Swedish Society for Nature Conservation

Report
Bad shoes stink

– product survey focusing on certain hazardous chemicals in leather shoes

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Article number: 9036
ISBN: 978-91-558-0016-1

Many thanks to all who gave valuable input to this report.
Produced with economic support from the Swedish International Development Authority (Sida). Sida has not participated in the production of the publication and has not evaluated the facts or opinions expressed.

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Preface

For a 100 years, the Swedish Society for Nature Conservation (the SSNC) has been working to protect the environment in Sweden, and in the past 20 years with consumer power and ecolabelling. The SSNC is since long also engaged internationally in various environmental issues, cooperating with environmental organisations in many countries.

The SSNC is an active party in raising the awareness among consumers and producers in Sweden about sector specific problems related to chemicals. A tool for this is product surveys exposing the problems. This methodology has been successful in Sweden. We now want to bring it to our collaborating environmental organisations abroad, to spread the use of consumer power to bring about change, and to widen the discussions about chemicals hazardous to health and the environment.

Much advertence has been given to chemicals in the textile industry lately. The SSNC has released three reports on this subject in the past two years, creating a lot of attention in the media. This has resulted in positive efforts from the Swedish textile producers to get rid of the exposed problems. We now believe time is ripe to focus attention on the shoe industry. Shoes are complex products, composed of many different materials, the preparation of which requires a wide spectrum of chemicals. Many consumers have no idea of what they put their feet into. Some of the chemicals are hazardous to health and the environment. In the view of SSNC, such chemicals should be substituted by less hazardous alternatives, but unless exposed, there will be no drive for change in the shoe industry.

Earlier this year, the SSNC released the report Chemicals Close Up - Plastic Shoes from All over the World, a study on chemicals in plastic sandals and flip-flops. Six collaborating organisations from all over the world were part of that study. In this study, focus is placed on chemicals in leather shoes. Five collaborating organisations participated in this study:

- GroundWork, South Africa
- National Association of Professional Environmentalists (NAPE), Uganda
- EcoWaste Coalition Inc., the Philippines
- Toxics Link, India
- Center of Environmental Solutions (CES), Belarus

With this report we show that toxic metals and semi-metals, such as arsenic, lead and mercury, can be found in leather shoes together with high levels of trivalent chromium, carcinogenic aromatic amines, the compound 2,4,6-tribromophenol that may affect levels of certain hormones, potentially leading to developmental effects, and low levels of the highly allergenic and toxic organic compounds dimethylfumarate and formaldehyde. Issues related to shoes as waste and risks of landfilling or incinerating leather waste rich in trivalent chromium are discussed. We want politicians, nationally and internationally, to intensify efforts on phasing out chemicals hazardous to health and the environment from all material flows in society, and meanwhile strengthen legislation on product safety, in order to protect consumers. Producers are, obviously, not able themselves to make products safe for health and the environment.

Mikael Karlsson
Chairman of the Swedish Society for Nature Conservation

Summary

The leather industry generates large volumes of wastewater, rich in organic compounds consuming oxygen upon degradation, salt, and various other chemicals. It also generates solid waste in the form of contaminated sewage sludge and leather waste. Some of the tanning chemicals stay in the leather, as it is further processed into various consumer goods, such as shoes. A shoe is a complex product assembled from many different materials, requiring various chemicals in the making. Finally, when the shoe reaches the consumer, it contains a cocktail of chemicals. During the whole life-cycle, from the tanning of the leather until the shoe is finally discarded as waste, a shoe can be hazardous to health and the environment.

The Swedish Society for Nature Conservation (SSNC), in collaboration with environmental organisations from South Africa, Uganda, The Philippines, India, and Belarus, analysed a selection of metals, semi-metals, and organic compounds in leather shoes of well-known brands bought in the countries of the respective collaborating organisations. Most of the studied chemicals can be assumed to originate from the tanning, preservation, or dyeing of the leather.

Metals and semi-metals in various concentrations were found in all shoes. Although the risk for the bearer of the shoe may not be immediate, metals and semi-metals can be hazardous to the long-term health of humanity and the environment, as shoes end up as waste and their content of metals and semi-metals eventually are released into the environment. This discussion is further developed in the report.

Not surprising, very high levels of trivalent chromium were found in the shoes. Chromium tanning accounts for some 80-85% of all tanning globally. Upon incineration or landfilling of leather waste containing chromium, the most common and least toxic trivalent form of chromium may oxidise into the highly toxic and carcinogenic hexavalent form.

Highly toxic semi-metals and metals, such as arsenic, lead, and mercury, were found in some shoes at concentrations higher than the background level detected in an untanned raw hide. Arsenic and mercury in the form of organic compounds can be used as leather preservatives, which in that case could facilitate direct uptake from a shoe by the bearer. In this study, however, it was not possible to deduce in what form arsenic and mercury were found in the leather. All shoes, except one, bought in Sweden are with respect to mercury at risk of not complying with Swedish Law.

Organic compounds hazardous to health and the environment were detected in a few shoes. Based on a small sample of 21 shoes, it is not possible to deduce how widespread the use of these compounds are in leather and shoe manufacturing, but our study shows that they are sometimes used, which is bad enough.

Two shoes contain azodyes capable of formation of carcinogenic amines. In one shoe, bought in the Philippines, the concentration of a carcinogenic aromatic compound is more than twice the threshold concentration stipulated in the European Union (EU) chemicals regulation Registration, Evaluation, Authorisation and Restriction of Chemical Substances (REACH). The other shoe, bought in Sweden, passed the threshold concentration for carcinogenic amines stipulated in REACH.

A high level of the bactericide/fungicide 2,4,6-trichlorophenol was found in one shoe bought in Sweden. This compound is difficult to degrade in the environment, bioaccumulative, highly toxic, and suspected to interfere with the supply of thyroid and sex hormones in the body. Hormonal disruption of this kind may lead to detrimental developmental effects in foetuses and obesity in adults.

The highly allergenic compound dimethylfumarate, a mould preservative, was found in a Swedish shoe at the threshold concentration defined in a ban that is valid in the EU since May the 1st 2009.

Low concentrations of the highly allergenic and possibly carcinogenic compound formaldehyde were detected in some shoes.

We also tested a few shoes for chlorinated paraffins, but could not find the carcinogenic short-chained forms regu-

lated by REACH. Chlorinated paraffins of longer chain lengths, however, were found in some of the shoes. Chlorinated paraffins, in general, are toxic in various ways. In addition, they are not easily degradable and bioaccumulative. The SSNC is of the opinion that:

- Considering the risk for oxidation of trivalent chromium into hexavalent, chromium containing leather waste must be regarded as hazardous waste, and should be treated accordingly. The leather and shoe manufactures should, as soon as possible, switch to chromium free leather, as now emerging chromium free tanning techniques yield high quality leather.
- The presence of carcinogenic compounds in consumer products is unacceptable, irrespective of concentration. It is a well-established fact in toxicology that the risk for cancer is linear with concentration for compounds capable of reacting with the DNA, such as certain aromatic amines. Consequently, there is no safe concentration for such compounds.
- The use of chemicals capable of interfering with the supply and distribution of hormones in the body is unacceptable in consumer products.
- Intentional addition of the highly toxic semi-metals and metals arsenic, lead and mercury to consumer products is not acceptable.
- Highly allergenic compounds do not belong in consumer products.
- Compounds that are not easily biodegradable and bioaccumulative should be phased out from the material flows of human society.

As manufacturers of leather and shoes do not seem to be able to deliver products free of chemicals hazardous to health and the environment to the consumers, we urge politicians to strengthen product safety legislation in Sweden, the EU and globally. We would also like to see more efforts voluntarily from the manufactures to remove hazardous chemical in their products.

Introduction

The transformation of raw hide into manufactured products requires a series of complex treatments, for which large amounts of chemicals and water are traditionally used. The leather industry is one of the most polluting industrial activities in terms of volume and complexity of the effluent discharged. In India, for example, some 75,000 m^3 wastewater per day is released from tanneries[2]. Many small-scale Indian tanneries do not have their own wastewater treatment facilities[2]. Pollutants in tannery wastewater discharges include fat, acids, salts, chromium and other metals, dyes and other chemical additives[3]. Some of these pollutants are toxic, persistent, and bioaccumulative, which is a problem. Degradation of high loads of organic pollutants from wastewater discharges consumes oxygen in the recipient water body and may, thus, affect organisms there negatively[4]. The annual global production of tanned hides amount to about 215 million pieces[5]. A large share of this production is nowadays located in countries where wastewater treatment, regulations on the use of chemicals and control of compliance with such may be inadequate. Environmental consideration in Swedish tanneries has improved considerably over the past 30-50 years[6], but was probably not better prior to that than the present situation in some tanneries in countries which now hold a large share of the global leather production.

Occupational health hazards connected to leather production include allergies and eczema from dermal contact with processing chemicals, respiratory problems such as dysponea and inflammation in the nasal cavity and bronchia, irritated mucosa, cough, hoarsness and headache[7]. Some investigations also indicate an elevated risk for liver disease, nasal and lung cancer[8, 9, 10].

Some chemicals used in processing leather remain in the finished products[11, 12]. These chemicals may pose health hazards to retailers, consumers, and upon final disposal of the shoe as waste also to the environment[11, 13, 14, 15, 16].

The aim of this study is to raise public awareness of problematic chemicals used in leather processing, so that producers, retailers, and consumers can demand products void of such chemicals. This will be beneficial for the long-term quality of environment, as well as for the health of individuals at all levels in the production-consumer chain. The SSNC has performed a survey on a selection of problematic chemicals (metals, aromatic amines from azo dyes, chlorinated phenols, dimethylfumarate, and chlorinated paraffins, see the following chapter) in leather from shoes, in cooperation with environmental organizations from different parts of the World. The cooperating organizations are:

- GroundWork, South Africa
- The National Association of Professional Environmentalists (NAPE), Uganda
- Toxics Link, India
- EcoWaste, Philippines
- Center of Environmental Solutions (CES), Belarus

For a brief presentation of each cooperating organization, please see appendix I.

Studied chemicals

The making of a shoe, involves many different manufacturing steps and materials for which various chemicals (for tanning, preservation, production of plastics, rubber, glues, polishes, and so on) are used[11]. Some of these chemicals are problematic from a health and environmental perspective. Attention is paid in this study to a selection of problematic chemicals that can be used for tanning, dyeing, and preservation of leather. The studied chemicals are presented more in detail in the sections below. Each section begins with a general presentation of the qualities of the chemical/group of chemicals, and ends with the elemental symbols, Chemical Abstracts Service (CAS) numbers (an international registry system for chemicals), and official risk classification of the chemicals (with reference to risk phrases in Annex III of the EU directive 2001/59/EC) of the respective chemicals analysed in the shoes of this study. For most metals, the official classification of the elemental form is given. It is important to understand that the official classification of the elemental form of metals may differ from their ionic form, such as in salts, or when they are part of organic compounds. Furthermore, it is important to point out that even though scientific experiments are revealing effects on organisms, the official classification may take quite some time to complete. For that reason, the official classification is far from always updated.

