Sources and hazards associated with the substances on the *Substitute It Now! (SIN*)-list

Les sources et les risques associés aux substances sur la liste « SIN* (*Substitute It Now!) »

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RÉSUMÉ

La liste *Substitute It Now! (SIN*-list) a été créée par l'«International Chemical Secretariat» pour protéger la santé des personnes et l'environnement face à leur exposition à 267 substances qualifiées de «substances extrêmement préoccupantes». Ces substances devraient être remplacées et ne plus être présentes dans les produits de consommation, produits chimiques et dérivés. Dans cette communication, on a confirmé que ces substances constituent un risque pour les personnes ou les espèces aquatiques. Une analyse de l'origine et des utilisations de ces substances démontre qu'elles ont déjà été abandonnées, et que certaines d'entre elles sont utilisées dans des processus chimiques fermés et facilement remplaçables par d'autres produits. Cependant, comme certaines de ces substances ne peuvent pas être remplacées, ce sont les produits chimiques et de consommation, et/ou procédés qui doivent être entièrement modifiés, ou un traitement approprié qui doit leur être appliqué.

ABSTRACT

The *Substitute It Now! List (SIN*-list) has been created by the International Chemical Secretariat (ChemSec) to protect human health and the environment from exposure to 267 substances that can be classified as Substances of Very High Concern. These substances should be substituted so that they are not present, either as functional chemicals or by-products, in commodities and chemicals. Here it has been confirmed that these substances constitute a hazard to humans or aquatic organisms or that hazards cannot be excluded due to the partial lack of inherent data. An analysis of the sources and uses of these substances shows that some already have been phased-out, some are used in closed chemical processes and some are readily exchanged with suitable substitutes. However, for some substances substitutions cannot be made, and thus the whole chemical/commodity/process needs to be exchanged or suitable treatment should be applied.

KEYWORDS

Hazard identification, industrial chemicals, phase-out, source identification, substitution, uses

1 INTRODUCTION

Chemical substances, composite materials, day-to-day commodities and personal care products are every day items in our lives and part of the foundation of our economy. The substances have different uses in the commodities; for example as flame retardants in textiles and plastics, as preservatives in paints and cosmetics as well as ultraviolet light filters in sunscreens. Many of the commodities are intended to release substances; biocides in paints are intended to mitigate growth of algae on painted surfaces, and naphthalene in mothballs is intended to deter moths. Other commodities are not intended to release substances but still do an example being flame retardants which migrate and vaporize from electrical and electronic equipment. Releases may also occur unintentionally through other processes such as combustion processes. Some substances are functional chemicals; they have an intended application in the commodity. Others are by-products from incomplete chemical reactions or residues from the production process, such as nonylphenol ethoxylates in textiles from the finishing process after dyeing. All the released substances may potentially affect humans and, being discharged into the environment; potentially result in adverse effects in the aquatic ecosystem. A major part of the substance flow is conveyed by way of sewage or separate stormwater systems to be managed by wastewater treatment plants (WWTPs) or stormwater constructed best management practices (BMPs) before discharge into the receiving environment. Treatment trains are thus important to mitigate pollution due to substances already released into urban water flows. It is also vital to ensure mitigation of unnecessary and unwanted releases by substituting the concerned substance or overseeing the use process of the commodities so release is minimized.

It is especially important to address the Substances of Very High Concern (SVHC) which are substances with known unwanted effects such as substances that are carcinogenic, mutagenic or repro-toxic (CMR); substances that are persistent, bioaccumulative and toxic (PBT); substances that are very persistent and very bioaccumulative (vPvB); or substances classified as being of “equivalent level of concern” (EQLC), e.g. endocrine disrupting chemicals, (European Union, 2006; 2008) as defined by the EU Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) process.

The non-governmental organisation The International Chemical Secretariat (ChemSec) and 12 business partners including IKEA, Sony Ericsson, and L’Oreal have chosen a pro-active approach and identified 267 substances that would be classified as SVHC according to the criteria in REACH. These 267 substances form the SIN*-list (*Substitute It Now!) 1.0 (ChemSec, 2008). The SIN*-list was launched at the ChemSec Substitution Conference on September 17th, 2008 in Brussels, Belgium, and the associated business partners strive to substitute the substances on the list. It is intended that others also should focus on removing these harmful substances from consumer related commodities and chemical products. The revised version (SIN-list 1.1) comprises of 356 substances.

