food and cosmetic products imported into the country have to be approved by the FDA. The FDA does not approve products with such a high lead content, or any lead for that matter.

Turmeric is practically an everyday product in most South Asian households. How does this news affect the way you view and use turmeric particularly for households with children? As for some of our female readers, if we use “sindoor” or related products, does this affect anything or will we continue using it? Or are we of the opinion that such studies are “alarmist”?

Imported Indian spices and Tests for Lead

Indian spices and ceremonial powders have entered the long list of sources where lead has been found. The study in the journal *Pediatrics* identified Indian spices and cultural powders as a more recent source of lead poisoning. You can read the original study or its abstract, "Pediatric Lead Exposure From Imported Indian Spices and Cultural Powders."

Four cases of pediatric lead poisoning from Indian spices or cultural powders are described in that study published in the journal *Pediatrics*. Chronic exposure to spices and cultural powders may cause elevated BLLs. A majority of cultural products contained $>1 \mu\text{g/g}$ lead, and some sindoor contained extremely high bioaccessible lead levels. Clinicians should routinely screen for exposure to these products.

The *Pediatrics* journal study is reported to have been undertaken after several reports of lead poisoning in Indian children in Boston were found. How does lead get into the spices? Actually, the lead can penetrate into spices if they are grown in lead contaminated soil or can be inadvertently added during the manufacturing or drying process.

Also lead may be intentionally added to add color or weight to the product. Some health care providers also observed that many of these products are brought into the United States when people go back to their home countries or when their families come to visit them here. Many people seeking to save money on the higher cost of organic turmeric at local health food stores and food markets go to the ethnic grocery stores that import spices from India and other countries and buy brands imported from other countries.

For example, many Indian grocery and ethnic food markets in Sacramento sell a wide variety of turmeric and curry brands and blends. Labels usually are in English. And a huge bag of turmeric is priced low compared to a small bottle of organic turmeric sold in supermarkets or food stores in small spice bottles.

How do we know what brands were tested for lead, even if we pay more money for a tiny spice bottle of organic turmeric or if we buy capsules of curcumin or turmeric in supplement forms from various vitamin/supplement companies? How do we know who tested and measured the spices for bioavailability, absorption, and lead or other toxic metal content that could have come from the growing soil or added as a filler or a coloring agent?

Consumer Lab tested turmeric and curcumin for lead

The biggest problem with turmeric is that those tested had little curcuminoid compounds in them. Curcumin is supposed to do the most good as far as the anti-inflammatory health benefits are said to happen from consuming a small amount of curcumin, usually found in turmeric.

Supplements containing the herb turmeric or its key compound, curcumin, have become popular in the U.S. ConsumerLab.com cautioned that two out of ten turmeric products recently selected for quality testing were found to provide only 7.7% and 14.7%, respectively, of expected curcuminoid compounds. Unlike some turmeric supplements tested in the past, however, none of the recently tested products exceeded strict limits for lead and cadmium contamination.

Turmeric has been shown to have anti-inflammatory and anti-oxidant activities

Recent research has focused on curcuminoids, the specific compounds in turmeric including curcumin which give turmeric its orange-yellow color. Studies suggest a role for curcuminoids in the treatment of a range of diseases including ulcerative colitis, rheumatoid arthritis and chronic anterior uveitis (an autoimmune disease of the eye), as well as for indigestion. According to Nutrition Business Journal, sales of turmeric and curcumin supplements grew to \$59 million in 2009, up from \$43 million in 2008.

How do we know whether we're getting a product with curcumin in the turmeric?

The products that failed Consumer Lab.com's testing would deliver only a small fraction of the doses expected from their labels. The problem also is with the poor absorption of curcumin. We would need specially formulated products that can show us how that product will be absorbed. And testing needs to prove the bioavailability.

ConsumerLab.com calculated the cost to obtain a 500 mg dose of curcuminoids, which ranged from 13 cents to 52 cents among products that passed testing, some of which included bioavailability enhancers. For the two products that failed testing, the costs were \$3.44 and \$7.88, due to the small amounts of curcuminoids that they actually contained.

TURMERIC

Turmeric (*Curcuma longa*) is a rhizomatous herbaceous perennial plant of the ginger family, Zingiberaceae (**Chan, 2009**). It is native to tropical South Asia and needs temperatures between 20°C and 30°C (68°F and 86°F) and a considerable amount of annual rainfall to thrive (**Materia Indica, 1826**). Plants are gathered annually for their rhizomes, and propagated from some of those rhizomes in the following season.

When not used fresh, the rhizomes are boiled for several hours and then dried in hot ovens, after which they are ground into a deep orange-yellow powder commonly used as a spice in curries and other South Asian and Middle Eastern cuisine, for dyeing, and to impart color to mustard condiments. Its active ingredient is curcumin and it has a distinctly earthy, slightly bitter, slightly hot peppery flavor and a mustardy smell.

In medieval Europe, turmeric became known as **Indian saffron** since it was widely used as an alternative to the far more expensive saffron spice.

Etymology

India and Pakistan are significant producers of turmeric (**Tahira, 2010**) which has regional names based on language and country. The name appears to derive from the Latin, *terra merita* (merited earth) or *turmeryte*, possibly related to saffron (**Dictionary.com, 2012**). As turmeric is a natural botanical compound, it is not patentable.

Production and Trade

India is the biggest producer of turmeric, supplying 94% of the world's demand. It is cultivated on a commercial scale and enters the market usually in the form of dried rhizomes which are then prepared according to their end use. It is widely used in South Asia as a spice.

The main producing countries of turmeric include India, Pakistan and Bangladesh. India is the biggest producer, supplying some 20,000 t each year. It enters the international market in the form of dried whole rhizomes, or as ground rhizomes. The major importers of this spice are Iran, Sri Lanka, Middle Eastern and North African countries.

