Chemicals and Materials

# Substitution of Chemicals - Considerations for Selection

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## Why is substitution important?

Substitution of currently used products with less hazardous products is one of the most effective ways of eliminating or reducing exposure to products that are toxic or pose other hazards. A hazard includes any product, chemical or material that has the ability or a property that can cause an adverse health effect or harm to a person under certain conditions.

Other occupational hygiene methods for controlling employee exposure to chemicals include elimination, isolation, enclosure, local exhaust ventilation, process or equipment modification, good housekeeping, administrative controls, and personal protective equipment. All these methods are part of the hierarchy of control to help reduce or eliminate the risk of injury or harm by interrupting the path of exposure between the hazardous product and the worker. Elimination and substitution are preferred methods for hazard control as they remove the hazard at the source.

For more details about hazards and risk, please see the OSH Answers "Hazard and Risk". Use of chemical products in a workplace may involve the implementation of a chemical safety management program.

NOTE: This document is written for workplaces who are considering how to assess safety and health risks of new or existing products. The manufacturing of products or adjusting ingredients within products can be very complex and is beyond the scope of this document, although similar methods can be used.

## Why should the substitute product be chosen very carefully?

Extreme care must be taken to make sure that one hazard is not being exchanged for another, especially one that could even be a more serious hazard. Before deciding to replace a product, one must know what risks the new product poses to the employees, the environment, the equipment, and facilities. If the risks are serious, then other alternatives should be considered. A thorough understanding of the potential risks associated with the current and alternative product is necessary.

The selection of a substitute can be a very complex process. In large organizations the selection process may involve a committee with representatives from engineering, purchasing, occupational hygiene, safety, maintenance, research and development, environmental control, waste management, shipping, and the supervisors and workers who directly work with the product. In smaller organizations, one person may carry out many of these functions.

According to the Centers for Disease Control and Prevention, one case study includes the substitution of a chlorinated solvent, an environmentally hazardous solvent, with an alternate solvent. An ingredient in brake cleaning products (used by auto mechanics) was regulated for pollution control reasons (chlorinated solvents, primarily methylene chloride). n-Hexane was one choice that was used to replace the chlorinated solvents. However, physicians began to report that auto mechanics using the new brake cleaner were suffering nerve damage, n-Hexane has been associated with neurotoxicity.

## When should a workplace look at substituting existing products?

All workplaces should regularly inventory and review the products used. Products with higher toxicity or safety concerns, or when there have been illnesses reported after use with a product, could be examined for alternatives.  Be aware that manufacturer's may also change their product formulations over time, and these changes may result in different ingredients within products of the same name.
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## What are some points to consider when doing a hazard assessment?

A hazard assessment should be done to help decide if alternative products are an appropriate choice.

Use safety data sheets (SDSs) and other sources of chemical information to compare the hazards of various products. For easier comparison, set up a table with the following categories for each potential substitute. The important properties to compare are:

1. **Chemical and Physical Properties**. For example, vapour pressure is an indicator of how easily a chemical evaporates into the air. Exposure by inhalation is the primary route of exposure for many products; therefore, the vapour concentration in the air largely influences the potential degree of exposure. If a solvent is not very volatile (does not evaporate easily), the potential for exposure by inhalation may be very low. On the other hand, fire and explosion are sometimes the greatest hazards from a product. Properties that must be examined include autoignition temperature, flash point, flammability limits, and reactivity.
2. **Short Term Health Effects.**Comparing animal toxicity values of various chemicals can suggest their relative short-term toxicities (i.e., effects that happen quickly). Examples of acute toxicity data include LD50s and LC50s (the lethal doses or concentrations that kill 50% of test animals exposed to the chemical). It is important to remember that toxicity may vary widely between animal species. Furthermore, biological effects or adverse health effects caused by short-term exposures to high concentrations of a chemical may not be the same as those resulting from low level, long-term exposures. For example, two closely related aromatic hydrocarbons, benzene and toluene, have similar acute toxic properties but only benzene is associated with cancer following long-term or chronic exposure.
3. **Long-Term Health Effects**. Long term health effects such as chronic lung disease may be more significant than short term health effects.
4. **Skin Toxicity**. Both the potential for direct irritation and allergic sensitization must be examined. One also must consider that, besides breathing in chemicals, some solvents (and even some solvent vapours) can also be absorbed through intact skin. This route of exposure can contribute significantly to the overall uptake of chemicals in the body.
5. **Sensitization of the Respiratory System**: If repeated exposure to the chemical by inhalation can cause hypersensitive reactions, like an asthma attack, then special exposure control methods and workplace practices should be set up and maintained.
6. **Cancer-Causing Potential and Reproductive Effects.** If there is sufficient evidence that a compound is associated with cancer or reproductive effects in humans, special handling precautions need to be considered.

7. **Exposure Assessment**. The physical-chemical properties can also be used to determine likely or unlikely routes of exposure based on measured exposure data or properties such as physical state, vapour pressure, molecular weight, water solubility, low Kow, boiling point, melting point, Henry's Law Coefficient, and particle size. Use the relevant exposure routes to identify if the alternative is likely to result in greater, equal, or less exposure.