1.1 Objectives

The objective of this study was to evaluate the human and environmental hazards associated with the 267 substances listed on the SIN*-list and assess its feasibility by addressing and responding to the questions: I) Is there one or more of the substances that should not be on the list due to lack of hazardous properties? II) Will the SIN-list be effective in improving the conditions of ecosystems and human health? For the latter, indicator substances of the SIN-list will be chosen and exemplified.

2 APPROACHES

The potential hazard of the 267 substances was addressed with two different approaches, and the effectiveness of the SIN*-list was assessed by evaluating the outcome of a literature review.

2.1 Metals and inorganic substances: international priority lists and human long-term effects

Metals and metal salts on the SIN*-list were evaluated based on their presence on two well-known lists containing hazardous and unwanted substances: the EU Water Framework Directive environmental quality standards (WFD-EQS) and the World Health Organization’s (WHO) drinking water quality guidelines. In addition, data on human and animal carcinogenic studies were collected from the online Hazardous Substance Data Bank (HSDB) (US National Library of Medicine, 2009) and included as criteria for hazardous effects.

2.2 Organic substances: hazard identification based on inherent properties

The potential environmental hazards associated with organic substances and organometals were identified based on their inherent properties and environmental fate as well as short and long term toxicity by applying the tool: 'Ranking and Identification of Chemical Hazards' (RICH) originally developed to evaluate stormwater priority pollutants (Baun et al., 2006). Inherent data originate from reference books and online databases (HSDB, CCRIS, GENETOX, IUCLID and ECOTOX) as well as Rippen (2008) and Verscheuren (1996)). Health hazards were identified based on short term (acute) and long term (CMR and endocrine disrupting) effects originating from the same databases. Additionally, the 30 substances classified as being of 'equivalent level of concern' by ChemSec had been subjected to an evaluation by a group of experts subcontracted by ChemSec (ChemSec, 2008); their collected data, evaluation and conclusions were fed into RICH.

2.3 Review of indicator substances' manufacturing, uses and releases

To review uses and releases of all the 267 substances, though interesting and highly relevant, was beyond the timeframe and scope of the study, and hence indicator substances were selected to represent different categories.

2.3.1 Selection of indicator substances

Eight substances were selected based on their i) application (uses) and ii) representing different SVHC categories (CMR; PBT, and EQLC) as well as iii) data availability. Thus a list of acrylonitrile, aniline, erionite, naphthalene, octabromodiphenyl ether, styrene, tetraethyl lead, and tetramethyl lead were utilised in the literature and database review.

2.3.2 Literature review and database mining

Well-known and established databases (HSDB, and ECB RAR documents) were utilized to identify manufacturing, uses and releases. Subsequently, the search engine Web of Science was utilized to search for the keywords; 'use', 'production' and 'release' as well as 'substitute' and 'alternative' and truncations thereof in combination with the substances names and/or CAS registry numbers. Google was also used for searching for the same keywords as in Web of Science, but here the information from the queries was also checked to ensure that the sources were credible.

3 RESULTS AND DISCUSSION

Forty inorganic substances (including beryllium as the single element), 15 organometals, and 215 organic substances made up the SIN*-list; in total 268 substances. Nonylphenol were included as both straight chain and branched chains hence receiving two CAS registry numbers.

The SIN*-list as published by ChemSec contains 220 substances classified as CMR; 30 as EQLC; 9 PBT; 6 PBT/CMR and 2 PBT/vPvB (ChemSec, 2008). Many well-known pollutants such as polycyclic aromatic hydrocarbons (PAHs), several phthalates, aromatic amines and many of the substances listed on the WFD-EQS such as nonyl- and octylphenol, are included as well as dyes, brominated flame retardants (octabromodiphenyl ether (OBDE) and tetrabromobisphenol A (TBBPA)) and other halogenated substances.