It is cultivated commercially as an annual crop, by planting small rhizomes or pieces of rhizome either on flat soil or in furrows between ridges. The growing plants require heavy manuring to get the best yield possible.

Turmeric is ready for harvesting 7 to 10 months after planting, when the lower leaves turn yellow. Harvesting is done by digging the rhizomes up. Leafy tops are then cut off and the roots and adhering earth is removed. Rhizomes are then washed. Some of these are retained for replanting as a future crop. The remainder are processed into turmeric.

To develop the yellow colour and characteristic aroma, cleaned rhizomes are cooked in boiling water for one hour under slightly alkaline conditions. The cooked rhizomes are then dried either artificially or in the sun for 6 to 8 days. Dried rhizomes are polished to smooth their exterior and also to improve the colour. They are then sold in this form or ground into powder.

Indian Turmeric Powders

Indian turmeric powder is produced by grinding the properly cleaned, graded and polished turmeric fingers. In the polishing process the upper layer of the turmeric fingers gets peeled off. If turmeric fingers are ground as is without any polish, black spots are visible in the powder which are not there if the fingers are polished before grinding.

Nizam Turmeric Powder

This quality is produced by grinding the cleaned and graded polished Nizam Turmeric Powder / Nizam quality turmeric fingers. This quality is popularly known as Nizam Quality as is largely grown in and around Nizambad area of Andhra Pradesh state which is one of the leading turmeric producing states in India. Nizam quality turmeric fingers when finely ground, gets transformed into bright yellow shade powder which is a characteristic color of Nizam origin turmeric.

Quality Parameters

Moisture	Maximum 10%
Fineness	98% passes through 80 mesh sieve
Total ash content	Maximum 7.0 %
Acid insoluble ash	Maximum 1.5%
Starch	Maximum 60%
Lead chromate test	Negative

Sudan Dye I,II,III,IV
Salmonella

Absent
Absent in 25 g

Rajapuri Salem Turmeric Powder

Rajapuri Salem Turmeric Powder is considered to be the most premium quality which is available in India. It is largely grown in Maharashtra state of India especially in and around Sangli area. On grinding cleaned, graded and polished Rajapuri Salem turmeric finger we get a saffron yellow shaded and a strong flavored turmeric powder which is a characteristic of this quality. Its color and flavor makes it stand apart from all the other available qualities in India. It is the most preferred quality by all premium spices brands which sell in India.

Quality Parameters

Moisture	Maximum 10%
Fineness	98% passes through 80 mesh sieve
Total ash content	Maximum 7.0 %
Acid Insoluble Ash	Maximum 1.5%
Starch	Maximum 60%
Lead chromate test	Negative
Sudan Dye I,II,III,IV	Absent
Salmonella	Absent in 25 g

In the past we had some discussions about using the spice turmeric as something that possibly had properties that might help achalasia. It seems that because a lot of the spices come from India where they still use leaded gas in their cars, the spices may have too much lead in them, especially for children. Not a big deal for most adults or those that just use them on occasion in a western diet. If you eat a lot of foods with Indian spices such as turmeric and curry you may want to consider the lead content of them. This would be most important for anyone that is using these as supplements especially for children. There are a lot of spices and herbs that come from areas that have lead exposure. Something to consider, especially for our children.

Usage

Turmeric root has been used for centuries in India as a dye, spice and herbal remedy. The root is dried and ground into a yellow-orange powder and is a common ingredient in curry and other Asian dishes. The main medicinal compound in turmeric is curcumin which is a powerful antioxidant, antibacterial and anti-inflammatory, according to the "Natural Standard Herb & Supplement Reference: Evidence-based Clinical Reviews." Turmeric powder and curcumin extract are used to treat heartburn, stomach upset and a variety of gastrointestinal complaints. Acid reflux disease, or chronic heartburn, is a significant cause of esophageal strictures, so turmeric might help reduce the risk. Furthermore, turmeric is a good anti-inflammatory that reduces antioxidants, deters infection and promotes healing, which are potentially beneficial for esophageal strictures. Ask your doctor if turmeric is contraindicated if you have chronic inflammation of the esophagus.

Culinary Uses

Turmeric powder is used extensively in South Asian cuisine.

Turmeric grows wild in the forests of South and Southeast Asia. It is one of the key ingredients in many, Pakistani, Indian, Persian and Thai dishes. Ancient Indian medicine, Ayurveda has recommended its use in food for its medicinal value, much of which is now being researched in the modern day. Its use as a coloring agent is not of primary value in South Asian cuisine.

In Indonesia, the turmeric leaves are used for Minangese or Padangese curry base of Sumatra, such as rendang, sate padang and many other varieties.

Although most usage of turmeric is in the form of rhizome powder, in some regions (especially in Maharashtra, Goa, Konkan and Kanara), leaves of turmeric are used to wrap and cook food. This usually takes place in areas where turmeric is grown locally, since the leaves used are freshly picked. This imparts a distinct flavor.

In recipes outside South Asia, turmeric is sometimes used as an agent to impart a rich, custard-like yellow color. It is used in canned beverages and baked products, dairy products, ice cream, yogurt, yellow cakes, orange juice, biscuits, popcorn color, sweets, cake icings, cereals, sauces, gelatins, etc. It is a significant ingredient in most commercial curry powders. Turmeric is mostly used in savory dishes, as well as some sweet dishes, such as the cake sfouf.

Although typically used in its dried, powdered form, turmeric is also used fresh, like ginger. It has numerous uses in Far Eastern recipes such as fresh turmeric pickle which contains large chunks of soft turmeric.

Turmeric is used to protect food products from sunlight. It is coded as E100 when used as a food additive, indicating how it is used as a food coloring since it normally gives food slightly yellow color. The oleoresin is used for oil containing products. The curcumin/polysorbate solution or curcumin powder dissolved in alcohol is used for water containing products. Over-coloring such as in pickles, relishes and mustard, is sometimes used to compensate for fading.