Metals

In this section, metals and the semi-metal arsenic are presented. Arsenic is in the rest of the report classified as a metal, since this is often common practise. Metals are used for tanning, and as components of pigments, dyes and preservatives[5, 17, 18, 19]. Metal contamination is a widespread environmental problem, particularly in aquatic ecosystems which are final sinks for metals. Some metals have no known biological function, e.g. arsenic, cadmium, chromium, lead, and mercury, whereas others are essential in minute concentrations for normal cellular function, e.g. copper, nickel and zinc[20]. Most metals are toxic to organisms at high concentrations, and some of the non-essential metals even at minute concentrations. There are three main mechanisms behind the toxicity of metals[20]:

I: their ability to replace other metals normally complexed to and necessary for the activity of enzymes (these complexed metals are called enzyme co-factors),

II: their ability to attach themselves to certain chemical groups on amino acids constituting enzymes and proteins, thereby altering the physical shape and activity of the proteins and enzymes, and

III: the ability to enhance formation of free radicals.

Free radicals are atoms, ions, or molecules with excessive electrons, which makes them prone to oxidise other molecules in the cell. Metals often enhance formation of oxygen containing radicals[21]. Cells have inherent systems to counteract free radicals, but when the capacity of these is exceeded, DNA, proteins and lipids in the cell membranes may be oxidised – a situation known as oxidative stress[22]. Oxidative stress may cause anything from metabolic disturbance, cellular degeneration to formation of tumours[23, 24, 25]. Detrimental effects of metal exposure at the level of a cell are summarized in Fig. 1.

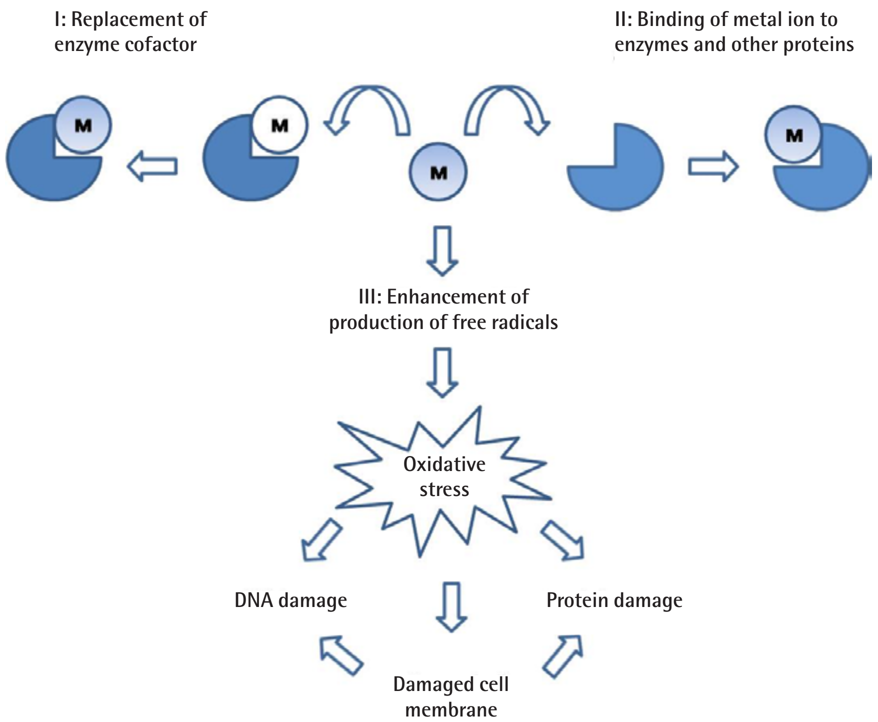

Fig. 1. Summary of detrimental effects due to metal exposure. Metals (indicated by spheres with a M in the figure) inside cells may generate free radicals that overwhelm the inherent free radical defence systems of the cells, resulting in oxidative stress with damages to DNA, proteins and cell membranes. Metals may also bind directly to proteins/enzymes, sometimes replacing other metals complexed to enzymes, thereby changing their structure and activity.

The metals analyzed in this study were arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, and zinc.

Arsenic

Arsenic as an environmental pollutant is serious. Inorganic forms of arsenic are toxic to organisms by causing metabolic disturbance[26]. Such occur when arsenic attaches itself to certain chemical groups on amino acids constituting enzymes and proteins[27]. Detoxification of inorganic arsenic in organisms results in formation of organic arsenic compounds, some of which are considered to be cancer promotors[28]. Arsenic compounds are in humans suspected to promote cancer in skin, lungs, bladder and prostate[29, 30]. It is classified as a human carcinogen (class I) by the International Agency for Research on Cancer (IARC)[31]. There is plenty of evidence for transfer of arsenic between organisms in food chains. Arsenic transfer from plants to herbivores has been reported from terrestrial and aquatic ecosystems[32, 33, 34]. Further transfer along the food chain may occur from herbivores to carnivores[34].

Elemental symbol: As
CAS: 7444-38-2
Official risk phrases of the elemental form: R23/25 (toxic by inhalation and if swallowed), and R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Cadmium

Cadmium is a widespread and serious environmental pollutant. The mechanisms responsible for cadmium toxicity are not well-understood, but they somehow involve oxidative stress[35, 36, 37]. Cadmium represents a serious hazard, because it can easily be absorbed via the alimentary tract, and penetrates through the placenta during pregnancy[38]. In addition to oxidative stress, which ultimately may promote tumour formation (cadmium is classified as human carcinogen (class I) by the IARC[39], it has other detrimental effects in the body. Cadmium is efficiently retained in kidney (halftime, 20-30 years), where it is physically damaging the structures involved in blood filtration, ultimately resulting in renal failure[40]. Cadmium can also cause bone damage, either directly via effects on the bone tissue, or as a result of renal failure[41]. It is known to interfere with female reproduction by modulating hormonal levels[42, 43]. Recent data suggest an elevated risk for cancer and higher mortality in general in environmentally exposed populations[40]. Cadmium is transferred among organisms in food chains of ecosystems, and accumulates in top consumers[44, 45].

Elemental symbol: Cd
CAS: 7444-43-9
Official risk phrases of the elemental form: R26 (very toxic by inhalation), R45 (may cause cancer), R48/23/25 (danger of serious damage to health by prolonged exposure through inhalation and if swallowed), R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment), R62-63 (possible risk of infertility and harm to the unborn child), and R68 (possible risk of irreversible effects).

Chromium

Chromium is a common and sometimes serious pollutant in the environment. The most common and stable forms of chromium are trivalent (Cr III) and hexavalent (Cr VI)[20]. The hexavalent form is water soluble and mobile in the environment, and easily crosses cell membranes, but once inside a cell it is reduced to trivalent chromium and is trapped[31, 46]. When reduced, hexavalent chromium promotes formation of oxygen containing radicals, causing DNA and tissue damage which eventually may result in cancer[36]. Hexavalent chromium is accordingly classified as a human carcinogen (class I) by IARC, whereas trivalent chromium is not classifiable as carcinogen (IARC class III)[47]. Not classifiable in this case implies that carcinogenicity has not been able to confirm, not that it is excluded. If inhaled, hexavalent chromium can cause asthma, bronchitis, and pneumonitis[20]. In addition, skin contact may induce allergies, dermatitis, and skin death[31]. Chromium reduced inside cells to the trivalent form may attach to DNA and other intercellular macromolecules, and is thereby suspected to be mutagenic[31]. Chromium is known to accumulate in food chains of ecosystems[48, 49, 50].

Elemental symbol: Cr
CAS: 7444-47-3
Official risk phrases chromium III: R41 (risk of serious damage to eyes).
Official risk phrases chromium VI: R43 (may cause sensitisation by skin contact), R45 (may cause cancer), R49 (may cause cancer by inhalation), and R50-53 (signifying, very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Cobalt

Cobalt pollution from human activities causes environmental risk. Cobalt mediates its toxicity via formation of oxygen containing radicals[31]. Inorganic cobalt, both soluble and particulate forms, caused lung tumours in animal experiments, whereas epidemiological studies on humans are not conclusive, because of co-exposure to other carcinogenic substances[51, 52, 53]. Cobalt disturbs repair of certain types of DNA damage, thereby potentiating DNA damage[54, 55]. Cobalt accumulation and transfer along food chains is poorly studied, although data suggest that it takes place[56].

Elemental symbol: Co
CAS: 7444-48-4
Official risk phrases of the elemental form: R22 (harmful if swallowed), and R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Copper

Copper is a problematic contaminant in aquatic environments, since it is highly toxic to microalgae forming the base of aquatic food chains[57, 58, 59]. It enhances formation of oxygen containing radicals, and thereby causes oxidative stress[21, 60]. Furthermore, it potentiates formation of free radicals from oxidation of by products formed in metabolism of certain groups of organic compounds[61, 62]. It is mutagenic, but not considered to be a human carcinogen[21]. Copper is easily accumulated by organisms in both aquatic and terrestrial ecosystems, and can be transferred along food chains[38, 63]. Chronic exposure, for example dietary, to copper may result in hepatic injuries[21].

Elemental symbol: Cu
CAS: 7444-50-8
Official risk phrases of the elemental form: R22 (harmful if swallowed), and R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Lead

Lead is another widespread and serious environmental pollutant. It has the ability to cross the blood-brain-barrier separating the cardiovascular from the central nervous system, as well as cross the placenta from mother to offspring during pregnancy[38]. The toxicity of lead and its compounds are well-known, with damage to the central nervous and cardiovascular systems being the most prominent effects[64]. In recent years, however, focus has also been directed to the probable carcinogenic effects of lead compounds. Many lead compounds are now classified as probable human carcinogens (class II A, by the IARC, and category II, by the German Commission for Investigation of Health Hazards of Chemical Compounds in the Work Area)[31, 65]. The exact mechanisms behind the lead triggered carcinogenicity are not known, but oxidative stress, disturbed DNA repair systems, and cell divisions in an uncontrolled manner appears to be involved somehow[66]. All these mechanisms promote formation of tumours. A few studies have shown that lead can be transferred along food chains in ecosystems[33, 67].

Elemental symbol: Pb
CAS: 7439-92-1
Official risk phrases of the elemental form: R33 (danger of cumulative effects), R40 (limited evidence of a carcinogenic effect), R48/23/25 (danger of serious damage to health by prolonged exposure through inhalation and if swallowed), R50-53 (very toxic to aquatic organisms, may cause

long-term adverse effects in the aquatic environment), and R61 (may cause harm to the unborn child), R62 (possible risk of impaired fertility).

Mercury

Mercury is a very serious environmental pollutant. In a regulation by the U.S. Environmental Protection Agency, it was ranked third among substances posing a serious risk to human mortality[20]. Mercury is easily absorbed in the alimentary tract, it crosses both the blood-brain barrier, and placenta during pregnancy[38]. The ability of mercury to react with sulphur rich amino acid groups on enzymes and proteins are well known[68]. This results in metabolic disturbance in various ways. Elemental, inorganic, and organic forms of mercury exhibit neurotoxicity, toxicity to kidneys, and the alimentary tract, where ulceration and hemorrhage may result[21]. As some of the inherent defence systems against oxidative stress depend on sulphur rich proteins, depletion of sulphur groups by mercury results in oxidative stress[69]. From aquatic ecosystems, where bacteria transform inorganic mercury into organic methyl and ethyl mercury, organic mercury is transferred along food chains[20]. It has been demonstrated that about 95% of methyl mercury ingested from fish is absorbed in the alimentary tract[70]. The serious health consequences of methyl mercury exposure was first dramatically illustrated in 1953, when an epidemic methyl mercury poisoning occurred in humans consuming fish from the Minamata Bay, Japan, and then again in 1970-1971, in Iraq, where people were consuming grains treated with a mercury based fungicide[70]. Many died, and other effects included mental retardation, deafness and blindness, especially in children exposed in utero.