3.1 Hazard identification of metals and inorganic substances

Neither the WFD-EQS nor the WHO guideline contain all the 40 inorganic substances considered on the SIN*-list. However, some of the pure metallic elements are considered on the two lists, i.e. cadmium, nickel and lead on the WFD-EQS and arsenic, cadmium, chromium, nickel, lead and antimony on the WHO list. As the 40 inorganic substances are derivatives of the aforementioned metallic elements, the WFD-EQS and the WHO guideline indirectly consider 19 and 33 of the 40 inorganic substances, respectively. Consulting the HSDB, 39 of the 40 inorganic substances are revealed either to be confirmed carcinogenic or suspected carcinogenic substances. Lead azide is the only inorganic substance not associated with carcinogenicity; however, the substance is a well-known explosive (HSDB). Of the 39 inorganic substances, 21 have confirmed human carcinogenic properties, six have confirmed animal carcinogenic properties and 10 have either confirmed, suspected or anticipated carcinogenic properties. The reason why the latter group is made up of different statements of the carcinogenic potential is that different studies have shown different results for the same substance. With respect to EU regulation 2006/11/EC there was found an overlap with the species of As, Be, Cd, Co, Cr, Ni, Pb and Sb. Figure 1 shows the carcinogenic potential of the 40 inorganic substances grouped by metallic element. An example is cadmium, which is a constituent of six inorganic substances, of which five are confirmed carcinogenic and one is suspected or anticipated carcinogenic. In general, derivatives of aluminium, arsenic, beryllium, cadmium, chromium (only hexavalent) and nickel are confirmed carcinogens. Derivatives of cobalt, lead and antimony are “only” confirmed animal carcinogens or suspected human carcinogens.

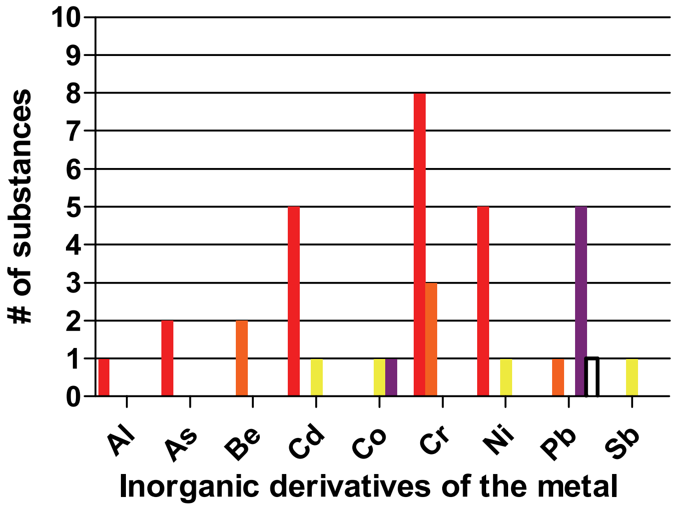

Figure 1. Carcinogenic potential of the various inorganic derivatives of the metals.
■: Confirmed human carcinogen; ■: Confirmed human carcinogen, suspected human carcinogen and anticipated carcinogen; ■: Either suspected or anticipated carcinogen; ■: Confirmed animal carcinogen; □: No data found on carcinogenicity.

3.2 Hazard identification of organic substances

For the 230 organometals and organic substances, inherent data were obtained from the abovementioned databases for 198 substances or groups of substances. Of these 198, 177 substances were classified as ‘black’, i.e., none of these organic substances or organo-metallic substances could be disregarded in hazard/risk assessments due to hazardous inherent properties, Figure 2. Of the 177, 81 were classified as ‘black’ based on their PBT properties, 88 on their CMR/E properties and eight on their acute human oral, dermal, and inhalational toxicities. Twenty-one substances were classified as ‘grey’, i.e. hazard cannot be either confirmed or contradicted and hence, according to the precautionary principle, these should also be considered as ‘black’ substances. Hence, none of the evaluated 198 substances could be classified as ‘white’, or non-hazardous, Figure 2.

