



## Differences in cadmium transfer from tobacco to cigarette smoke, compared to arsenic or lead

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### ABSTRACT

Arsenic, cadmium and lead levels in tobacco filler and cigarette smoke were determined in a 568-sample worldwide survey. Median tobacco levels for arsenic, cadmium and lead were 237, 769 and 397 ng/g respectively, comparable to those previously reported albeit somewhat lower for lead and cadmium. Median mainstream smoke yields for arsenic, cadmium and lead were <3.75, 18.2, and <12.8 ng/cig. under ISO, and <8.71, 75.1 and <45.7 ng/cig. under Health Canada Intense (HCI) smoking regime respectively. In the case of cigarettes with activated carbon, a selective retention of cadmium but not lead or arsenic was observed. This effect was more pronounced under ISO than under HCI smoking regimes. Cadmium selective retention by activated carbon was confirmed by testing specially designed prototype cigarettes and the causes for this selective filtration were investigated. The differences between cadmium, arsenic and lead in terms of their speciation in tobaccos and in cigarette smoke could be related to their distribution in the ash, butt, mainstream (in gas-phase and particulate-phase) and sidestream smoke of a smoked cigarette. The possible formation of organometallic cadmium derivatives in the smoke gas-phase is discussed, the presence of which could adequately explain the observed cadmium selective filtration.

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### 1. Introduction

The health effects of environmental or workplace exposure to heavy metals and arsenic have been the subject of extensive research [1,2]. Cadmium, in particular, has been linked with overall cancer mortality [3] and, more specifically, with cancers of the lung, pancreas, breast, prostate, endometrium and urinary bladder [4]. It has also been linked with non-cancer morbidity, kidneys and bones being major target organs [5–8].

Heavy metals have been reported to be associated with the toxicity of tobacco products and tobacco smoke [9,10] and a number of elements have been identified as contributors to this toxicity. Canadian regulations require that levels of cadmium, lead, arsenic, nickel, chromium, selenium and mercury be reported in tobacco, mainstream and sidestream smoke [11]. Among these elements, arsenic and cadmium appear in the abbreviated list of harmful and potentially harmful constituents whose level in tobacco should be reported according to a guidance document issued by the U.S. Food and Drug Administration (FDA) [12]. In particular, cadmium was listed by the International Agency for Research on Cancer as a Group 1 human carcinogen [4]. It was also selected as a priority toxicant by the

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World Health Organization for smoke delivery reporting [13] and recommended for regulatory policy in a subsequent report [14]. Cadmium has been included in different prioritization lists of smoke constituents based on risk assessments [15–17].

In the absence of specific occupational exposure, the main sources of cadmium uptake are food and tobacco smoke. The body burden of cadmium was assessed as being approximately two-fold higher in smokers than in non-smokers [18,7,19]. The impact of smoking on the lead body burden is observed through a sequestration in bones [20–22], but not in blood [23,24], while no effect from smoking could be observed in the case of arsenic [25], or mercury [26,27]. Surveys also showed that smoking is not an important source for nickel [28]. Finally, the smoke delivery levels of nickel, chromium and selenium are in most cases below the quantification limits of the protocols commonly used for their determination [29]. Conversely, sizeable amounts of cadmium, lead and arsenic can be found in tobacco smoke [30]. In the light of these observations, the present study focuses on cadmium (Cd), lead (Pb) and arsenic (As).

The cigarette delivery of elements to mainstream smoke can be addressed as a combination of two factors, the amount of these elements present in tobacco and their transfer rate, which is specific to element speciation and is impacted by cigarette design. The transfer of elements during smoking has been the subject of a number of studies over decades. Nevertheless, despite this wealth of information, it is difficult to obtain a clear model of elements transfer to smoke (sidestream or mainstream), or their retention (in ash or butt). Even for the specific subject of the phase-distribution for each element in the smoke aerosol, there is a lack of agreement. This point is central to a discussion on transfer since a compound must be at least partly present in the gas-phase to be selectively removed from mainstream smoke by adsorbents. The uncertainty that prevails about the elements transfer or speciation is likely due to the complexity of the quantification of elements yields at trace levels, despite dramatic improvements in instrumentation and analytical methods over the years. Sample contamination is a constant problem. The small size of the data sets taken into account in many studies is an additional cause for discrepancies among authors' assessments.

Based on data from three worldwide market surveys of commercial cigarettes performed between 2008 and 2012, which included the determination of tobacco and mainstream smoke levels of As, Cd and Pb, we investigated the transfer of each of these elements from tobacco to mainstream smoke generated under both International Organization for Standardization (ISO) and Health Canada Intense (HCI) machine-smoking regimes. Of particular interest is the fact that market surveys data can very effectively evidence selective removal of an element by activated carbon through a comparison of its filtration to that of nicotine. Results, including data from specially designed prototypes, are discussed and the conclusions strengthened by a review of the relevant literature on elements specific filtration.

## 2. Materials and methods

### 2.1. Market surveys brands sampling

In order to best observe the impact of cigarette design and tobacco blend, brands were selected to cover as many cigarette design specificities as possible, rather than sampling based on local market share. 568 samples of commercial brands from 27 different manufacturers were bought in 2008 (205 samples), 2009 (63 samples) and 2012 (300 samples) at the point of sale in 23 countries. Because in some cases a same brand could be analyzed in different market surveys, 489 brands were actually investigated by the 568 samples. With the exception of one papirosi cigarette, all were conventional cigarettes, excluding e.g., bidis and herbal products. Different blend types were included in the sampled set, with a large proportion of American and Virginia blends. The dimension of sampled cigarettes covered the whole available range, with diameters between 5.2 mm (superslim) and 8.0 mm (magnum), and rod lengths between 70 mm and 100 mm. Among the sampled brands, filter designs included single and multiple-plug configurations with up to 4 plugs. In some brands, filters contained activated carbon, present either in the tow or in a cavity between two plugs. Some non-filter brands were also sampled. The numbers of samples selected per country are presented in Table 1, including information regarding their filter design.

### 2.2. Prototype cigarettes investigating a high activated carbon loading

Prototype cigarettes were manufactured to study the impact of adsorbents on cadmium, arsenic and lead filtration. The control cigarette (without activated carbon) was designed to mimic a commercial king-size American blend with a 27-mm cellulose acetate plug, a ventilation set at 35% and a resistance to draw of 100 mm H<sub>2</sub>O. The cigarette had a 7.5-mg tar delivery under ISO machine-smoking regime. The test prototype differed only from the control in the filter design. The test prototype filter was a 27-mm composite filter, consisting of a 7-mm plug of cellulose acetate at the mouth end abutted to a 20-mm Dalmatian plug into which 80 mg of activated carbon was embedded. The prototype cigarette was designed to same resistance to draw as the control. The test had a 7.2-mg tar delivery under ISO machine-smoking regime.

### 2.3. Smoke and tobacco analyses

The analyses of the different components in both tobacco filler and smoke were conducted under contract to Philip Morris International by Labstat International ULC (Kitchener, Ont., Canada), an ISO 17025 accredited laboratory, and were performed according to the official Health Canada methods [31]. Alkaloids in tobacco fillers were analyzed by gas chromatography according to method T-301 [32]; three replicates per sample were conducted. Cadmium, lead and arsenic were analyzed in tobacco fillers according to method T-306 [33]. Three replicates per sample were conducted. After conditioning according to ISO

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