Elemental symbol: Hg
CAS: 7439-97-6
Official risk phrases of the elemental form: R23 (toxic by inhalation), R33 (danger of cumulative effects), and R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Nickel

The use of nickel in society is substantial and it can locally be a serious environmental problem. Nickel has long been known to cause nasal and lung cancer in exposed workers[71]. Nickel compounds are classified as human carcinogens (class I) by the IARC[31]. Nickel dermatitis is one of the most common forms of allergic reactions, with 4-9% of persons with contact dermatitis responding positively to nickel[68]. Nickel exposure results in oxidative stress, which is one of the underlying causes for its carcinogenicity. The exact mechanism behind formation of oxygen containing radicals, however, is not known[21, 31]. Nickel is also likely to induce metabolic disturbance. It replaces zinc co-factors in proteins and enzymes, thereby modifying their activities[55, 72]. Its interference with enzymes and proteins in all major pathways for DNA repair, leads to increased susceptibility for mutations[73, 74, 75, 76]. Nickel is easily accumulated by plants, which indicates a risk for transfer to herbivores[77]. In a study where the potential for transfer of various metals along the food chain from a species of marine zooplankton, the conclusion was that nickel might be transferred[78].

Elemental symbol: Ni
CAS: 7444-02-0
Official risk phrases of the elemental form: R40 (signifying limited evidence of a carcinogenic effect), and R43 (may cause sensitisation by skin contact).

Zinc

Zinc is a common environmental pollutant and of concern due to its high toxicity[79]. The mode of action is likely to be metabolic disturbance, as zinc competes for iron and copper binding sites in the cell[80]. This could indirectly cause oxidative stress. In contrast to many other metals, however, zinc also counteracts oxidative stress. Various investigators have proposed that zinc maintains cell membrane structure and function so that lipids in the cell membranes are not oxidised[81]. Zinc is also a co-factor of a crucial enzyme component of the inherent defence system of cells against oxidative stress[82]. Zinc deficiency, thus, increases susceptibility to oxidative stress[83]. Plants accumulate zinc and, thus, may transfer zinc to herbivores[84]. Zinc has also been suggested to be transferred in aquatic food chains, based upon a study with a species of marine zooplankton[78].

Elemental symbol: Zn
CAS: 7444-66-6
Official risk phrases of the elemental form: R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Azo dyes

Azo dyes are by volume the largest group of synthetic dyes used in textile and leather industry, and paper printing[85]. Considerable amounts of dyes from such industrial activities often end up in the sewage water, because of the inefficiency of the dyeing process. Azo dyes were synthesized to be resistant to biological degradation. As a result, only 30-70% of the dyes on average are degraded in the treatment process of sewage water[86, 87, 88, 89]. In addition to poor degradability, inappropriate disposal of dye sewage water is of concern to the public health[90]. Azo dyes usually display low toxicity, but some form aromatic amine intermediates upon metabolic breakdown, and these compounds can be highly carcinogenic by promoting formation of expoxide compounds damaging the DNA[86, 91, 92, 93]. Many cases of urinary bladder cancer were reported among dye workers, due to aromatic amines[94, 95]. The epoxide detoxification systems of cells are also involved in protection against oxidative stress, so when depleted secondary damage to the cell may occur due to oxidative stress[96, 97]. Some azo dyes taken in by food may be reduced by bacteria in the alimentary tract to aromatic amines and further metabolism may result in production of oxygen containing radicals leading to oxidative stress[98]. Skin bacteria also possess the capacity to reduce azo dyes[99], which may increase the risk for exposure to carcinogenic aromatic amines from azodyes in materials in contact with the skin.

In this study, 22 aromatic amines classified as carcinogenic by European Commission (regulated in foodstuff by Directive 2002/72/EC and annex 17 of REACH) were analyzed (see table 5 in appendix II for the amines, CAS numbers and official risk classification).

Chlorinated phenols

The use of large volumes of chlorinated phenols as biocides, so also in leather industry, have made this group of organic compounds a common environmental pollutant[100, 101, 102]. There is a positive relationship between the degree of chlorination and the toxicity of a chlorinated phenol[101]. Pentachlorophenol and its sodium salt sodium-pentachlorophenol are extremely toxic chemicals, and the most well-studied chlorinated phenols[101]. Chlorinated phenols are easily absorbed across skin, lungs and the lining of the alimentary tract[103]. Many mechanisms appear to be responsible for the toxicity of chlorinated phenols. They have been reported to interfere with the metabolism of steroid hormones, and may thus disturb reproduction[104, 105, 106]. Pentachlorophenol has been shown to negatively affect the immune system in several ways[107, 108]. Furthermore, pentachlorophenol has recently been shown to induce tissue death by oxidative stress[109, 110]. Recent studies also indicate that even at low levels, pentachlorophenol exerts synergistic effects with other pollutants, such as cadmium, copper, ammonium and polycyclic aromatic hydrocarbons[111, 112]. Chlorinated phenols are persistent in the environment and can bioaccumulate[113, 114, 115]. Only from pentachlorophenol and sodium-pentachlorophenol, at least 32 abiotic or biotic degradation products have been identified, and many of them are potentially toxic, mutagenic or may damage the development of foetuses during gestation[116, 117]. Upon heating and burning of chlorinated phenols, they can be converted into even more toxic polychlorinated dibenzo-p-dioxins and dibenzofurans[118].

Compound: pentachlorophenol
CAS: 87-86-5
Official risk phrases: R24/R25 (toxic by inhalation and if swallowed), R26 (very toxic by inhalation), R36/37/38 (irritating to eyes, respiratory system and skin), R40 (limited evidence of a carcinogenic effect), and R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Compound: 2,3,4,5-tetrachlorophenol
CAS: 4901-51-3
Official risk phrases: R24/25 (toxic in contact with skin and if swallowed), R26 (very toxic by inhalation), R36/37/38 (irritating to eyes, respiratory system and skin), R40 (limited evidence of a carcinogenic effect), and R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Compound: 2,3,4,6-tetrachlorophenol
CAS: 58-90-2
Official risk phrases: R25 (toxic if swallowed), R36/R38 (irritating to eyes and skin), and R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Compound: 2,3,5,6-tetrachlorophenol
CAS: 935-95-5
Official risk phrases: R25 (toxic if swallowed), R36/R38 (irritating to eyes and skin), and R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Ortho-phenylphenol

Ortho-phenylphenole is a broad-spectrum fungicide and anti-bacterial agent with many different applications[119]. It can be used as a preservative in leather products[101]. Several studies have shown that metabolism of *ortho*-phenylphenole results in oxidative stress, DNA damage, and that this may cause cancer in the urinary bladder of at least rats (for reviews, see Bomhard *et al.* (2002) and Brusick (2005))[120, 121]. According to IARC, however, based on the present knowledge, ortho-phenylphenol is not classifiable as a human carcinogen[122]. This pesticide is not considered to be persistent in the environment or bioaccumulate, but can be found in bodily fluids of humans, such as urine and amniotic fluid[123, 124]. Tolerable daily intake of various pesticides for adults is probably not applicable to foetuses. Lack of reliable exposure data complicates pre-natal risk assessment. *Ortho*-phenylphenole and its sodium salt are very toxic to many aquatic species[125, 126].

Compound: *ortho*-phenylphenol
CAS: 90-43-7
Official risk phrases: R22 (harmful if swallowed), R37/38-41 (irritating to respiratory system and skin and risk of serious damage to eyes), and R50 (very toxic to aquatic organisms).

2,4,6-tribromophenol

2,4,6-tribromophenol is used as a fungicide, bactericide, and increasingly as a flame retardant[127]. It is highly fat soluble and persistent[126], which leads to accumulation in the environment[128], and bioaccumulation in organisms, including in humans, where it has, e.g., been found in fat, blood and milk[129, 130, 131]. In the indoor environment, it has been detected in dust[132]. Inhalation and ingestion of dust is, thus, one way of exposure. Although not officially classified as a disruptor of hormonal levels, there is plenty of evidence for such effects. Thyroid hormones regulate the cellular metabolic rate, and are essential for differentiation and development of several tissues, especially the brain[133, 134]. 2,4,6-tribromophenol easily binds to the proteins that transport and distribute thyroid hormones in the body[135, 136], consequently competing with thyroid hormones for these proteins. Disturbed supply of thyroid hormones during foetal development has been linked to effects on brain development, and to lower IQ in adulthood[137, 138, 139, 140]. Disrupted regulation of thyroid hormones may result in obesity[141, 142, 143]. Moreover, 2,4,6-tribromophenol also affects synthesis of sex hormones in the body, and hormones regulating the activity of the kidneys[144]. 2,4,6-tribromophenol is highly toxic to many aquatic species[145].

Compound: 2,4,6-tribromophenol
CAS: 118-79-6
Official risk phrases: No official classification, but in material safety data sheets often R36/37/38 (irritating to eyes, respiratory system and skin), and R50-53 (may cause long-term adverse effects in the aquatic environment).

Chlorinated paraffins

Chlorinated paraffins are members of a complex group of compounds that in leather industry sometimes are used in the tanning process for assisting removal of fat from raw hide, and then after tanning to assist re-fatting of the leather[146]. Chlorinated paraffins also have many other applications, such as being used as adhesives, lubricants and flame retardants for plastics and fabrics, and additives in paints, which has made them widespread environmental pollutants[147]. Chlorinated paraffins are hazardous to the environment because of their toxicity towards aquatic and soil species[148, 149], persistence and potential of magnification in food chains of ecosystems[149, 150, 151]. They are often found in sewage sludge, as well as in soil, sediments, water and organisms[149, 151, 152, 153, 154, 155], even in remote areas[151]. In organisms, chlorinated paraffins can be transformed into chlorinated fatty acids which are transferred along food chains and may have various toxic effects[156]. Chlorinated paraffins have been found to modulate thyroid hormone levels in experimental animals[157], which should raise concern (possible effects were discussed in the above section for 2,4,6-tribromophenol). Furthermore, the short chain chlorinated paraffins have proven to be carcinogenic to rats and mice[147], and IARC has classified short chain length chlorinated paraffins as possibly carcinogenic to humans (class II B)[158]. There is also some evidence for the carcinogenicity of medium chain length chlorinated paraffins, and low molecular weight chlorinated paraffins, or their breakdown products[155, 159, 160].

Compounds: Chlorinated paraffins, chain length C10-C13
CAS: 85535-84-8
Official risk phrases: R40 (limited evidence of a carcinogenic effect), and R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Compounds: Chlorinated paraffins, chain length C14-C17
CAS: 85535-85-9
Official risk phrases: R64 (signifying may cause harm to breast-fed babies), R66 (repeated exposure may cause skin dryness or cracking), and R50-53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Compounds: Chlorinated paraffins, chain length more than C17
CAS: 85535-86-0
Official risk phrases: R52-53 (harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

Dimethylfumarate

Dimethylfumarate can be used as a preservative for protecting leather goods and fabric from mold during transportation and storage. Sachets containing dimethylfumarate are placed inside shoe boxes, couches and clothes, from where dimethylfumarate disseminates and impregnates the product[161]. This compound was recently shown to be a potent agent able of causing contact dermatitis (an immune system related allergic skin response, resulting in eczema)[162, 163]. Exposure to dimethylfumarate has produced eczemas very difficult to treat in patients from several countries. The first cases in Europe, reported in 2006, were linked to couches and chairs manufactured in China, and were followed by several new cases linked to various consumer goods, among them footwear[161]. The use of dimethylfumarate is, as far as known, primarily a health issue.

