A More Sustainable Approach to Everyday Cleaning

The General Issue:

Current chemical technology for the production of household and commercial cleaning detergents is not sustainable. This means that the sources of most raw materials for current products are not renewable, and that the environmental and health effects of current products are often detrimental and possibly cumulative. Society has no viable choice but to begin to shift from the old ways of cleaning things, to newer, more sustainable and more biologically compatible ways of cleaning things.

The Environmental Problem:

Residual amounts of surfactants and other synthetic chemicals typically found in many household and commercial cleaning detergents continue to find their way into our waterways, despite our best attempts to remove most of them at water treatment plants. These surfactants affect aquatic life adversely and also potentiate other more toxic chemical residues that are also present in our environment.

The Health & Safety Problem:

Many cleaning compounds also contain volatile chemicals and perfumes that decrease indoor air quality during and after cleaning, and can adversely affect the health of human beings. Cleaning compounds are one of the primary sources of indoor pollution, and a major contributor to sick building syndrome and environmental hypersensitivity. In addition, some cleaning compounds are corrosive and can present a safety hazard to users.

The Sustainable Solution:

To move towards a more sustainable technology, we must as a society shift away from synthetic substances to 100% natural biological ingredients, and we must move towards substances that have reduced impact in terms of both human health and the health of other organisms in our external environment.

The expertise already exists to develop natural, biologically-produced cleaning products that are cost effective, that are on par in performance to existing products, that do not contribute to indoor pollution, and that do not deposit persistent residues in the environment that could disrupt the delicate web of life on our planet.

This “white paper” presents the evidence surrounding the aquatic toxicity of surfactant residues and makes the case for the introduction of new and more sustainable cleaning technologies.

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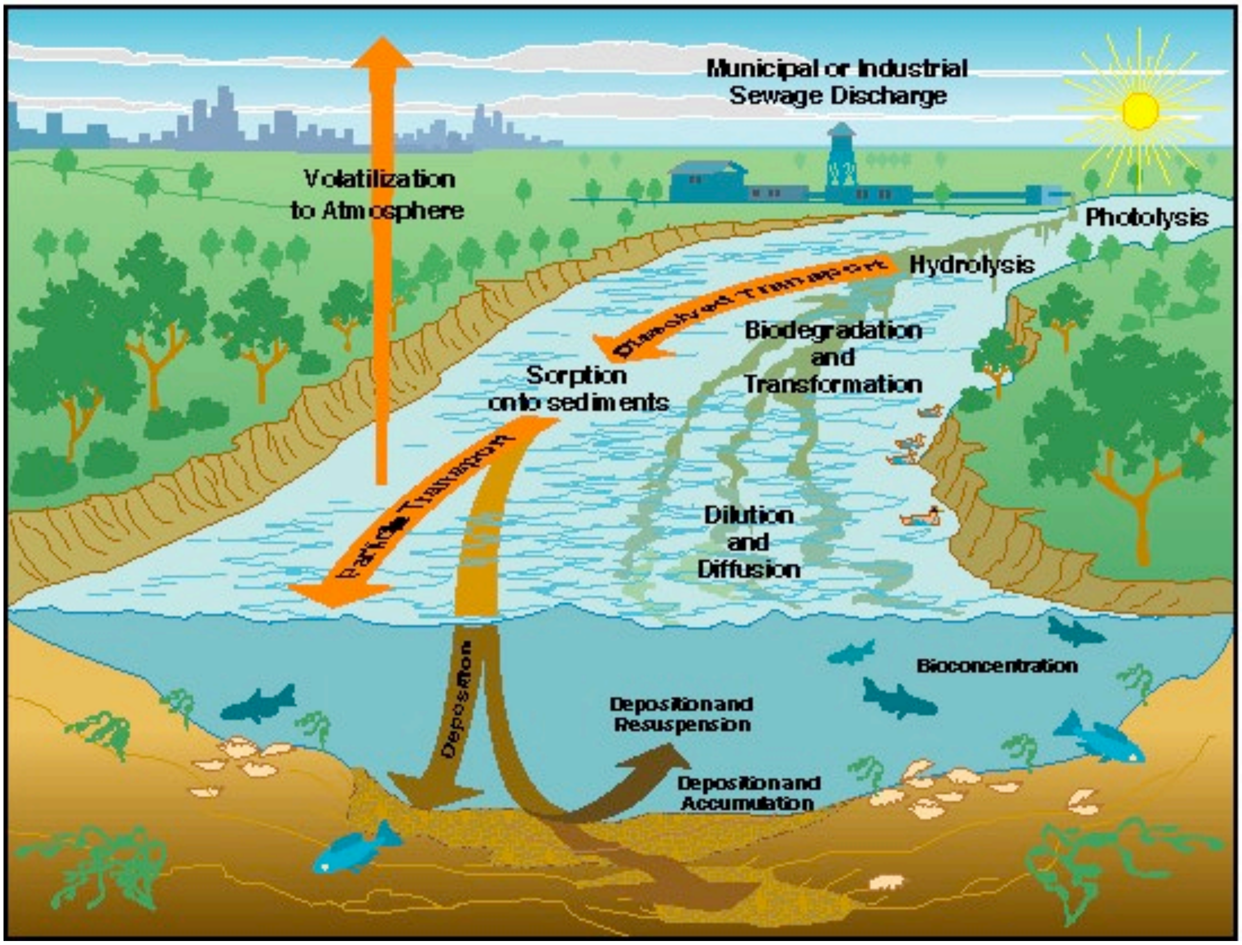
How Waterways and Bed Sentiments Get Contaminated:

The following diagram illustrates how contaminants enter our waterways and waterbed sediments. (Meade, 1995)

Figure 51--*Fate of Contaminants in the River*



The Detailed Evidence:

Environment Canada Environnement Canada

Recently, scientists have seen a variety of endocrine-related effects in fish and wildlife in many parts of the world, including Canada. Environment Canada's recent paper entitled "Endocrine Disrupting Substances in the Environment" (Environment Canada, 1999) emphasizes that a number of endocrine disrupting substances are widespread in the environment, and that "even at relatively low levels, these can affect growth, reproduction and development of organisms in Canadian ecosystems. They include substances in industrial and municipal effluents and in agricultural runoff, natural estrogens in plants (phytoestrogens), and specific chemicals such as alkylphenols and tributyltin and those found in pesticides."

The United States Environmental Protection Agency's "Special Report on Endocrine Disruption" (U.S. EPA, 1997) finds also that "compelling evidence has accumulated that endocrine systems of certain fish and wildlife have been disturbed by chemicals that contaminate their habitats". Endocrine disruptors are external agents that interfere in some way with the role of natural hormones in an organism. There are in fact many man-made chemicals in our environment that have a wide variety of adverse consequences (including cancer and reproductive effects) both for wildlife and for human beings.

The Environment Canada report specifically cited alkylphenolics, a family of surfactants which are among the primary ingredients of detergents, as being problematic. People know them as the chemicals that reduce surface tension in water and allow aqueous solutions to spread and penetrate more easily. This very property is what affects aquatic life adversely, for example, by altering the properties of a fish's gill and changing the way the fish takes in other substances.

Surfactants are toxic by themselves at high enough levels. For example, akylbenzene sulphonic acid, also known as LAS or "linear alkylbenzene sulfonates", quaternary ammonium compounds, alcohol ethoxylates and nonylphenol ethoxylates, also known as NPE's, all have specific toxic properties. At lower levels, often referred to as "sublethal concentrations", they still have effects which disrupt the normal body chemistry of aquatic species.

Low-level mixtures of various toxic chemicals also have unpredictable effects. Sometimes they are additive, sometimes they cancel out, and sometimes they work synergistically (that is, they together produce effects far larger than they could produce individually). Surfactants are among those chemicals that can act synergistically with other chemicals in our aquatic environment. They can sometimes predispose aquatic organisms to be more vulnerable to other more toxic compounds such as petroleum products, pesticides, chloramines, heavy metals and metal ions.