NOTE: Recommended occupational exposure limits such as the American Conference of Government Industrial Hygienist's (ACGIH) Threshold Limit Values (TLVs) must **not** be used in the comparison of products since the basis for establishing these values varies from substance to substance (e.g., protection from irritation, becoming unconscious, or impairment of health). The TLV booklet clearly states that the TLVs are **not** a relative index of toxicity.

NOTE: Choosing a suitable alternative can be a complicated matter. It may be necessary to consult with experienced safety professionals or occupational hygienists, ideally those who are familiar with the products and processes used in your workplace. Other factors may take priority in your decision-making process.

## What are steps to take when considering substitution?

While there are many methods or tools that can be used to screen products, each have common steps. These steps include:

1. **Identifying hazards and assessing risks.** This step involves deciding whether the current product or process is a hazard. What products are on-site? Is there a significant risk involved in storing, using, or disposing of a product? To answer these questions, be sure to have an accurate inventory of all products, as much information as possible about each product including technical information, amounts, and life-cycle considerations (use, storage, handling, transportation, and disposal). Also, determine if any of the products (or their ingredients) are identified on a regulatory list as toxic, restricted, prohibited, etc. (for example, the Domestic Substance List under the Canadian Environmental Protection Act).

2. **Identifying alternatives**. Investigate a wide range of options. Compare all of the hazard assessment information.
    - Will the replacement product meet the technical requirements (e.g., solubility, drying time, etc.)?
    - Compare the different states of a chemical (e.g., will a granular form create less dust than a powder form?)
    - Is the product compatible with the process, other products, or the equipment?
    - Is the job is necessary or not (e.g., can the part be replaced rather than cleaned)?
    - Do existing control methods adequately control the substitute (e.g., a less toxic substitute may evaporate more rapidly and the existing ventilation system may not adequately capture the vapours)?
    - Will the current waste disposal system meet technical and regulatory requirements when dealing with any new waste created by using the substitute?

3. **Complete the hazard assessment and think about what could happen if you use the alternatives.** It is important that you have gathered all available information before this step so that you can make a realistic comparison of both the good and bad points.
    - the way the work is done,
    - how and where the product will be used,
    - who will be affected or exposed,
    - the quantity used,
    - the kind of equipment or parts (e.g., O-rings, gaskets or hose materials) needed to be compatible with the substitute,
    - the ventilation system that may be required,
    - the disposal methods, and
    - regulatory requirements that may apply.

4. **Comparing alternatives.** In this step, compare the alternatives with each other, and with the substance or process currently being used. It can be hard to compare the risks of one chemical that is very flammable with one that is very toxic. Think of the effects in simple terms such as "Is the substitute going to explode, or poison people? Will it only affect people who work with it, or could it affect other people in the area?" Remember to consider how and where the alternative will be used.

5. **Decide whether to substitute.** This step is the most difficult. Remember that a change in one step of a process can affect many others. Consult with the workers who will be handling the product directly for their input. It is a good practice to introduce the substitute on a trial or small quantity basis at first.

6. **Introducing the substitute.** Plan the change in material or process carefully. Remember to train and educate the workers involved.
7. **Assessing the change.** Check to see if the substitution has produced the intended results. You may find monitoring the health of the workers, monitoring the level of contaminants in the air, or fulfilling legal requirements useful parameters to measure.

* Adapted from: Substance Substitution (no date) by the Health and Safety Executive, United Kingdom.

## Where can I find sample substitution programs or tools?

Use caution when choosing a risk assessment process for the evaluation of chemical alternatives as it is a highly technical process and involves professional judgement of what is a 'safe' level of risk.  The following resources* are methods for substitutions and tools that can be used to help screen substitutes:

- CANADA Examining opportunities to support the transition to safer chemicals in Canada (See Annex 1: Methodology and the tables in Annex 3: Landscape of alternatives assessment tools and methods
- Ontario Toxics Reduction Program - Reference Tool for Assessing Safer Chemical Alternatives
- Transitioning to Safer Chemicals - Basics of Informed Substitution & Alternatives Assessment - Occupational Safety and Health Administration (osha.gov)
- US National Research Council's Framework to Guide Selection of Chemical Alternatives.
- OECD: Guidance on Key Considerations of the Identification and Selection of Safer Chemical Alternatives
- OECD Substitution toolbox: A compilation of resources relevant to chemical substitution and alternatives assessments.
- UK's Health and Safety Executive - COSHH e-tool

(*We have mentioned these organizations as a means of providing a potentially useful referral. You should contact the organization(s) directly for more information. Please note that mention of these organizations does not represent a recommendation or endorsement by CCOHS of these organizations or methods over others of which you may be aware).

## What should a worker do if they believe they know about an alternative product?

Your employer should provide you with training on use, handling, and storage of products, such as through WHMIS education and workplace specific training. If you become aware of other products that may perform equally or better for the task, let your supervisor know about it so they can have a competent person evaluate the other product for use at the workplace. You can also consult with the health and safety committee or representative about the use of safer products.

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