Compound: Dimethylfumrate
CAS: 624-49-7
Official risk phrases: R21 (harmful in contact with skin), and R36/37/38, R43 (irritating to eyes, respiratory system and skin, may cause sensitisation by skin contact).

Formaldehyde

Formaldehyde has long been used as a preservative, and, more recently in several industrial applications, including production of adhesives and binders for wood, plastic, textiles and leather[164]. It is also used in the production of tanning resins for leather[165], and, therefore, potentially present as a by-product in finished leather. Formaldehyde is a common air pollutant in tanneries[166]. Studies on experimental animals has shown that inhalation of high levels of formaldehyde induces cancer in the nasal cavity[164]. Whether it is a human carcinogen is still debated[167, 168], but many international agencies and organizations classify it as a "suspected" or "potential" carcinogen with respect to cancer in the nasal cavity and pharynx[166.] Formaldehyde is well-known to be a potent inducer of contact dermatitis[169, 170]. The formaldehyde containing compound para-tertiary bytulphenol formaldehyde, used in adhesives in footwear, has been shown to elicit contact dermatitis on feet[171]. Formaldehyde can, thus, be an occupational hazard, as well as a hazard for the consumer of products with formaldehyde remnants. The use of dimethylfumarate is, as far as known, primarily a health issue.

Compound: Formaldehyde
CAS: 50-00-0
Official risk phrases: R23/24/25 (toxic by inhalation, in contact with skin and if swallowed), R34 (causes burns), R40 (limited evidence of a carcinogenic effect), and R43 (may cause sensitisation by skin contact).

Chemicals regulation and policy

In the EU and Sweden

No legislation in the EU specifically regulates the content of chemicals in shoes, but the use of some of the chemicals in this study is restricted within the framework of the EU regulation REACH (EC1907/2006), directly valid as Swedish law. In addition to REACH, the general rules of the national environmental legislation the Swedish Environmental Code (in Swedish miljöbalken) also apply to shoes produced or sold in Sweden. The rules of chapter 2 of the Swedish Environmental Code, stipulates that a producer is obliged to obtain sufficient knowledge of the environmental and health impacts of her/his products, and if the impacts are not clear, the precautionary principle shall be applied. Any chemicals posing risks to environment and health shall be substituted by less dangerous alternatives. The statutes in the Code are implemented by, e.g., supervision and the Code is further operationalised in a number of Ordinances with relevance for chemicals management. Furthermore, in order to comply with Swedish Product Safety Ordinance (2004: 469), consumer goods must be safe for the health of the consumers to be allowed for selling on the market.

The only metals in this study for which REACH, or Swedish law, is applicable to leather goods are mercury and nickel. There is a national ban in Sweden on the intentional use of mercury in consumer goods (Ordinance 1998:944, issued pursuant to chapter 14, §8 of the Swedish Environmental Code). Nickel is prohibited in consumer goods in prolonged contact with skin, if the emission of nickel exceeds 0,5 µg/cm^2/week (REACH, annex XVII).

Carcinogenic amines from azo dyes must not exceed 30 µg/g in shoes and other leather goods (REACH, annex XVII).

Short-chained chlorinated paraffins are not allowed at concentrations exceeding 1% in products intended for fat liquoring of leather (REACH, annex XVII). However, this stipulation does not protect consumers from imported leather goods prepared with short-chained chlorinated paraffins. In 2001, EU included short-chained chlorinated paraffins in the list of priority substances in the field of water policy, amending the Water Framwork Directive (WFD 2000/60/EC). The WFD defines water quality standards for European waters, with respect to the priority substances. Substances listed in the WDF, will be subject to phase out with an appropriate time table that shall not exceed 20 years.

From 1998, dimethylfumarate is banned as a biocide for products manufactured in the EU (Directive 98/8/EEC), but producers outside the union still use it, so it has until now entered the EU market. Since May the 1st 2009, dimethylfuramate is also banned in imported products (see 2009/251/EEC), in order to protect EU consumers from this compound. Products, or part of their accessories, containing at least 0,1 µg/g dimethylfumrate, shall be withdrawn from the market.

Globally

The Strategic Approach to International Chemicals Management (SAICM) aims at sound management of chemicals throughout their life cycle so that, by 2020, chemicals are produced and used in ways that minimize significant adverse impacts on human health and the environment. This "2020 goal" was adopted by the World Summit on Sustainable Development in 2002 as part of the Johannesburg Plan of Implementation. In February 2006, the first International Conference on Chemicals Management (ICCM) adopted the completed SAICM, which comprises the Dubai Declaration on International Chemicals Management, expressing high-level political commitment to SAICM, and an overarching policy strategy which sets out its scope, needs, objectives, financial considerations, underlying principles and approaches, implementation and review arrangements. One important outcome was the agreement to make available relevant documentation on health and environmental assessments for all chemicals in international trade, and to provide information on the contents of hazardous chemicals in articles.

Materials and methods

Selection of shoes for the study and reference material

Shoes selected for this study are well-known brands, bought from major retailers in the respective countries participating in the study. They represent a wide selection of different kinds of leather shoes for adults, gents and ladies (see table 1). A total of 21 pairs of shoes were bought during the period end of July to the mid of October 2009 (11 pairs from Sweden, and 2 pairs in South Africa, Uganda, India, the Philippines and Belarus respectively). The shoe by El Naturalista, bought in Sweden, was claimed by assistants in the shop of purchase to be vegetable tanned, and the shoe by Veja was prior to purchase confirmed by the producer to be vegetable tanned.

Reference material for getting an idea of the background levels of metals in raw cow hide, prior to tanning, was provided by the Swedish leather producer Elmo Leather AB.

Analyses

All analyses were performed by Swerea IVF, Mölndal, Sweden, except for the analysis of hexavalent chromium, performed by Eurofins, Lidköping, Sweden.

Analyses of the total metal content

Leather samples (1 g each) from the shoes were finely shredded, whereupon oxidised and dissolved in concentrated nitric acid (10 ml/sample) for 24 hours. The acid in the samples was then diluted to 20% (volume/volume) and the samples were left for another 24 hours for additional metal leaching and stabilisation of the metal salts. All samples were during the two days kept in small and sealed tubes, to minimize loss of volatile compounds and avoid contamination. An ICP-OES (Perkin-Elmer Optima 2100DV with a Meinhard nebuliser and cyclonic spray chamber) was used for the analyses according to a modified version of the method US EPA 200.7. For quantification, a certified standard solution was used.

Analyses of chromium VI

Chromium was leached from the leather (5 g) samples in Milli-Q (50 ml) water using an ultrasound bath for 15 min. Trivalent and hexavalent chromium were subsequently separated by HPLC (Perkin Elmer 200 with a C-8 column), whereupon the hexavlent chromium was analysed with ICP-MS (Eland DRC II). The handling of samples and analyses were done according to EN ISO 5567-3:2004, and a modified method in Chang and Jiag (2001)[172]. The analyses of chromium VI were complicated by the high total levels of chromium, which masks the content of chromium VI. The detection limits had to be individually adjusted with respect to the total chromium level, other disturbances, and dilution.

Analyses of carcinogenic aromatic amines from azo dyes

Preparation of the samples was done according to ASU B, 03-03-97, Nachweis bestimmter Azofarbstoffe in Leder. Leather samples (1 g each) were first washed with hexane to remove the surplus of fat. The azo bonds in the dyes were then reduced by ditionite and the samples cleaned using columns packed with diatomaceous earth. The eluates from the columns were analysed in scanning mode with a GC-MS (Agilent 6890N gas chromatograph with a split/splitless injector coupled to an Agilent 5973N mass spectrometer with EI ionisation. A 30 m 0.25/0.25 Zebron ZB-5 column from Phenomex was used.). For quantification, an internal standard and calibration solutions containing the aromatic amines of interest were used. The detections limits for the amines were individually less than 20 mg/kg, and as low as 1 mg/kg for some, such as 4-aminodiphenyl and benzidine.

Analyses of chlorinated phenols, ortho-phenylphenol, and 2,4,6-tribromophenol

The analyses were carried out according to the method M-7 by Öko-Tex. Phenols were extracted in two cycles from the leather samples (5 g each) using potassium carbonate solution (50 ml) and an ultrasound bath.They were subsequently derivatised by anhydrous acetic acid. The formed phenolic esters were separated from the solution by hexane extraction, whereupon analysed in SIM mode by GC-MS (Agilent 6890N gas chromatograph with a split/splitless injector coupled to an Agilent 5973N mass spectrometer with EI ionisation. A 30 m 0.25/0.25 Zebron ZB-5 column from Phenomex was used.). Calibration was done with a certified reference material and the analyses carried out with an internal standard containing the phenols of interest. Also the internal standard was derivatised by anhydrous acetic acid.

Analyses of chlorinated paraffins

Four pairs of shoes (number 4, 14, 17, and 21 from table 1) which had distinctive odours and leather textures different to the rest of the shoes were selected for a qualitative screening for chlorinated paraffins. Leather samples (1 g each) were extracted in hexane (10 ml/sample) for 15 hours. The extracts were then analysed by GC-MS (Agilent 6890N gas chromatograph with a split/splitless injector coupled to an Agilent 5973N mass spectrometer with EI ionisation. A 30 m 0.25/0.25 Zebron ZB-5 column from Phenomex was used.) without the possibility to exactly quantify the chlorinated paraffins. The screening was done to look for the short-chained (C10-13) chlorinated paraffins regulated in the EU water framework directive 2000/60/EC.

Analyses of dimethylfumarate

The analyses were done according to the method Swerea IVF 80-09. Dimethylfumarate was extracted in two cycles from leather samples (1 g each) using methanol (about 20 ml, depending upon how much was absorbed by the sample) and elevated temperature (80° C) and pressure (2000 psi) in a Dionex ASE200. The extracts were analysed in SIM mode by GC-MS (Agilent 6890N gas chromatograph with a split/splitless injector coupled to an Agilent 5973N mass spectrometer with EI ionisation. A 30 m 0.25/0.25 Zebron ZB-5 column from Phenomex was used.) using an internal standard. The quantification was done with aid of an external standard.

Analyses of formaldehyde

The analyses were done as a screening according to the chromotrophic acid method. The leather material was cut into small pieces, wetted by water and then placed in vessels (< 1 dm^3) with a white porcelain cup filled with chromotrophic acid. There is no direct contact between the leather and the acid. In the closed vessel, the volatile aldehydes will first go into gaseous phase, whereupon dissolve in the acid. The acid reacts with aldehydes and changes colour. It is a change in colour proportional to the amount of aldehyde, but the method is considered only semi-quantitative. An experienced analyser can detect low amounts of aldehydes (at 15 mg/kg, the acid starts to change colour in the direction of blue). In practise aldehydes other than formaldehyde may influence the result, but formaldehyde is the only volatile aldehyde expected to be commonly found in leather.

Correction of wet to dry weight

When the raw reference material arrived to the laboratory, it was wet and salted. Consequently, the metal levels detected had to be corrected for wet to dry weight. A sample of the raw hide was dried overnight at 80° C, and subsequently weighed after removal of the hair. Half of its weight was lost upon drying.