For the remaining 30 substances (mainly summary parameters or mixtures of substances), only partial data could be obtained, and thus no hazard identification could be conducted. In the justification of the SIN*-list, all these 30 substances are classified as CMR-substances, but it has not been possible to confirm this in the present study. In total 51 organic substances (21+30) require a more thorough investigation to be fully assessed.

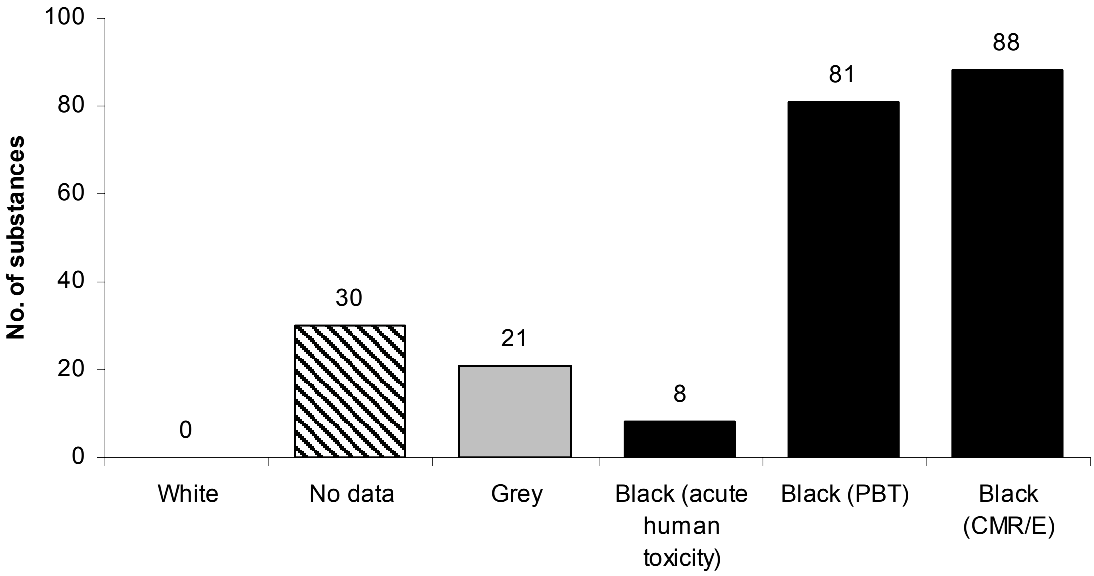

Figure 2. Results form the RICH ranking of organic substances and organometals.

3.3 Indicator substances' manufacturing, uses and releases

Eight of the 267 substances were subjected to a further review focusing on their uses (application in commodities), point of release and substitution options, Table 1.

Substance	CAS no.	SVHC	Use	Point of releases	Substitutes/alternatives
Acrylonitrile	107-13-1	CMR	Chemical intermediate	Industrial processes (plastic); by-products in commodities; vehicle exhaust; and cigarette smoke	No substitutes for plastic polymers (acrylonitrile butadiene styrene (ABS)) but natural fibres may be used for clothes, upholstery etc
Aniline	62-53-3	EQLC	Chemical intermediate	Industrial production of aniline and other substances	No substitutes could be found for the identified applications
Erionite	66733-21-9	CMR	Zeolite, catalyst	Natural geological deposits	Have been replaced by non-fibrous zeolites
Naphthalene	91-20-3	EQLC	Chemical intermediate, natural by-product	Naphthalene production and industrial processes; fuel/oil production; application of commodities (pyrotechnics, mothballs, wood impregnation); and combustion processes	Substitutes are available for some industrial processes (dichlorobenzene and smaller aromatic substances); alternatives for wood impregnation exist; but to avoid naphthalene as by-product in combustion processes, new or alternative technologies are needed.
Octabromo diphenyl ether (OBDE)	32536-52-0	CMR + PBT	Flame retardant	Industrial processes; release from commodities during use (volatilization, dust etc); and waste disposal	In ABS-plastic, which account for 95% of the OBDE uses, substitutes with similar or comparable properties are available.
Styrene	100-42-5	EQLC	Chemical intermediate	Industrial processes (plastics, resins, rubber); releases during commodity use and waste	Styrene use in polystyrene plastic can not be substituted. Alternative composite materials exist, but cannot be