In combination with annatto (E160b), turmeric has been used to color cheeses, yogurt, dry mixes, salad dressings, winter butter and margarine. Turmeric is also used to give a yellow color to some prepared mustards, canned chicken broths and other foods, often as a much cheaper replacement for saffron.

Turmeric is widely used as a spice in South Asian and Middle Eastern cooking. Many Persian dishes use turmeric as a starter ingredient. Almost all Iranian fried dishes typically consist of oil, onions and turmeric followed by any other ingredients that are to be included. In Nepal, turmeric is widely grown and extensively used in many vegetable and meat dishes for its color, as well as for its potential value in traditional medicine. In South Africa, turmeric may be used to give boiled white rice a golden color.

In India, turmeric plant leaf is used to prepare special sweet dishes, patoleo, by layering rice flour and coconut-jaggery mixture on the leaf, and then closing and steaming it in a special copper steamer.

Medical Uses

Turmeric has been used in India for hundreds of years and is a major part of Ayurvedic medicine. It was first used as a dye and then later for its possible medicinal properties.

Phytochemicals found in turmeric have been investigated in preliminary research for their potential effects on diseases (NCCAM, 2012) such as cancer, arthritis, diabetes (Boaz, 2011) and other clinical disorders. As an example of such basic research, turmeric reduced the severity of pancreatitis-associated lung injury in mice.

According to one report, research activity into curcumin and turmeric is increasing. The US National Institutes of Health currently has registered 71 clinical trials completed or underway to study use of dietary curcumin for a variety of clinical disorders (dated September 2012).



Turmeric rhizome

Some research shows compounds in turmeric to have anti-fungal and anti-bacterial properties; however, curcumin is not one of them.

In another preliminary research example, curcumin is being studied for whether it alters the response to chemotherapy in patients with advanced bowel cancer, as found in a laboratory study.

Cosmetics

Turmeric paste is traditionally used by Indian women to keep them free of superfluous hair and as an antimicrobial. Turmeric paste, as part of both home remedies and Ayurveda, is also said to improve the skin and is touted as an anti-aging agent. Turmeric figures prominently in the bridal beautification ceremonies of India, Nepal, Bangladesh and Pakistan. Staining oneself with turmeric is believed to improve the skin tone and tan. Turmeric is currently used in the formulation of some sunscreens.

The government of Thailand is funding a project to extract and isolate tetrahydrocurcuminoids (THC) from turmeric. THCs are colorless compounds that might have antioxidant and skin-lightening properties, and might be used to treat skin inflammations, making these compounds useful in cosmetics formulations.

Dye

Turmeric makes a poor fabric dye, as it is not very light fast. However, turmeric is commonly used in Indian and Bangladeshi clothing, such as saris and Buddhist monks' robes.

Ceremonial Uses

Turmeric is considered highly auspicious in India and has been used extensively in various Indian ceremonies for millennia. Even today it is used in every part of India during wedding ceremonies and religious ceremonies.

It is used in Pujas to make a form of Hindu god Ganesha. Lord Ganesha, the remover of obstacles, is invoked at the beginning of almost any ceremony and a form of Ganesha for this purpose is made by mixing turmeric with water and forming it into a cone-like shape.

Gaye holud (literally "yellow on the body") is a ceremony observed mostly in the region of Bengal comprising Bangladesh and Indian West Bengal. The gaye holud takes place one or two days prior to the religious and legal Bengali wedding ceremonies. The turmeric paste is applied by friends to the bodies of the couple. This is said to soften the skin, but also colors them with the distinctive yellow hue that gives its name to this ceremony. It may be a joint event for the

bride and groom's families, or it may consist of separate events for the bride's family and the groom's family.

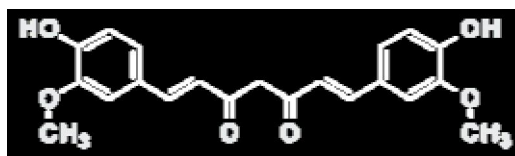
During the south Indian festival Pongal, a whole turmeric plant with fresh rhizomes is offered as a thanksgiving offering to Surya, the Sun god. Also, the fresh plant sometimes is tied around the sacred Pongal pot in which an offering of pongal is prepared.

In southern India, as a part of the marriage ritual, dried turmeric tuber tied with string is used to replace the Mangalsutra temporarily or permanently. The Hindu Marriage Act recognizes this custom. Thali necklace is the equivalent of marriage rings of west. In western and coastal India, during weddings of the Marathi and Konkani people turmeric tubers are tied with strings by the couple to their wrists during a ceremony called Kankanabandhana.

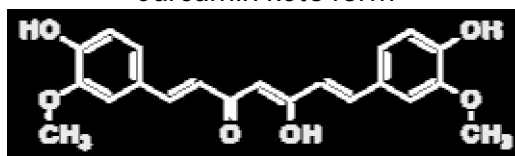
Modern Neopagans list it with the quality of fire, and it is used for power and purification rites.

Friedrich Ratzel in *The History of Mankind* reported in 1896 that in Micronesia the preparation of turmeric powder for embellishment of body, clothing and utensils had a highly ceremonial character. He quotes an example of the roots being ground by four to six women in special public buildings and then allowed to stand in water. The following morning, three young coconuts and three old soma nuts are offered by a priestess with prayer, after which the dye which has settled down in the water is collected, baked into cakes in coconut molds, wrapped in banana leaves, and hung up in the huts till required for use.

Composition



Curcumin keto form



Curcumin enol form

Turmeric contains up to 5% essential oils and up to 5% curcumin, a polyphenol. Curcumin is the active substance of turmeric and curcumin is known as C.I. 75300, or Natural Yellow 3. The systematic chemical name is (1E,6E)-1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione.