Table 1 Information about the shoes in the study (number of the shoe sample, producer/agent, country of purchase, shop of purchase, name of the shoe/article number/model number, type of shoe, country of manufacture, price in domestic currency, and price in US dollar).

Number	1	2	3	4	5	6	7
Producer/ Agent	Nilson	Ara	Timberland	Björn Borg	Converse	Scorett	Din Sko
Country of purchase	Sweden	Sweden	Sweden	Sweden	Sweden	Sweden	Sweden
Shop of purchase	Nilson	Eurosko/ Skohornet	Eurosko/ Skohornet	Eurosko/ Skohornet	Scorett	Scorett	Din Sko
Name of the shoe/article nb./model nb.	Brouge Bootie BLK21	Jennie by Ara, Columbia Ocean	Speke MTC	67406882	Chuck Taylor One Star leather	0103112701 4006	Jordan
Type of shoe	gents boots	ladies loafers	gents boots	gents black polido loafers	gents boots	ladies pumps	ladies pumps
Country of manufacture	Portugal	Indonesia	China	No data	Indonesia	No data	Vietnam
Price, domestic currency	SEK 950	SEK 699	SEK 1199	SEK 899	SEK 999	SEK 250	SEK 199
Price. US Dollar	138	101	174	130	145	36	29

Number	8	9	10	11	12	13	14
Producer/ Agent	Vagabond	Lino Moda	El Naturalista	Veja	Groundcover	Groundcover	Bata Shoe Company Ltd
Country of purchase	Sweden	Sweden	Sweden	Sweden	South Africa	South Africa	Uganda
Shop of purchase	Vagabond	Crispin	Knulp	Scoop	Groundcover	Groundcover	Bata Shoe Company Uganda Ltd
Name of the shoe/article nb./model nb.	Portillo	11008103	Iggdrasil N104	Veja grama leather GR2007, black velour	Slip on	Oxford	751-6026
Type of shoe	ladies mid cut boots	gents shoes	ladies shoes	ladies sneaker	ladies loafers	gents shoes	ladies pumps
Country of manufacture	Vietnam	No data	Spain	Brazil	South Africa	South Africa	No data
Price, domestic currency	SEK 1 200	SEK 800	SEK 1 065	SEK 1 299	ZAR 345	ZAR 285	UGX 40 000
Price. US Dollar	174	116	154	185	47	39	21

							
Number	**15**	**16**	**17**	**18**	**19**	**20**	**21**
Producer/ Agent	Bata Shoe Company Ltd	Bandolino	Rusty Lopez	Bata India Ltd	Bata India Ltd	San Marko	San Marko
Country of purchase	Uganda	Philippines	Philippines	India	India	Belarus	Belarus
Shop of purchase	Bata Shoe Company Uganda Ltd	SM Centerpoint	SM Centerpoint	Liberty Retail Revolutions Ltd	Bata India Ltd	San Marko	San Marko
Name of the shoe/article nb./model nb.	Premium collection	Bandolino boot	Rusty Lopez laced up	Generation you gliders	Pinoso Black	13252	27188
Type of shoe	gents shoes	ladies boots	gents shoes	ladies loafers	gents shoes	ladies boots	gents shoes
Country of manufacture	No data	Philippines	Philippines	India	India	Belarus	Belarus
Price, domestic currency	UGX 85 000	PHP 1 400	PHP 2 000	INR 999	INR 1 599	BYR 137 570	BYR 150 390
Price. US Dollar	44	29	42	21	33	50	54

Results

Metals

In most of the shoes, the levels of metals are higher than in the reference material (see table 2 compared with 3).

Variable levels of the studied metals were detected in the shoes (see table 3). Trivalent chromium is by far the most common metal in the shoes. Also the shoe by El Naturalista, claimed to be vegetable tanned, has a high total level chromium. Hexavalent chromium was found in a shoe by Bata (sample number 14). Cadmium and nickel are the only studied metals absent in some of the shoes (16 shoes are free of cadmium; 9 free of nickel). Only a few shoes are free of both cadmium and nickel (sample number 2, 7, 9-11, 16, and 21), and most of them were bought in Sweden. The shoe by Timberland (sample number 3) has a high level of copper compared to the rest of the studied shoes, the shoes by Scorett, Groundcover, and Rusty Lopez (sample number 6, 12, 13, and 17) have the highest levels of lead, and the shoe by Scorett and two by Bata (sample number 6, 14, and 18) have the highest levels of zink.

Carcinogenic aromatic amines from azo dyes

Two of the carcinogenic aromatic amines regulated in REACH were found in the studied shoes. In the shoe by Din Sko (sample number 7), 4-amiodiphenyl was detected, and benzidine was detected in the shoe by Rusty Lopez (sample number 17) (see table 4).

Chlorinated phenols

No chlorinated phenols were detected in the studied shoes (see table 4).

Ortho-phenylphenol

Ortho-phenylphenol was found in the shoes by Nilson, Vagabond, Lino Moda, and Rusty Lopez (sample number 1, 8, 9, and 17) (see table 4).

2,4,6-tribromophenol

2,4,6-tribromophenol was found in the shoe by Veja (sample number 11) (see table 4).

Chlorinated paraffins

Chlorinated paraffins were detected in a few shoes scanned for this class of compounds (sample number 4, 17 and 21) (see table 4). However, no further analyses or quantifications were carried out, since the scanning did not indicate the presence of short-chained chlorinated paraffins (of chain lengths with 10-13 carbon atoms) in the studied material. Quantification standards are not commercially available for long-chained paraffins.

Dimethylfumarat

Dimethylfumarate was detected in one shoe by Jennie by Ara (sample number 2) (see table 4).

Formaldehyde

Two shoes, the shoe by Scorett and one by Bata (sample number 6 and 18), were tested positive for formaldehyde (see table 4).

Table 2 Total content of arsenic, cadmium, chromium (total), cobalt, copper, lead, mercury, nickel and zinc in raw cattle hide. In the table, the detection limits are preceded by the "less than sign" (<) and denote the lowest concentrations detectable by the method of analysis in question.

Sample	Land of purchase	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (total) (mg/kg)	Cobalt (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Nickel (mg/kg)	Zink (mg/kg)
Reference material	Sweden	0.68	<0.05	<0.3	<0.3	1.8	0.36	0.22	<0.3	14

Table 3 Sample number of shoe, land of purchase and total content of arsenic, cadmium, chromium (total + VI), cobalt, copper, lead, mercury, nickel and zinc. In the table, the detection limits are preceded by the "less than sign" (<) and denote the lowest concentrations detectable by the method of analysis in question. The "negative sign" (-) denotes no value.

Sample number	Land of purchase	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (total) (mg/kg)	Chromium (VI) (mg/kg)	Cobalt (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Nickel (mg/kg)	Zink (mg/kg)
1	Sweden	29	0.05	28 000	<0.98	1.1	5.1	1.4	1.1	<0.3	6.4
2	Sweden	18	<0.05	26 000	<0.17	2.1	1.5	0.22	1.0	<0.3	12
3	Sweden	16	<0.05	24 000	<0.01	2.2	490	0.48	1.0	0.6	42
4	Sweden	10	<0.05	13 000	<0.2	0.52	2.9	11	1.2	1.0	14
5	Sweden	15	0.07	18 000	<0.14	0.94	<0.3	1.0	1.1	0.4	140
6	Sweden	14	<0.05	18 000	<0.12	0.84	8.9	91	1.0	0.4	850
7	Sweden	17	<0.05	21 000	<0.14	1.3	1.3	1.0	0.89	<0.3	16
8	Sweden	9.3	<0.05	11 000	<0.23	2.6	72	33	1.9	0.8	5.2
9	Sweden	22	<0.05	26 000	<0.22	1.9	1.6	1.5	1.1	<0.3	99
10	Sweden	18	<0.05	24 000	<0.2	1.0	8.3	0.31	1.2	<0.3	10
11	Sweden	0.84	<0.05	42	-	<0.3	1.9	0.72	0.13	<0.3	28
12	South Africa	14	<0.05	18 000	<0.17	2.8	5.7	110	0.91	0.3	10
13	South Africa	16	<0.05	20 000	<0.17	11	0.8	130	0.93	0.4	9.2
14	Uganda	4.3	0.07	4 500	0.025	3.1	<0.3	4.8	0.51	0.4	340
15	Uganda	13	0.06	17 000	<0.02	1.0	8.9	19	0.80	<0.3	68
16	Philippines	20	<0.05	27 000	<0.12	16	3.2	1.3	1.0	<0.3	37
17	Philippines	21	0.15	28 000	<0.3	2.2	9.5	72	0.93	3.5	38
18	India	18	<0.05	25 000	<0.16	1.4	9.3	7.4	0.95	0.8	260
19	India	14	<0.05	19 000	<0.1	11	3.8	2.0	0.88	0.4	29
20	Belarus	19	<0.05	24 000	<0.11	1.5	7.2	3.5	0.93	0.3	29
21	Belarus	22	<0.05	29 000	<0.22	1.2	15	0.40	1.1	<0.3	160

Table 4 Sample number of shoe, land of purchase and total content of 4-aminodiphenyl, benzidine, pentachlorophenol, tetrachlorophenol, *ortho*-phenylphenol, 2, 4, 6-tribromophenol, chlorinated paraffines (all chain lengths), chlorinated paraffins (chain lengths C10-C13), dimethylfumarate and formaldehyde. In the table, the detection limits are preceded by the "less than sign" (<) and denote the lowest concentrations detectable by the method of analysis in question. The "negative sign" (-) denotes no value.

Sample number	Land of purchase	4-amino-diphenyl (mg/kg)	Benzidine (mg/kg)	Pentachloro-phenol (mg/kg)	Tetrachloro-phenols (mg/kg)	*Ortho*-phenyl-phenol (mg/kg)	2, 4, 6-tri-bromophenol (mg/kg)	Chlorinated paraffins (all chain lengths)	Chlorinated paraffins (chain lengths C10–13)	Dimethyl - fumarate (mg/kg)	Formaldehyde (mg/kg)
1	Sweden	<1	<1	<0.04	<0.04	2.9	-	-	-	<0.1	no
2	Sweden	<1	<1	<0.04	<0.04	<0.1	-	-	-	0.1	no
3	Sweden	<1	<1	<0.04	<0.04	<0.1	-	-	-	<0.1	no
4	Sweden	<1	<1	<0.04	<0.04	<0.1	-	yes	no	<0.1	no
5	Sweden	<1	<1	<0.04	<0.04	<0.1	-	-	-	<0.1	no
6	Sweden	<1	<1	<0.04	<0.04	<0.1	-	-	-	<0.1	<30
7	Sweden	2*	<1	<0.04	<0.04	<0.1	-	-	-	<0.1	no
8	Sweden	<1	<1	<0.04	<0.04	8.9	-	-	-	<0.1	no
9	Sweden	<1	<1	<0.04	<0.04	1.2	-	-	-	<0.1	no
10	Sweden	<1	<1	<0.04	<0.04	<0.1	-	-	-	<0.1	no
11	Sweden	<1	<1	<0.04	<0.04	<0.1	30**	-	-	<0.1	no
12	South Africa	<1	<1	<0.04	<0.04	<0.1	-	-	-	<0.1	no
13	South Africa	<1	<1	<0.04	<0.04	<0.1	-	-	-	<0.1	no
14	Uganda	<1	<1	<0.04	<0.04	<0.1	-	no	-	<0.1	no
15	Uganda	<1	<1	<0.04	<0.04	<0.1	-	-	no	<0.1	no
16	Philippines	<1	<1	<0.04	<0.04	<0.1	-	-	-	<0.1	no
17	Philippines	<1	68	<0.04	<0.04	4.3	-	yes	no	<0.1	no
18	India	<1	<1	<0.04	<0.04	<0.1	-	-	-	<0.1	<20
19	India	<1	<1	<0.04	<0.04	<0.1	-	-	-	<0.1	no
20	Belarus	<1	<1	<0.04	<0.04	<0.1	-	-	-	<0.1	no
21	Belarus	<1	<1	<0.04	<0.04	<0.1	-	yes	no	<0.1	no

*) In sample number 7 there were also other amines, indicative of the dye stuff C.I. Acid Red 26 (CAS 3761-53-3), which in itself is officially classified as carcinogenic.