					applied for all known uses. Styrene-butadiene rubber may partially be replaced by natural rubber.
Tetramethyl and tetraethyl lead	75-74-1 and 78-00-2	CMR and PBT	Anti-knocking agents in fuel.	Banned in automobile fuel in most countries; the main release occurs during use of aviation fuel.	Methyl *tert*-butyl ether have substituted alkyl leads on a wide scale, though now also under consideration for unwanted effects. New unleaded aviation fuel is under development.

Table 1. Uses, releases and substitutes for the eight selected substances.

3.4 Indicator substances' uses and associated substitutes

Substitution refers to replacement or reduction of hazardous substances in commodities (products) and processes by non-hazardous or less hazardous substances. Alternatively, another technical solution or organisation measurement achieving an equivalent functionality can also be included as 'substitution' (Lohse et al, 2003).

Acrylonitrile and styrene are used in manufacture of fibres, resins, rubber (styrene) and rigid plastics (acrylonitrile) which are then used for the manufacture of a wide range of consumer and industrial commodities such as clothing, upholstery, fibres, asbestos replacement products, household appliances, vehicle parts, pipes and food containers (PCI, 1996; ECB, 2004), Table 1. In the specific polymers where they are used, there are no substitutes; thus, the production of the polymer needs to cease. Alternative fibres, such as natural fibres, including cotton, wood and sisal from plants and silk, wool and leather from animals, can be used for many of the substituting applications. Also, the resource burden is different as e.g. cotton requires less energy than polyester but demands significantly larger volumes of water (Kalliara and Nousiainen, 1999). Similarly, aniline is an intermediate and in most identified uses there seems to be no substitute, and therefore it is necessary to substitute the entire material for which aniline is used as an intermediate.

Octabromodiphenyl ether was banned in the EU in 2004 after a risk assessment (EU, 2003; ECB, 2003a) and there exists substitutes which also comprise of brominated adducts such as TBBPA. But TBBPA is also listed on the SIN*-list which makes it an unsuitable substitute. However, bromine-free options are under development (ChemSec meeting 2008).

Erionite is a natural fibrous material similar to asbestos, but it is no longer marketed for commercial purposes (in the USA, NTP, 2005) but has been replaced by non-fibrous zeolites, Table 1.

Naphthalene is also a natural substance present in coal and oil, and it is used in a wide range of chemical processes and in many commodities. Some of these are addressed here. In production of phthalic anhydride, naphthalene can be substituted by ortho-xylene and in mothballs by 1,4-dichlorobenzene, but both these substances are also known to have unwanted effects on human health and in the environment. So an alternative replacement of mothballs could be overseeing the handling and packaging of textiles in sealed containers which will hamper the access of insects. For naphthalene use in dye production it has not been clear if the substance's colouring properties will be affected, however in pyrotechnics alternatives to naphthalene are under consideration for production of 'black smoke' (Chen, 2003). For creosote (naphthalene) impregnation of wood, alternatives exist, but they consist of heavy metals and chlorinated organic solvents, substances which also are present on the SIN*-list. Although alternatives such as borates, cyproconazole, propiconazole exist (US EPA, 2008), the latter two mentioned are closely related to pharmaceuticals to treat fungal infections. However, an alternative was to exchange the use of impregnated wood with composite minerals and metals, which omit the use of impregnation chemicals. It is here important to evaluate and ensure that the substitutes not cause other negative or degenerative effects.

Tetramethyl and tetraethyl lead have been substituted by methyl *tert*- butyl ether (MTBE) in automobile fuel, but tetraethyl lead is still permitted in aviation fuel for piston powered aircraft, Table 1. However, unleaded fuel is being developed (Shell, 2009) and some aircraft in the USA have been permitted to use automobile fuel (EAA, 2000). Alternatively, diesel engines do not use leaded fuel and can thus be seen as a substitute for leaded fuel, with the corresponding higher emissions of particles.