It can exist at least in two tautomeric forms, keto and enol. The keto form is preferred in solid phase and the enol form in solution. Curcumin is a pH indicator. In acidic solutions (pH < 7.4) it turns yellow, whereas in basic (pH > 8.6) solutions it turns bright red.

Adulteration and Substitutes

In India, the deliberate contamination and bulking out of turmeric is a serious problem in local markets. On an international scale, the problems may not be so serious, but closely related species are frequently substituted for true turmeric. Fortunately, chemical analysis can to some extent establish how pure a product is.

Ground turmeric is the most vulnerable product, particularly in local markets. Here, it is not uncommon to find turmeric powder adulterated with lead chromate, yellow earth, sand or even cheap talc.

In the international market, concern over possible adulteration is associated mainly with the mixing of related *Curcuma* species containing similar pigments. Species that have been used as a substitute include *C. xanthorrhiza*, *C. aromatica* and *C. zedoaria*.

In Asian producing countries, these three species are used as a source of starch, dyes and in folk medicine as a substitute for true turmeric. It is often difficult to identify these species by microscopic examination of the powder. But, adulteration of true turmeric by *C. aromatica* and *C. zedoaria* can be detected by chemical methods.

Heavy Metal Contaminants in Turmeric

Table 1. Permissible limit in parts per million by weight of the metal contaminant in turmeric

1. Lead		5. Zinc	
Turmeric whole and powder	10.0	Turmeric whole and powder	25.0
2. Copper		6. Cadmium	
Turmeric whole and powder	5.0	Turmeric whole and powder	0.1
3. Arsenic		7. Mercury	
Turmeric whole and powder	0.1	Fish	0.5
4. Tin		Other foods	1.0
Turmeric whole and powder	Nil	8. Methyl Mercury	
		All foods (Calculated as the element)	0.25

100 turmeric powder samples were picked up from Mathura markets and were tested quantitatively for heavy metals. Around 30 % of the samples were found to be adulterated, particularly with lead and chromium crossing the limits to an alarming extent.

Recommendations

Curry dishes are rich in turmeric, although we can also take the herb in capsule form. Consumed as a health supplement, recommended dosages of turmeric powder are usually between 250 to 500 milligrams daily. The toxicity of turmeric has not been established because it causes so few side effects in large dosages. We should ask a herbalist about appropriate daily dosages.

BLACK PEPPER

Black pepper spices is one of the most internationally traded spice belonging to the family of Piperaceae. The plant is cultivated for its fruit and is popularly used as a spice and seasoning after drying.

Indian Name: Kali Mirch

Botanical Name: *Piper nigrum*

Family Name: Piperaceae

Parts Used: Fruit

Habitat: Southern states of India, Vietnam and few other Asian countries

The Plant

The black pepper plant is grown in a soil that is moist and well drained and is rich in organic matter. The normal height of the plant is around four meters. The leaves of the plant is five to ten centimeters long and three to six centimeters broad.

The plants usually bear plants every fourth or fifth year and continues to do so for seven years. Every stem consist of 20 to 30 fruiting spikes.

Origin

Since many centuries black pepper spices has been cultivated in Malabar region of Kerala in south India. The pepper that has been cultivated is white and black pepper whereas green and red pepper is a recent invention.

Pepper spices is also grown in South East Asia for more than two thousand years. Malaysia and Indonesia are the major and the earliest producers of pepper in South East Asia. In 20th century the cultivation of Black Pepper spices reached to Thailand, Vietnam, China and Sri Lanka. Outside Asia, Brazil is the major producer of black pepper. But taking world as a whole India followed by Indonesia are the major producers.

Composition

The essential oil content of black pepper spices is 3%. The major constituent of essential oil is sesquiterpenes. Other constituents that define the aroma and odor are monoterpenes hydrocarbons that includes sabinene, terpinene, α -pinene, myrcene, β -pinene, limonene, 3-carene derivatives of monoterpene like borneol, carvone, carvacrol, 1,8-cineol, linalool.

Odorants that are chiefly found in black pepper spices are linalool, α -phellandrene, limonene, myrcene and α -pinene. In white pepper the essential oil is nearly 1%.

Black Pepper Cultivation

Black pepper spices after being moderately riped are dried at moderate temperature. Just after the berry starts to show the traces of redness, the fruit is plucked and stored in room temperature and thereafter soaked into boiled water to give surface disinfection. This results in the fermentation which finally leads to the changing of green pepper fruits into black. Later the pepper is dried in direct sunlight. For good flavor and aroma pepper should be plucked when the fruits show the first sign of yellow orange. This type of pepper is mainly produced in India, whose corns are larger than typical black pepper corns.

Other Pepper Variants

White Pepper

When pepper fruits are completely ripened, they are used for making white pepper. For processing white pepper, firstly the outer hull or mesocarp is removed. After this, in a slow moving water berries are soaked which results in the disintegration of the mesocarp which is later removed mechanically from the kernel (endocarp). The seed grain so remained is sold as white pepper. In white pepper the pungency of the black pepper is retained whereas flavor is altered due to loss of aroma compounds

Green Pepper

To process green pepper it is harvested very early. The freshly harvested pepper corns are are pickled in salt or vinegar, or they are dried at elevated temperature. Since they are still

unripe, they exhibit small pungency and a fresh, herbal, "green" flavor. The aroma of dried green pepper corns are fantastic but they have less pungency. This make the m suitable for delicate dishes.

Red Pepper

Red pepper is rare. It has good pungency and smell and can be compared to black pepper. The sugary taste makes them unique in the pepper world. For producing them, the ripe peppercorns are harvested at the right time. The drying process is fast and suppress fermentation to preserve the color. While processing extra care is taken in order to prevent the separation of the outer hull from the kernel

Trade in Black Pepper Spices

Indian Scenario

India is one of the major countries exporting large volumes of international grade pepper to a number of countries. According to an estimate, the Southern state of Kerala accounts for 90% of the total pepper production. Tamilnadu and Karnataka are other major Indian production centres. The exports of black pepper spices has been rising in terms of volume for the past few years.