**) The extraction efficiency for 2,4,6-tribromophenol has not been determined, so the detected concentration in sample number 11 can be even greater than 30 mg/kg.

Discussion

Exposure to the studied chemicals from manufacturing, consumption and waste

With this study, the SSNC demonstrates that several chemicals hazardous to health and the environment are present in leather from ordinary shoes bought in six countries around the globe. These chemicals can be hazardous during the whole life cycle of the shoe.

Nowadays, leather processing and manufacturing of shoes is often located in developing countries. Legislation relating to occupational safety, health and the environment, and the control of compliance with such, is frequently weak in these countries[173, 174]. The workers are often not properly informed about how to handle hazardous chemicals[174], and the working conditions often poor[175]. Twenty two percent of workplace fatalities and work-related diseases worldwide are due to improper handling of chemicals[176]. Environmental degradation in areas with heavy leather industry can be substantial. In India, e.g., the Supreme Court placed a ban on tanneries in 1995, leading to their temporary closure, and imposed fines for compensating farmers for loss of arable land due to pollution[177]. Most of the Indian tanneries, however, are now back in operation with wastewater treatment plants. Metal pollution of soils and water due to leather processing is, however, common[178]. Considering the high levels of metals left in the leather of the shoes, it can be assumed that the wastewater from the processing must have been heavily contaminated. Mutagenic and carcinogenic activity in drinking water from a river in Brazil polluted by azo dyes has been confirmed[179]. Several studies have also shown that complex tannery effluents containing the classes of organic chemicals detected in this study (e.g. benzidine, 4-aminodiphenyl, and formaldehyde) may influence hormonal levels and lead to developmental and reproductive disorders in animals[180].

People handling and consuming the shoes can be exposed to the chemicals via dermal uptake, or by inhalation of the volatile compounds.

Although dermal uptake of metals is not a major exposure route, it can take place, particularly if the metals are in organic form. Uptake of cobalt, nickel and chromium applied to human skin samples in a synthetic sweat solution, and increased uptake when the skin was damaged, has been demonstrated[181]. Chromium in its hexavalent form readily crosses skin[46, 182]. It has also been shown that arsenic and mercury may cross human skin[182, 183]. Arsenic and mercury can be part of leather preservatives. Salts of the organic mercury compounds, e.g., such as phenylmercury acetate, have been used by the leather industry as fungicides[184]. Salts of organic mercury compounds damage the DNA in various ways, and may thus promote formation of cancer[185, 186, 187, 188], although these salts are not officially classified as carcinogens. In this study, it could not be deduced in which form, inorganic and/or organic, arsenic and mercury were in the leather. For cadmium, copper and zinc, no data on penetration of human skin was found, but at least cadmium can be taken up through the skin of rodents[189]. If foot sweating is profusive, and if thin or no stockings at all are used, it seems plausible that metals are leached from the leather of shoes into the sweat and cross the skin into the body. Blisters and other lesions on the foot may perhaps enhance the uptake. Varying levels of metals exceeding those in the reference leather were detected in all shoes of the study.

It is known that azo dyes may penetrate human skin, and that skin cells possess enzymes that reduce azo bonds, potentially leading to the formation of carcinogenic aromatic amines[190]. Similar enzymes have also been found in skin bacteria[99]. Azo dyes can be leached from leather into sweat, which facilitates their dermal uptake[191]. The carcinogenic aromatic amine benzidine was found in the leather of a shoe by the Philippine shoe manufacturer Rusty Lopez at concentrations more than twice the allowed 30 µg/g according to REACH. This finding is alarming. The shoe by the Swedish shoe manufacturer Din Sko contained 4-aminodiphenyl under the 30 µg/g limit stipulated in REACH, but other amines (xylidines) found in this sample suggest that the mother dye may have been C.I. Acid Red 26 (CAS 371-53-3), which in itself is carcinogenic. There is, however, no available analytic method for verification that the mother dye was C.I. Acid Red 26[146].

Ortho-phenylphenol is fat soluble and has been shown to penetrate human skin[192]. *Ortho*-phenylphenol was found in the shoes by the Swedish manufacturers Nilson, Vagabond, Lino Moda and by the Philippine manufacturer Rusty Lopez.

No information on skin penetration of 2,4,6-tribromphenol was found, but with respect to the high fat solubility of this compound, it seems plausible that such can take place.

Industrial workers, shop assistants and consumers are at risk of allergic responses, such as eczemas, when handling or using shoes containing the highly allergenic compound dimethylfumarate. It is, however, surprising that dimethylfumarate is still found in products on the EU market. The dimethylfumarate ban decrees products containing this compound to be withdrawn from the market with immediate action, as the ban came into force in May the 1st 2009. The level of dimetylfumarate found in the shoe by Jennie by Ara, corresponds to the allowed 0.1 µg/g limit, as stipulated in the directive 2009/251/EEC.

Low levels (less than 30 mg/kg) of the highly allergenic and potentially carcinogenic compound formaldehyde were found in a shoe by the Swedish shoe manufacturer Scorett and in a shoe by Bata, bought in India. Formaldehyde is volatile and thus evaporates with time after its application. Industrial workers, shop assistants unpacking newly arrived shoes are at risk of exposure, as are buyers of the shoes. The shoe by the Swedish shoe manufacturer Scorett was on sale, and appeared to have been on shelf in the shop for a while, but formaldehyde was still detectable in it.

The final life stage of a shoe is as waste. In the period 2000 to 2008, almost 71 500 tonnes of leather shoes of the type used for this study were imported to Sweden[193]. About a quarter of the total weight of an ordinary leather shoe is leather, as estimated from the shoes bought in Sweden. If this holds, and if the detected levels of metals in the leather in this study are representative of an average Swedish shoe sample, about 38 kg arsenic, 32 kg lead, 46 800 kg chromium, 3.3 kg cobalt, 138 kg copper, 0.7 kg nickel, 2.6 kg mercury and 263 kg zinc, on average, were annually imported to Sweden between 2000 and 2008. Eventually the metals end up as waste with the shoes. Globally, about 600 000 tonnes of solid leather waste is produced annually by the leather industry[194]. Worn out shoes and leather waste from the industry are sent to a dump or an incinerator.

In many parts of the world it is still common to landfill waste. As precipitation percolates the landfill, chemicals can be leached out of the waste, and if no appropriate treatment of the leacheate is in place, the chemicals may eventually reach surface and groundwaters. This is of concern for the safety of drinking water. Chromium, commonly found at high concentration in leather waste, is of particular concern in this respect. Disinfection of drinking water usually takes place under strong oxidising conditions, which may promote oxidation of the less toxic trivalent chromium to the more toxic hexavalent form[195]. Hexavalent chromium may also react with magnesium in the drinking water, producing carcinogenic magnesium and calcium chromate or dichromate salts[195]. Arsenic and lead are other metals of concern in drinking water[196, 197]. In a risk assessment, it was pointed out that azo dyes may be leached from landfilled leather waste[198], which can lead to formation of carcinogenic aromatic amines in the environment. In the EU, the targets set by the Landfill Directive (1999/31/EC) are to reduce the amount of biodegradable waste landfilled to 50% of the 1995 value no later than July 16th 2009, and to 35% of the 1995 value no later than July 16th 2016[199]. The reason is to cut emissions of greenhouse gases from decomposition of organic matter. This implies that increasingly more waste of the type that leather products belong will be incinerated in the EU. In the countries outside the union, landfilling and incineration of waste are both commonly practised[200].

The chemicals found in leather in this study can also be problematic when incinerated. Metals are not destroyed upon incineration, but volatilised at the high temperature, and subsequently condensed to form metallic particles during the cooling of the flue gas. These particles are submicron in size and may be hazardous to human health[201, 202]. Depending upon the composition of the waste, such as its content of hydrogen, chlorine, oxygen, sulphur, sodium, and calcium, as well as the temperature of incineration, trivalent chromium may oxidise into hexavalent[203]. Combustion of halogenated compounds, such as chlorinated and brominated phenols, may result in formation of dioxins and furans[204, 205, 206]. Dioxines and furans are highly toxic, detrimental to the development of foetuses and infants in many ways, and may cause neurocognitive deficits, hormonal disturbances leading to reproductive dysfunction and cancer[207, 208].

With appropriate filters, metals, dioxins and furans can to a high degree be removed from flue gas[209, 210]. Emissions of hazardous chemicals, including metals, dioxins, and furans, from incinerators are regulated in the EU Waste Incineration Directive 2000/76/EC , which necessitates the use of filters for cleaning flue gas. However, metals, dioxins and furans remain in the filters and may be leached from them, depending upon how the used filters are finally disposed. The same goes for the fly ash formed in the incineration process. Due to the high metal content, the use of fly ash from incinerators today is limited in many countries. In Sweden, there is a wish to able to use waste incineration ashes in, e.g., road construction and cement production, but the high metal content of the ashes means that they often instead must be landfilled in special dumps for dangerous waste[211]. Hexavalent chromium, e.g., has been shown to be leachable to various degrees from fly ashes, and mortars and cements composed of fly ash[212, 213].

In countries where environmental regulations and compliance with such is weaker than in the EU, and good technology for cleaning flue gas may not be affordable, incineration can be as large a problem as landfilling.

The SSNC is of the opinion that most of the detected chemicals do not belong in consumer products, such as leather goods, at all. The chemicals are discussed in the paragraphs below.

Metals

In 2007, the SSNC analysed towels for chemicals, metals among them[214]. This year, metals were also studied by the SSNC in plastic shoes[215]. More metals, in general, were found in the shoes than in the towels. This study has shown that metals are more abundant in leather than in plastic shoes, with a few exceptions.

Since metals are natural constituents of leather, it was necessary to get an idea of the background levels of metals by analysing a reference hide. Background levels of metals in an animal depend on many factors, such as the geographic origin of the animal, species, sex, its age upon slaughtering, and life-style related factors[216, 217, 218, 219], so caution must be taken when interpreting the results from the reference material. However, metal levels of similar magnitude detected in the reference hide and in the leather from the studied shoes, can be interpreted as indicative of background levels.

High levels of lead were found in one Swedish shoe (sample number 6, by Scorett), and two South African shoes (sample number 12 and 13, by Goundcover), compared to the reference material. The shoe by Scorett is with respect to lead close to the maximum acceptable concentration of the EU flower ecolabel for shoes, and the shoes by Groundcover exceed the concentration. Groundcover claims in their homepage to be environmentally responsible[220], but to live up to this claim, Groundcover should not have lead in their shoes.