The above mentioned uses all refer to the intentional uses of the 8 substances, but the 8 substances may also be produced and emitted as by-products, such as combustion by-products, that may form unintentionally during reduction-oxidation reactions. Acrylonitrile can be found in vehicle exhausts. And it has historically been found in cigarette smoke because it was used as a tobacco plant fumigant; this is no longer the case, so it is unlikely that it still can be found in cigarette smoke. Naphthalene is released during combustion processes from automobile exhausts and waste incineration but also present in spills and formation water in connection with oil drilling. The ECB (2003b) concludes that the primary release of naphthalene occur in connection with vehicle exhausts.

Life cycle assessment (LCA) is a tool used to evaluate substances, commodities or processes from their cradle to their grave with the goal to compare the full range of social and environmental costs, in order to identify the least burdensome one. The tool is often used to assess costs and effects in several categories such as acidification, ecotoxicological effects, eutrophication, global warming, human health, ozone depletion, and resource depletion, to mention a few. When choosing a suitable substitute, it is of vital importance to include many aspects so that the outcome of the substitution has an overall beneficial effect compared to the substance being substituted, and so that it can work as a decision support for risk assessment and risk reduction. It is also important that the relevant stakeholders are included in the managerial process.

3.5 Emission control strategies

Emission control strategies for controlling SVHC stretch beyond substitution because of the unintentional production of combustion by-products which is out of the industries' control. Here it is important that new technologies are developed that result in lower emissions or the introduction of new fuels which resulting in a lower generation of by-products. It is also important that already released or discharged substances are managed in an appropriate manor. In order to achieve a good protection of the environment, the substances can be addressed on different levels in a catchment: i) pre-application control (before release) including substitution, new techniques, preventive measures and legislation, ii) pre-environmental release treatment (after release from the products or processes), include municipal and industrial WWTPs and management of combined sewer overflows, and iii) post-environmental release treatment – which covers treatment options put in place to remove substances after they have been released into the natural environment such as stormwater BMPs, dredging of contaminated sediments and in-stream treatments (Eriksson et al., 2009).

3.6 Revisions

The SIN*-list can be expanded as more substances become classified according to the SVHC criteria and one year after the launch of the original SIN*-list a supplement of 89 new substances were added, thus, yielding a list of 356 substances. All of the 89 obtained their classification due to their CMR properties (ChemSec, 2009).

4 CONCLUSIONS

The 267 substances listed on the SIN*-list needed to be counted as 268, as nonylphenol was considered both as a straight chain and a mixture of branched isomers. While applying the RICH-tool, a total of 51 organic substances need a more thorough investigation to be fully assessed as 30 (often mixtures or summary parameters) could not be assessed due to lack of data and 21 could neither be confirmed hazardous nor exempted from side effects. The remaining 177 organic substances were all classified as hazardous. 39 of the 40 metals and inorganic substances have either confirmed or suspected animal or human carcinogenicity. One inorganic substance did not have data for such evaluation. None of the substances on the SIN*-list can be disregarded in hazard/risk assessments based on the assessment carried out in this study, but the recommendation is to keep the list as it is, however further assessment of the 52 substances having no solid data to be fully assessed need to be initiated.

Not all substances on the SIN*-list are in use, marketed or permitted, and therefore no positive impact will be seen from the inclusion of these substances on the list. Direct use of the SIN*-list substances is not always the main pathway for emission, so substitution is only part of the solution for these substances. Direct substitution with less harmful alternatives is possible for some substances, which fits well with the intention of the list. However, substitution with a substance that is more harmful than the substance being replaced, giving an effect opposite of the one desired, may happen and has to be avoided. For some substances, the entire commodity in which the substance is used must be substituted. Here it is important to use LCA to evaluate the environmental impacts to ensure that the new commodity is less harmful than the old.

The SIN*-list is a frontrunner in the process of reducing the use of harmful chemicals, but for it to become more effective, it is important that use, release and the substitution potential are considered in the substance selection process. It is also vital to identify the substances that are in use or is released as by-products in order to optimize water and wastewater treatment.

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