Global Scenario

The global production and trade of pepper is on the rise. Vietnam is the largest manufacturer and trader of pepper in the global market. Indonesia, India, Brazil, Malaysia, Srilanka, Thailand and China are among the top producers of pepper in the world. Singapore, Rotterdam and New York are the largest trading centres of pepper.

Uses of Black Pepper Spices

The spice derives its flavor from piperine compound. Black pepper spices is widely used for food flavoring and preservation.

Black Pepper is widely used in traditional medicinal systems including ayurveda, Siddha and Unani systems. It is used for manufacturing medicines, curing illnesses and diseases like heart disease, indigestion, constipation, insomnia, joint pains, liver problems, sneezing etc.

History of Pepper

Black pepper spices has been used by the human beings for two thousand years. The earliest pepper was grown in southern part of India. After Greek invasion to India the western market was open for Indian pepper. Greek invasion led to the establishment of new route to the west. Pepper became soon the valuable items of commerce worldwide.

In 7th and 8th century AD the spice trade was monopolized by the Arabs who traded the pepper with the west through spice route that passes from the Arabian peninsula and Egypt. In Medieval age spice trade came to be monopolized by Italian traders also. The growing demand led the European to discover the new sea routes to reach the eastern part and procure the spices directly from the producers.

At the end of the 15th century Portuguese discovered many sea routes and they established their colonies in South East Asia and south Asia which persisted until the second half of the 20th century. The early 20th century also saw many wars between British and Dutch to control this trade in which British emerge victorious.

Today in modern period pepper has not lost its importance. It is still important trading item. Black pepper along with other variants like long pepper, green pepper, red pepper and white pepper are demanded highly in the world market.

KITCHEN TRICKS TO EXPOSE SPICE ADULTERATION

In a country where official systems set for food safety and prevention are constantly outdone by a booming adulteration business, the onus of safeguarding one's family against contaminated food, unfortunately falls on citizens themselves. From loose packed ground spices, to wet produce such as milk, khoya, paneer, to dry spices and grains, almost everything we buy has a potential of being adulterated if purchased from an unauthorized vendor in a box unmarked and tested by either Agmark or ISI. Some of these could be less harmful such as water or bran, but chemicals and colouring agents such as Metanil Yellow, Lead Chromate and Sudan Red III are known to be carcinogenic. The chairman of the Consumer Guidance Society of India, Dr Sitaram Dixit lists a few commonly used food items, and suggests simple home tests to check for their most common adulterants. In case the test asks for the presence of an acid, we should use common toilet cleaning acid, or easily found citric acid or even lemon juice.

1. Turmeric, Dals and Pulses such as Moong or Channa Adulterant

Metanil Yellow and Kesari Dal (Added to enhance the yellow colour of a food substance)
Test

Dissolve half a spoon full of besan or turmeric powder in 20 ml of lukewarm water. Add a few drops of hydrochloric acid or any commonly available acid at home. If the water turns pink, violet or purple, it shows the presence of Metanil Yellow.

Harmful Effects

It is highly carcinogenic. If consumed over a continuous period of time, it can also cause stomach disorders.

2. Green Chillies, Green Peas and Other Vegetables Adulterant

Malachite Green (To accentuate the bright, glowing green colour of the vegetable)
Test

Take a small portion of the sample and place it over a moistened white blotting paper. Coloured impressions on the blotting paper indicate the presence of Malachite green.

Harmful Effects

It is a coloured dye. It has proven to be carcinogenic for humans if consumed over a long period of time.

3. Mustard Seeds and Mustard Oil Adulterant

Argemone seeds (To add bulk and weight)

Test

When pressed or crushed, argemone seeds are white inside and have a rough outer surface whereas mustard seeds are smooth on the outside and are yellow on the inside.

Harmful Effects

The consumption of these could cause epidemic dropsy and severe glaucoma. Young children and senior citizens with poor immunity are more susceptible this.

4. Black Pepper

Adulterant

Papaya seeds (To add bulk)

Test

Float the sample in alcohol. Mature black pepper corns sink whereas papaya seeds float to the surface in alcohol.

Harmful Effects

Papaya seeds can cause serious liver problems and stomach disorders.

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REMOVAL OF HEAVY METALS FROM ELECTROPLATING EFFLUENTS BY CARBONIZED AGROWASTES

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Abstract

Batch tests were conducted using an electroplating industry effluent that contained 18.0, 18.9, 8.6 and 15.6 ppm of Cr(VI), Ni(II), Cu(II) and Zn(II) respectively. The work aimed to evaluate the feasibility of using powdered pseudoactivated carbon prepared from agrowastes for the removal of heavy metals from electroplating effluents. The ability of coconut coir carbon (CCC), sagaun sawdust carbon (SSC), wheat stem carbon (WSC) and rice husk carbon (RHC) to remove heavy metals from the effluent was studied. The removal was in the order of Ni > Zn > Cu > Cr over a wide range of initial concentration 1-20 mg/l at sorbent dose 1 g/l, pH 4.8, temperature 25°C, rpm 250 for 5 h. The sorption increased with increasing contact time but the equilibrium was attained in 2 h for Cr, 3.0 h for Cu, 3.5 h Zn and 4 h for Ni. The order of metal removal capacities for these chemical sorbents was: RHC > CCC > WSC > SSC. Electroplating effluent showed 4 to 10% lower removal as compared to synthetic standard solution under similar conditions.