The level of copper was notably high in the shoe by the U.S shoe manufacturer Timberland (sample number 3), compared to the reference material. Copper is often used in dyes for producing blue, turquoise and green shades[221], but the shoe in question is brown, which makes us wonder why copper is there at such a high level. Timberland is a brand with an image strongly linked to the outdoors, and the company claims in their homepage to be environmentally responsible[222]. The high copper level soils this image. Within many ecolabels for textiles, including the Bra Miljöval Ecolabel of the SSNC (Good Environmental Choice), there is a long-term ambition of pushing the textile industry to phase out copper containing dyes. The SSNC urges that the leather and shoemaking industry should do such a phase out.

With the exception of the shoe by Veja (sample num ber 11), all shoes in this study had a much higher content of arsenic than the reference material, which suggests that arsenic could have been added in the processing of the leather. If not intentionally added, arsenic is perhaps an impurity from the tanning solution, since only the vegetable tanned shoe had an arsenic level comparable to the reference material.

The level of mercury in the majority shoes was also much higher than in the reference material, suggesting that mercury could have been added in the processing of the leather. It is particularly high in the shoe by Vagabond (sample number 8). In Sweden, there is a national on mercury. All shoes bought in Sweden, with the exception of the shoe by Veja, are consequently, at risk of not complying with Swedish law.

Highly variable levels of zink in the leather of the shoes clearly show that it is possible to produce shoes containing low levels of zink. The shoes by the U.S. shoe manufacturer Converse (sample number 5), the Swedish shoe manufacturer Scorett (sample number 6), the global giant shoe manufacturer Bata (samples number 14 and 18), and the Belarusian shoe manufacturer San Marko (sample number 21) stand out from the rest of the shoes in this study for having the highest levels of zink.

At present, 80-85% of all leather produced is chromium tanned[223], and not surprisingly, high levels of trivalent chromium were found in the shoes. The figure should be lowered, as there are emerging alternatives to chromium tanning, yielding high quality leather (this discussion is further developed below, in the section about tanning). Hexavalent chromium in a shoe is unacceptable (sample number 14 by Bata Uganda). If the hexavalent chromium arose as a result of improper tanning conditions, or use of certain leather chemicals, e.g. fish oil promoting chromium oxidation[224], can only be speculated.

Intentional addition of chemicals containing arsenic, lead, mercury and nickel to leather should not be allowed. At the UN summit in Johannesburg in 2002, an international undertaking for reducing sources of human exposure to lead was agreed upon[225]. The chemical guidelines of the Textile Importer´s Association in Sweden, organising some of the Swedish shoe producers and retailers, lists lead as a metal that should not be allowed in pigments and dyes[226]. Many countries are working to phase out mercury from areas of application where it is not yet banned. At the international level, this work is coordinated within the frames of the United Nations Environmental Programme UNEP, as national measures are not sufficient[227]. Shoes qualifying for the official ecolabel of the EU, the EU flower, are not allowed to contain arsenic, cadmium, and lead, among several other chemicals[228]. Reference to a standardised test method (DIN EN 14602:2005) for verification of the metal content is given in the criteria, and the detection limit for arsenic, cadmium and lead with this method is 100 mg/kg[229].

Organic compounds

Azodyes capable of producing carcinogenic aromatic amines should not be present at all in consumer products, according to the SSNC. Since long, it is widely accepted in toxicology that there is a linear relationship between concentration and cancer risk for chemicals capable of directly reacting with DNA[230], such as some amines[91]. This implies that there is no safe concentration for such chemicals. The SSNC is, consequently, of the opinion that the limit of 30 mg/kg for carcinogenic amines in products set in REACH is not strict enough. In our view, it is unacceptable to find a carcinogenic amine even at a concentration of 2 mg/kg, such as found in the shoe by the Swedish shoe manufacturer Din Sko (sample number 7). The level found in the shoe by the Philippine shoe manufacturer Rusty Lopez is alarmingly high (68 mg/kg) (sample number 17). The threshold concentration in REACH was defined with respect to possible detection limits some 15 years ago[146], and consequently needs to be revised.

With respect to *ortho*-phenylphenol, all shoes in this study pass the Oeko-Tex 110 standard, class II, for materials intended for contact with skin[231], but the shoes containing *ortho*-phenylphenol fail to comply with the Global Organic Textile Standard (GOTS)[232]. When it comes to the use of fungicides in general the SSNC means that the use of such compounds shall be avoided. If necessary, only fungicides with low toxicity, low capacity to bioaccumulate and good degradability should be used.

The discovery of 2,4,6-tribromophenol in the shoe by Veja (sample number 11) was accidental and unexpected. As this compound is part of the internal standard, it was possible to quantify it. A concentration of 30 mg/kg detected in the shoe by Veja is considered as high[146]. However, since samples with intentionally added 2,4,6-tribromophenol at known concentrations (so called “spiked” samples) have not been extracted to check for the extraction efficiency of this compound, the actual concentration in the shoe may be even higher[146]. Finding a highly toxic, persistent, bioaccumulative compound with suspected hormone disrupting effects in a shoe is totally unacceptable. Bactericides and fungicides, if necessary in the product, should not have such qualities.

Chlorinated paraffins are persistent in the environment, bioaccumulating, and harmful to aquatic organisms, as described above. Some of them are carcinogenic. They may also produce carcinogenic compounds upon combustion, as the described above in a paragraph of the discussion. Since no quantification was done of the chlorinated paraffins, it cannot be judged if they are just attributed to background levels, due bioaccumulation in the animals from which the hides were taken, or if they have been added intentionally in the leather processing. Chlorinated paraffins may be used in leather processing[233]. The SSNC is of the opinion that the use of persistent, bioaccumulating, or toxic and compounds, such as the chlorinated paraffins, shall be phased out from material flows in the human society.

Tanning

Chromium tanned leather has very good mechanical and shrinkage resistance, waterproofing qualities and is easy to dye[234], but has also considerable impact on the environment. As already discussed in the paragraphs above, there are potential problems with chromium containing waste, such as leather. However, also earlier in the leather production chain, chromium is problematic. Mining of chromite ore for trivalent chromium result in waste containing hexavalent chromium[235]. Chromium tanning is based on trivalent chromium salts, with an annual global demand being in the order of about 400 000 tonnes chromium salt in the tanning industry[224]. Since 40-70% of the chromium in the tanning solution is taken up by the leather in the tanning process, about 160 000 tonnes of tanning salt annually end up as waste[224]. Typical concentrations of chromium in conventional tanning wastewater are in the range 1700-3000 mg/l[224, 236], whereas environmental legislation the in many countries allow only 0.3-2.0 mg/l in the water discharged[237]. Various measures to reduce the loss of chromium from tanning have been developed, such as modifications of the tanning conditions (reaction time, temperature, and pH), increasing the affinity of chromium for the leather by chemical tanning boosters (so called exhaustion aids), modifying the tanning salt by removing inert trivalent chromium species that will not react with the leather, increasing the access to or the number of chromium binding sites in the leather by chemical modification of the proteins of the leather, chromium recycling, and so on[224, 236]. Loss of chromium reduction measures may bring down concentrations of chromium in the tanning wastewater to the order of 300-750 mg/l, which is still too high with respect to legislative requirements in most countries[236].

Alternatives to chromium tanning can broadly be classified as mineral (other metals than chromium), vegetable, aldehyde, and synthetic tanning[224]. Development of these processes, or combinations of them, nowadays yield leather with desired qualities, not lagging far behind that of chromium tanned leather[223, 224]. Vegetable tanning is based on tannins extracted from the bark of certain species of trees. Chestnut, mimosa, quebrachio, myrabolams, and valonia are some species commonly cultivated for tannins procuduction[238]. Böleby Tannery in Sweden use bark from Norway spruce[239]. Being from a renewable source, vegetable tanning is at first glance an appealing alternative to chromium tanning. There are, however, potential environmental problems connected also to vegetable tanning. In conventional vegetable tanning, about 85% of the tannins in the tanning solution is taken up by the leather, which annually generates 60 000-80 000 tonnes of wasted tannins from the global annual use of 350 000-400 000 tonnes tannins[240]. Many tannins are difficult to degrade for microbes[241], and thus consume a lot of oxygen (high biological oxygen demand (BOD)), which requires wastewater treatment facilities with high enough retention time to bring down the BOD in the effluent to acceptable levels. Pre-tanning processing (so called "pickling") of leather for vegetable tanning conventionally requires a lot of salt, but this can be overcome by enzyme-aided tanning[240]. Previous problems with waterproofing of vegetable tanned leather also seem possible to overcome[229].

Provided that the wastewater treatment is sufficient, and tannins are not extracted from rainforest trees, the SSNC is in favour of vegetable tanning. There are now also emerging mineral alternatives to chromium tanning. According to Seeram and Ramasami (2003), iron and zirconium tanning are promising in producing leather of high quality[224].

Classification of waste

The SSNC is of the opinion that risk classification of waste containing trivalent chromium often is insufficient. To take the speciation of metals, i.e. the forms in which they may occur, into consideration is necessary in risk assessments[242]. Still, in Sweden, classification of waste containing hazardous chemicals according to risk categories as specified in the Swedish Waste Regulation (2001:1063) is based only on too simplified calculations. In these calculations, use is made of official risk and safety phrases (defined in the EU directive 2001/59/EC), assigned to chemicals with respect to their intrinsic properties[243]. Potential speciation of metals depending upon how the waste is treated, however, is not considered. As a result, waste containing trivalent chromium is not considered to be "hazardous waste", yet may produce hazardous hexavalent chromium when further processed. If waste streams were properly separated and waste containing chromium and other hazardous metals were treated separately, ashes from incineration could have an added value.

Final comments

This study has demonstrated that problematic chemicals can be found in shoes irrespective of the geographic origin or price of the shoe. It is disappointing that brands claiming to have an environmental profile also contain problematic chemicals. This clearly shows that the leather and shoe manufacturers have not yet managed to take their responsibility for safety of consumers and the environment. Ecolabelling would be a useful tool for the manufacturers to carry out necessary improvements.

One thing noted by staff at the Swerea IVF laboratory is the overall high quality of the shoes bought outside the EU. Where adhesives had been used in many shoes bought in Sweden, proper seams were placed in many shoes bought outside the EU. If the shoes from outside the EU are representatives of high quality shoes on the respective domestic markets, it would be interesting to also investigate low-price products from non-EU markets in the future. Good quality is a prerequisite for a longer lifetime of a shoe. If the turnover of shoes in society is decreased, so is waste.

Furthermore, this study has also demonstrated the importance of getting proper information about the shoes in the shop. Without proper information at hand, the environmentally conscious consumer cannot make an active and proper choice. We were misinformed by shop assistants that the shoe by El Naturalista in this study is vegetable tanned, which the high chromium level and a search for information in the El Naturalista homepage proved to be wrong. Some products by El Naturalista are semi-vegetable tanned, and only one product of the now gone summer collection 2009 was completely vegetable tanned. The shoes by Veja are marketed as vegetable tanned and "ecological"[244], yet at least the tested shoe contained high levels of the hazardous chemical 2,4,6-tribromophenol. Consumers choosing to buy shoes from Veja, because they are supposed to be "ecological", will most likely somehow be deceived by the marketing. Shop assistants need to be properly informed by the retailers or producers about the products they are selling. The industry, in turn, needs to define how to market products in order not to mislead consumers in the absence of the shoes being ecolabelled. Advice by environmental and consumer organisations could be valuable in this job.

Many consumers are unaware of the fact that hazardous chemicals can be found in shoes, and therefore the leather and shoemaking industry have not yet been faced with demands from the consumers for safer shoes. Some chemicals should have been voluntarily phased out in consumer goods by the industry long ago, but are still used, such as shown by this study. Legislation on restricting the use hazardous chemicals also lags behind. The REACH regulation (EC1907/2006) on chemicals is weak and unclear when it comes to chemicals in consumer goods, particularly imported goods from outside the Union. Originally, the European Commission assumed some 1400 chemicals to be subjects for requiring authorisation for use[245], but so far authorisation has not begun, and resources in the individual EU member states are not sufficient to adequately speed up the process. Presently, only 7 substances are prioritised for eventual authorisation processes, out of as few as 15 compounds that are placed on the so-called candidate list for "substances of very high concern"[246]. Among the 15 are two arsenic compounds that possibly can be used in leather industry for depilation and preservation of hides (scant information about this found on the Internet).

In the EU, producers and retailers of products containing at least 0.1% (weight/weight of the relevant part of the product) of any compound listed in the candidate list, are obliged to be prepared to give customers the necessary information on how to handle the products safely (article 33, REACH). A consumer who asks a producer or retailer if any of the candidate list compounds are in a product, shall, free of charge, be given an answer within 45 days.

The International Chemical Secretariat (ChemSec), of which the SSNC is a member, has identified 356 substances, including the 15 listed in the REACH candidate list, fulfilling the criteria for "substances of very high concern" (see the SIN list in reference 247). Progressive and proactive companies should use the SIN list as a guide for phasing out hazardous chemicals.

On the global level, the United Nations Environmental Programme (UNEP) needs to be strengthened, and more resources needs to be given to the implementation of SAICM. Efforts should be made to develop legally binding agreements on the global phasing out hazardous chemicals.

Advice and requirements from the SSNC

Demands on politicians and agencies

- Strengthen legislation for prohibiting hazardous chemicals in consumer products. Producers have so far not shown that they are able to ensure product safety for consumers on their own.
- Increase resources in order to speed up full implementation of REACH.
- Strengthen the UNEP and SAICM, and promote global binding conventions for the phase out of hazardous chemicals, such as arsenic, lead and mercury, from the material flows in the human society.
- When international undertakings for phasing out hazardous chemicals are too slow, strengthen the national authorities dealing with these issues and speed up efforts nationally.
- Classify waste containing chromium (both trivalent and hexavanlent) as hazardous.
- Improve the management of hazardous waste.

Demands on manufacturers and retailers

- Demand full information from the supplier/upstream manufacturer on the materials and contents of hazardous chemicals in the shoes you intend to purchase or place an order on, and if the supplier/upstream manufacturer cannot provide information in this matter, do not purchase or place an order. The consumer has the right to safe products and full and correct information.
- Increase the use of chromium free leather in the shoe production. Support development of alternatives to chromium tanning.
- Purchase leather only from tanneries you know have adequate wastewater treatment facilities.
- When purchasing chromium tanned leather, ensure that it was prepared in a tannery with chromium reduction measures installed.
- Prioritise to build long-term relationships with suppliers/upstream manufacturers, and help them to improve the tanning facilities.
- Produce and buy shoes of high quality and long durability.
- If you are a manufacturer, ecolabel your shoes. This helps you to place the right demands on your suppliers/manufacturers. Retailers should provide ecolabelled shoes in their shops.
- Phase out substances that are hazardous to health and the environment voluntarily. A good help in this work is the SIN list by ChemSec (see ref. 247).

Consumer advices

- Ask for ecolabelled shoes. Only a few shoes on the EU market are currently ecolabelled with the EU flower.
- Ask for chromium free leather.
- Use your shoes as long as possible, and take them to the shoemaker if they need to be mended.
- Buy only shoes you need. This saves money and the environment.
- If you are a consumer in the EU, use your right to ask if any of the particularly hazardous substances listed in the candidate list of REACH can be found in a shoe you intend to buy or have bought.
- When the shoes have to be discarded, ask your local refuse collection department how to do it in order not to cause harm to health or the environment.

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Appendix I

GroundWork

GeroundWork South Africa, founded in 1999, is part of Friends of the Earth International. GroundWork is known for its successful work with industrial chemicals, but above all for how this organization strengthens the voice of the weak in society and for raising the question of the injustice that poor people often live in the most polluted areas with poor access to natural resources. GroundWork is active, above all, in South Africa, but also in the neighbouring countries, both at local level and at the level of policy making.

National Association of Professional Environmentalists in Uganda

The National Association of Professional Environmentalists in Uganda, NAPE, was founded in 1997. NAPE works, among other things, with sustainable management of chemicals, and preservation of natural resources (water, energy and preservation of forests and wetlands). NAPE actively engages in gender issues and human rights. NAPEs cooperation with the SSNC is about informing the public and decision makers that chemicals in manufacturing and finished products may be a problem for the environment and health of humans.

Toxics Link

Toxics Link India began in 1996 as a platform for exchanging information, and operates both at the local level and with policy making, through various networks. Toxics Link works for health care and provisions free from toxics, and with issues related to electronic waste, product safety, wastewater and recycling. With the financial support by the SSNC, Toxics Link in turn can support and educate lesser non-profit organizations in the work with chemical issues.

EcoWaste Coalition Inc.

The Ecological Waste Coalition Inc. of the Philippines, EcoWaste Inc., was founded in 2000, and is now a dynamic network with more than 75 movements and active interest groups, active in the Philippines. EcoWaste Inc. has a "zero waste" goal set up for 2020, and works for achieving the goal by informing on the most ecologically and climatically sustainable ways of dealing with waste. EcoWaste Inc. also works for a production of goods free of toxics. In cooperation with the SSNC, EcoWaste Inc. informs the public and decision makers that chemicals in manufacturing and finished products may be a problem for the environment and health of humans.

Center of Environmental Soilutions, Belarus

Center of Environmental Solutions (CES) is a non-profit NGO which was established in 2001. The center unites young and creative people for supporting environmental, cultural, social and educational initiatives. The goal for CES is to promote the principles of a sustainable toxic-free future for Belarus, by supporting initiatives aimed to protect the environment. Prioritised areas of work include toxics, waste, energy, organic agriculture and green consumerism.

Appendix II

Table 5 Primary aromatic amines classified as carcinogenic in the European Union, corresponding CAS numbers of the respective amines, official risk classification according to the classification database of the Swedish Chemicals Agency or the database Prevent, with reference to the risk phrases defined in European Union directive 2001/59/EC, and signification of the risk phrases.

Chemical	CAS	Offical risk phrases	Signification of risk phrases
4-aminodiphenyl	92-67-1	R22, R45	Harmful if swallowed, may cause cancer
Benzidine	92-87-5	R22, R45, R50-53	Harmful if swallowed, may cause cancer, very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
4-chloro-o-toluidine	95-69-2	R23/24/25, R45, R50-53, R68	Toxic by inhalation, in contact with skin and if swallowed, may cause cancer, very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment, possible risk of irreversible effect
2-naphthylamine	91-59-8	R22, R45, R50-53	Harmful if swallowed, may cause cancer, very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
o-amino-azotoluene	97-56-3	R43, R45	May cause sensitisation by skin contact, may cause cancer
2-amino-4-nitro-toluene	99-55-8	R23/24/25, R40, R52-53	Toxic by inhalation, in contact with skin and if swallowed, limited evidence of a carcinogenic effect, harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment
p-chloroaniline	106-47-8	R23/24/25, R43, R45, R50-53	Toxic by inhalation, in contact with skin and if swallowed, may cause sensitisation by skin contact, may cause cancer, very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
2,4-diaminoanisol	615-05-4	R22, R45, R51-53, R68	Harmful if swallowed, may cause cancer, toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment, possible risk of irreversible effects
4,4'-diaminodi-phenylmethane	101-77-9	R39/23/24/25, R43, R45, R51-53, R68	Danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed, may cause sensitisation by skin contact, may cause cancer, toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment, possible risk of irreversible effects
3,3'-dichloro-benzidine	91-94-1	R21, R43, R45, R50-53	Harmful in contact with skin, may cause sensitisation by skin contact, may cause cancer, very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
3,3'-dimethoxy-benzidine	119-90-4	R22, R45	Harmful if swallowed, may cause cancer
3,3'-dimethyl-benzidine	119-93-7	R22, R45, R51-53	Harmful if swallowed, may cause cancer, very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
3,3'-dimethyl-4,4'-diaminodiphenyl-methane	838-88-0	R22, R43, R45, R50-53	Harmful if swallowed, may cause sensitisation by skin contact, may cause cancer, toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
p-cresidine	120-71-8	R22, R45	Harmful if swallowed, may cause cancer
4,4'-methylene-bis-(2-chloraniline)	101-14-4	R22, R45, R50-53	Harmful if swallowed, may cause cancer, very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
4,4'-oxydianiline	101-80-4	R23/24/25, R45, R46, R51-53, R62	Toxic by inhalation, in contact with skin and if swallowed, may cause cancer, may cause heritable genetic damage, toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment, possible risk of impaired fertility
4,4'-thiodianiline	139-65-1	R22, R45, R51-53	Harmful if swallowed, may cause cancer, toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
o-toluidine	95-53-4	R23/25, R36, R45, R50	Toxic by inhalation and if swallowed, irritating to eyes, may cause cancer, very toxic to aquatic organisms
2,4-diaminotoluene	95-80-7	R21, R25, R36, R43, R45, R51-53	Harmful in contact with skin, toxic if swallowed, irritating to eyes, may cause sensitisation by skin contact, may cause cancer, toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
2,4,5-trimethyl-aniline	137-17-7	R23/24/25, R45, R51-53	Toxic by inhalation, in contact with skin and if swallowed, may cause cancer, toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
4-aminoazobenzene	60-09-3	R45, R50-53	May cause cancer, very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
o-anisidine	90-04-0	R23/24/25, R45, R68	Toxic by inhalation, in contact with skin and if swallowed, may cause cancer, possible risk of irreversible effect

The making of a shoe is a complex process, requiring many different kinds of materials and chemicals. In this report, the Swedish Society for Nature Conservation, in collaboration with environmental organisations abroad, presents results from an international product survey, focusing on certain potentially hazardous chemicals in leather. Variable levels of toxic semi-metals and metals, such as arsenic, lead, and mercury were found in some shoes, together with high levels of chromium. This generates a waste problem when the shoes are discarded. Carcinogenic aromatic amines from azo dyes were found in two of the twenty one analysed shoes, which is unacceptable. Low levels of the highly allergenic fungicide dimethylfumarate were found in one shoe, and the highly allergenic and potentially carcinogenic formaldehyde in a few. Chlorinated paraffins, which are toxic, persistent, bioaccumulative, were also detected in a few shoes.

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The Swedish Society for Nature Conservation is an environmental organisation with power to bring about change. We spread knowledge, map environmental threats, create solutions, and influence politicians and public authorities, at both national and international levels. Moreover, we are behind one of the world's most challenging ecolabellings,

"Bra Miljöval"(Good Environmental Choice). Climate, the oceans, forests, environmental toxins, and agriculture are our main areas of involvement.

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