INTRODUCTION

In India, there are over 50,000 large, medium and small electroplating units mostly scattered in the urban areas. Most large units are captive to some other large industrial units (Chauhan and Chauhan 2002). Medium units cater to selected business groups as feeder units. Small units mostly carry out job plating where, unlike captive and feeder units, most of operations are done manually in residential areas as family owned business and there is no space for effluent treatment. The variety of processes and methods of operation in the metal finishing industry give rise to a wide range of effluent compositions (Pigage et al. 2002). The processing baths contain high concentration of potentially polluting materials. In general, the wastewater can be expected to contain cyanides of potassium or sodium, complex cyanides, copper, nickel and zinc in acid solution, hexavalent chromium, oil wastes and solvents. Due to proprietary nature of many products used in the metal finishing, the precise composition is quite often not known. Dissolved chemicals and metals, which are not toxic to aquatic life at very low concentration levels are, however, the major concern. The permitted levels of metal contaminants in the electroplating wastewater to be discharged, as applicable in various parts of the world as well as in India, are very low but the electroplating effluents have their very high levels. A typical wastewater from an electroplating industry is likely to have in ppm 100-500 suspended solids, 20-100 Cr(VI), 30-150 total Cr, 15-90 CN^- , 5-25 Cu, 15-70 Ni and 10-200 Zn whereas the permitted levels of these contaminants in the electroplating wastewater to be discharged are 100, 0.1, 2.0, 0.2, 2.0, 2.0 and 5.0 ppm respectively. The pH is in the range of 4-10 that must be changed to 6.5 to 7.5 before water is released into the environment.

Though activated carbon is an ideal adsorbent for organic matter due to its organophilic character, it is not economical for wastewater and soil treatment owing to its high production and regeneration costs, and about 10-15% loss during regeneration by chemical or thermal treatment. High cost of activated carbon and synthetic resins has prompted search for substitutes that are abundant, cheap, renewable and ecofriendly (Dakiky et al 2002; Buerge-Weirich et al 2002). So the use of agricultural residues such as saw dust or industrial by-products like bagasse have received considerable attention (Achari and Anirudhan 1995; Gaghate et al. 1990; Siddique et al. 1999; Haribabu 1992; Rai and Surendra 1999; Rangaraj et al. 1999; Selvakumari et al. 2001; Singh et al. 2000). Most of these materials contain functional groups associated with proteins, polysaccharides like lignin, cellulose and hemicellulose. The pollutant uptake is believed to occur through coulombic attraction and ion exchange processes involving these groups. Though these materials generally do not have high sorption capacity as compared to activated carbon, they are plentiful, inexpensive and renewable. This offers an attractive approach to the removal of metal cations in solution. The sorption capacity of these materials could be enhanced by various physicochemical modifications to improve their physical and structural properties making them more suitable for full-scale filter applications. The goal of this research is to evaluate the ability of coconut coir carbon (CCC), sagaun sawdust carbon (SSC), wheat stem carbon (WHC) and rice husk carbon (RHC) to remove heavy metals from the electroplating effluent as effective, low cost, biomass sorption media.

MATERIALS AND METHODS

Sagaun saw dust used in this study was collected from the saw machine at Panchkuian, Agra. Coconut coir, rice husk and wheat stem were obtained from the local market. All the four agrowastes were dried in the sun, crushed, washed thrice with distilled water and rinsed with 1% HCl to remove water soluble impurities particularly metal ions and surface adhered particles. Then they were kept in 0.1 N NaOH solution overnight to remove lignin and in 0.1 CH₃COOH to remove alkalinity developed due to NaOH. Thereafter, they were washed well with distilled water till the wash water became colourless. Now they were dried at 110°C in an oven for 2 h to get rid of moisture and other volatile impurities. Their carbons were prepared by keeping 4 parts of the above agrowastes with 3 parts by weight of conc. H₂SO₄ in an air oven maintained at 150°C for 24 h. The carbonized agrowastes were washed with distilled water to remove free acid (SO₄²⁻ ions). Then they were soaked in 1% w/v sodium carbonate solution overnight to remove any residual acid. Again they were washed with distilled water and dried at 110°C for 2 h. The carbons so obtained were ground in a mortar with a pestle and sieved through a standard sieve to get the particle size less than 300 microns throughout the study.

All chemicals used were of analytical grade unless otherwise specified. Distilled deionized water (DDW) was used throughout the experiment. Five standard solutions of 1, 5, 10, 15 and 20 mg/l concentrations of Cr, Ni, Cu and Zn for instrument calibration and sorption study were prepared by diluting their stock solution of 1 g/l, i.e., 1 ml □□□1 mg metal. To prepare the Cr(VI) stock, 2.828 g anhydrous K₂Cr₂O₇ was dissolved in about 200 ml DDW, 1.5 ml conc. HNO₃ and diluted to 1 litre with DDW. The stock solution of Ni, Cu and Zn were prepared by dissolving 1.000 g of 99.5% AR 325 mesh metal powder from CDH, New Delhi in a minimum volume of 1:1 acid (HNO₃ for Ni and Cu, and HCl for Zn) and diluting to 1 litre with 1% (v/v) acid.

The capacity studies were carried out by transient batch tests. In 25 numbers (5 concentrations of 4 metals each + 5 controls one for each) of 100-ml capacity PVC bottles with screw caps, 0.05 g of sorbent was added to each bottle of 5 sets, each set having 6 bottles 5 for different concentrations of a metal and 1 for its control. 50 ml of the metal solution or effluent was added to each bottle. The solution was buffered with 0.07M sodium acetate - 0.03 M acetic acid to pH 4.8. Each bottle was shaken in a reciprocating shaker at 180 rpm for 5 h at room temperature, and the metal concentration was measured per hour until the solution reached equilibrium. The controls without sorbent are to demonstrate metal uptake due to the sorbent, not from other sources such as the walls of the container, centrifuge tube etc. The contents were centrifuged at 2000 rpm for 10 min and the supernatant liquid was filtered using a 0.45- μ m membrane filter. The filtrate was analysed for metal ions. The initial and final concentrations of the metal solutions were determined using a Perkin-Elmer AAnalyst 100 AAS by Standard Methods (APHA et al. 1998). Experiments were triplicated and results averaged.

RESULTS AND DISCUSSION

The characteristics are listed in Table 1. Such carbons are expected to be more than four times more effective than raw agrowastes (Manju and Anirudhan 1997; Perisamy and Namasivayam 1995).

Table 1. Characteristics of Adsorbents

Parameters	RHC	CCC	WSC	SSC
Composition (in %)				
Moisture	3.82	4.96	5.67	4.22
Ash	4.56	7.85	5.68	8.36
Carbon	79.89	80.32	78.9	81.73
Silica	2.76	4.36	3.02	4.64
Sodium	0.13	0.11	0.17	0.09
Potassium	0.29	0.31	0.27	0.23
Calcium	0.35	0.39	0.41	0.32
Magnesium	0.03	0.02	0.07	0.01
Phosphorous	0.05	0.04	0.06	0.03
Iron	0.27	0.19	0.32	0.12
Miscellaneous	7.85	1.45	5.34	0.25
Properties				
pH	8.32	7.64	7.34	7.83
Conductivity (μ S/m)	0.92	0.80	0.75	0.62
Specific gravity (g/L)	1.20	1.34	1.10	1.12
Porosity (ml/g)	1.01	0.92	0.83	0.72
Surface area (m^2/g)	456	397	328	298
Cation exchange capacity(meq/g)	0.70	0.90	0.53	Nil

The physicochemical properties of carbonized agrowastes vary widely from plant to plant and method to method of carbonization. They depend on variety of a plant and area in which it is cultivated, temperature of carbonization, operational features and efficiency of the heating

equipment like oven or furnace, The peaks of their X-ray diffractogram can be used to identify major components as crystalline quartz, amorphous silica, calcium orthosilicate, cristobalite, sillimanite, crystalline carbonate etc. (Swamy et al. 1998). Their scanning electron micrographs can depict their morphology particularly linear or curved type fibers with holes in fibers and at other places in skeletal structure. The number and size of pores of a carbon can also be determined. The greater the number and larger the size of pores but the smaller particle size make a better sorbent. The bands of their FTIR spectra can indicate the presence of carboxy, hydroxy, sulphonic etc. groups responsible for cation exchange.

Table 2. Effect of Cr, Ni, Cu and Zn concentration on their % removal at agitation time 4 h, rpm 240 and sorbent dose 1 g/l, pH 4.8 and temperature 25°C

Metal	Concentration (mg/l)*	RHC	CCC	WSC	SSC
Cr(VI)	1	92.1	90.9	88.3	85.1
	5	89.5	88.2	84.5	80.0
	10	84.2	82.4	76.8	70.9
	15	75.7	71.1	65.9	58.4
	20	68.1	62.3	56.1	48.5
Ni(II)	1	97.6	95.9	94.3	92.8
	5	97.0	94.7	92.7	90.4
	10	95.5	91.9	88.4	84.5
	15	91.3	86.0	79.6	71.2
	20	84.2	76.6	70.9	62.9
Cu(II)	1	94.2	93.6	91.9	88.0
	5	92.7	91.7	89.0	83.6
	10	89.2	86.9	83.9	76.1
	15	81.2	78.9	73.4	62.3
	20	72.5	68.6	63.4	54.1
Zn(II)	1	95.4	94.7	92.3	90.8
	5	94.2	93.2	90.6	87.0
	10	91.5	89.4	84.5	80.2
	15	85.2	80.9	75.2	68.1
	20	78.5	72.1	64.2	56.5
Cr(VI)	18.0	67.4	61.0	55.7	47.2
Ni(II)	18.9	83.0	75.2	68.5	60.3
Cu(II)	8.6	89.0	86.5	83.4	75.5
Zn(II)	15.6	81.0	75.4	68.3	60.7

*The second set of data is for metal ions present in electroplating effluents.

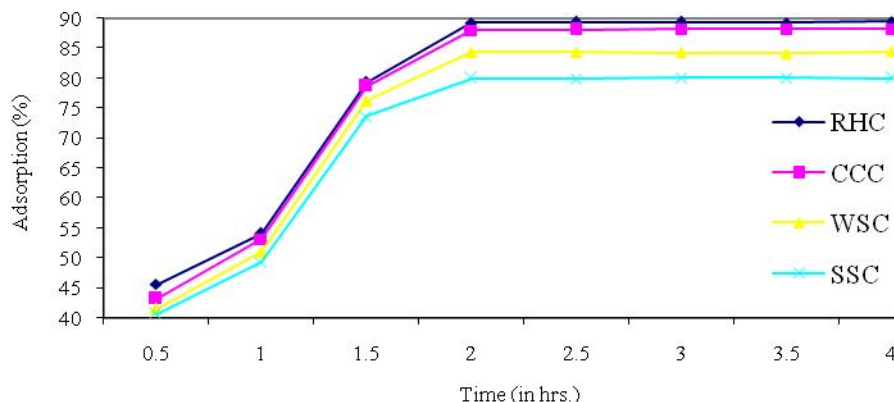


Figure 1. Effect of contact time on the % removal of Cr at 5 mg/l concentration, sorbent dose 1 g/l, pH 4.8 and temperature 25°C

The effect of contact time on sorption was also investigated (Figure 1)

The uptake of metal ions at 1, 5, 10, 15 and 20 mg/l concentrations by different sorbents was thus calculated and results are listed in Table 2.

The data were analysed using the Freundlich and the Langmuir equations:

$$\ln a = \ln k + 1/n \ln c \quad \text{Freundlich equation}$$

$$c/a = 1/Qb + c/Q \quad \text{Langmuir equation}$$

where a (mg/g) is the metal sorbed per unit mass of sorbent ($a = x/m$ where x mg of metal is sorbed on m grams of sorbent), c (mg/l) is equilibrium concentration in aqueous phase, k (mg/g) and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively, Q (mg/g) and b (l/g) are Langmuir constants related to adsorption capacity of sorbent and adsorption maximum (energy of adsorption) respectively. The Langmuir constants were calculated at five initial concentrations under optimal conditions (Table 3).

Table 3. Comparison of Langmuir and Freundlich constants and correlation coefficients (R^2 values) for the sorption of heavy metals by RHC, CCC, WSC and SSC

System	Langmuir constants and R^2			Freundlich constants and R^2		
	Q , mg/g	b , l/g	R^2	k , mg/g	$1/n$	R^2
Cr/RHC	15.5637	0.7730	0.9975	7.422	0.5057	0.9665
Cr/CCC	14.3753	0.7581	0.9986	6.985	0.4686	0.9529
Cr/WSC	13.1134	0.6130	0.9998	6.199	0.4605	0.9759
Cr/SSC	11.4383	0.5978	0.9999	5.102	0.4311	0.9531
Ni/RHC	18.7713	2.3191	0.9993	16.956	0.4823	0.9501
Ni/CCC	17.1763	1.4426	0.9998	11.884	0.4753	0.9484
Ni/WSC	15.8784	1.1181	0.9984	9.430	0.4782	0.9503
Ni/SSC	14.0016	0.9786	0.9965	7.413	0.4551	0.5266
Cu/RHC	17.1083	1.0063	0.9991	9.697	0.4839	0.9512
Cu/CCC	15.6278	0.9955	0.9998	8.936	0.4718	0.9523
Cu/WSC	14.2539	0.8527	0.9995	7.511	0.4501	0.9530
Cu/SSC	12.2523	0.6460	0.9977	5.539	0.4505	0.9534
Zn/RHC	18.3009	1.1852	0.9979	11.151	0.5088	0.9584

Zn/CCC	16.3204	1.1634	0.9987	9.922	0.4744	0.9488
Zn/WSC	14.9322	0.8557	0.9998	8.269	0.8023	0.9445
Zn/SSC	12.5572	0.8492	0.9139	6.878	0.4147	0.9468

Sorption capacity is found to decrease with increase in metal concentration. The higher uptake at lower initial concentration can be attributed to the availability of more isolated metal ions. Sorption rate is very rapid during initial period of contact due to the availability of more sites for sorption and more than 60 per cent of sorption is reached within 1 hour. However, equilibrium was attained after 2 h for Cr, 3 h for Zn, 3.5 h for Cu and 4.0 h for Ni. RHC could remove greater amount of these metals than any other carbon studied. It was found to remove 92.1% Cr (VI), 97.6% Ni, 94.2% Cu and 95.4% Zn at concentration 1 mg/l, sorbent dose 1 g/l, rpm 240, agitation time 4 h, pH 4.8 and temperature 25°C. The order of metal removal capacities for these chemical adsorbents was RHC > CCC > WSC > SSC. The order of removal/sorption of metals was Ni > Zn > Cu > Cr. The effect of various parameters affecting the adsorption such as initial metal concentration, adsorbent dose, contact time and pH was determined. Adsorption decreases with rise in metal concentration but increases with increase in adsorbent dose.

The rate of adsorption is high in the beginning as sites are available and unimolecular layer increases. Adsorption and desorption occur together and rates become equal at a stage called adsorption equilibrium when isotherms are applied. That is why there is little increase in % removal on increasing contact time from 4 to 5 h. The subsequent slow rise in curve may be due to adsorption and intra-particle diffusion taking place simultaneously with dominance of adsorption.

The pseudoactivated carbons may consists of oxides of silicon, calcium, magnesium, iron, etc. They may have anion adsorption sites similar to minerals like alumina and clay. Such sites are aquo groups (—M—OH_2^+) and hydroxo groups (—M—OH). The surface chemistry of an oxide in contact with an aqueous solution is determined to a large extent by deprotonation or a hydroxyl ion association reaction. However, some evidences suggest that an anion like $\text{Cr}_2\text{O}_7^{2-}$ can be adsorbed by ion exchange mechanism even though the surface is neutral. Had Cr(VI) not been in dichromate form, it would have been sorbed to the maximum extent based on its ionic size and potential.

The optimum pH for metal removal was found in the acidic medium (Singh et al. 2001). The reason may be attributed to the large number of H^+ ions in acidic medium neutralize negatively charged adsorbent surface, thereby reducing hindrance to diffusion of dichromate ions. At higher pH the abundance of OH^- ions create increased obstacle to diffusion of dichromate ions.

CONCLUSIONS

The following conclusions can be drawn from the above results:

1. CCC, SSC, WSC and RHC to remove heavy metals from the effluent in the order of Ni > Zn > Cu > Cr over a wide range of initial concentration 1-20 mg/l at sorbent dose 1 g/l, pH 4.8, temperature 25°C, rpm 250 for 5 h.
2. The sorption increased with decreasing metal concentration and increasing contact time, but the equilibrium was attained in 2 h for Cr, 3.0 h for Cu, 3.5 h Zn and 4 h for Ni.
3. The order of metal removal capacities for these chemical sorbents was: RHC > CCC > WSC > SSC.

3. Electroplating effluent showed 4 to 10% lower removal as compared to synthetic standard solution under similar conditions.
4. The sorption followed Freundlich as well as Langmuir isotherms.
5. The present paper shows the possibility of using agrowastes particularly rice husk abundantly available in our country to produce cheaper activated carbons. The data thus generated may be used for designing treatment plants for industrial effluents having low levels of heavy metals and hold a promise for commercial exploitation.

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