There is ample scientific evidence to show that surfactant residues are already present in our waterways and in lake- and river-bottom sludge, as are other synthetic chemicals with which they can combine or act synergistically. There is evidence that these combinations of pollutants are already having significant effects on aquatic life. The problem is not theoretical at all, it is here today.

In the sections that follow, detailed evidence concerning the potential environmental dangers of surfactants is presented.

1. Surfactants are present in our watershed and waterbed sediments.

Common synthetic chemicals in detergents used for cleaning in our homes, schools, offices and hospitals find their way into wastewater from these buildings. Wastewater treatment facilities receive on average 1 to 7 ppm influent of anionic surfactants and up to 20 ppm of total surfactants. (Rapaport et al 1987)

The effluent of waste treatment facilities in turn contains surfactants. Most jurisdictions limit the discharge of surfactants in the effluent to .5mg/liter. Typical removal rates for linear alkylbenzene sulfonates (LAS), the most widely used surfactant, are 98% for activated sludge, 80% for trickling filtration, and 27% for primary clarification. (Rapaport et al 1987) LAS and nonylphenol ethoxylates are found in the water of the Mississippi River at concentrations ranging from 0.1 to 10 μg/litre. LAS is found in the Mississippi riverbed sediment at concentrations ranging from 0.1 to 1 mg/kg. (Meade, 1995)

Results of a 1978-86 U.S. monitoring survey indicated that the concentrations of LAS in river water below effluent outfall ranged from .01-0.3 mg/l. The concentrations less than 5 miles downstream were 0.026-0.15 mg/l. while those greater than 5 miles downstream ranged from less than 0.005-0.12 mg/l. (Rapaport et al 1987)

Concentrations of 0.01 to 1.0 mg/l. of nonionic surfactant have been reported for rivers in the United Kingdom and 0.01 to 0.11 mg/l. for rivers in West Germany. A worldwide review of data on surface waters and groundwaters found a total range for nonionic surfactants from undetectable to 2 mg/l. (Swisher, 1987)

2. Surfactants can be toxic to aquatic life at sufficient concentrations.

Fish react to acutely toxic concentrations of surfactants with a sequential pattern of increased activity, inactivation, and immobilization, and if not removed from the exposure, death. The cause of death is suffocation, probably as a result of both physical and chemical disruption of the gill epithelium.

LAS (linear alkylbenzene sulfonates, or alkylbenzene sulphonic acid) has an aquatic toxicity of 25 µg/litre (or .025 mg/litre). (U.S. Geological Survey, 1995) Alcohol ethoxylate surfactants are toxic at concentrations as low as 0.37 mg/l. (Maki, 1979) Quaternary ammonium compounds display toxic effects on the gills and blood chemistry of Rainbow trout at concentrations as low as 1 ppm (1 mg/l.), (Byrne et al, 1989) and on *Daphnia pulex* at concentrations as low as 0.5 ppm (0.5 mg./l). (Moore et al, 1987)

3. Sublethal concentrations of surfactants can also affect aquatic species.

Subacute studies in fish show that the gills and the locomotive mussels are the sites most vulnerable to LAS toxicity. Low levels of LAS induce behavioral changes, such as a disruption in avoidance response and attraction. Early developmental stages, particularly the feeding sac–fry, are also very susceptible to LAS. (Chattopadhyay and Konar, 1985), (Fukuda, 1983), (Swedmark et al, 1976), (Saboureau and Lesel, 1977)

The sublethal effects of nonylphenol ethoxylates (C9APE10) on the activity of saltwater fish and invertebrates have also been studied. (Swedmark et al, 1971) At <1 mg/l., cod (*Gadus morhua*) maintained normal behavior for several months. At 5 and 10 mg/l., an initial period of normal behavior was followed by increased swimming activity and subsequent loss of equilibrium. Breathing rate and opercular movements increased in frequency. At 5 mg/l. the siphon retraction ability of the bivalve *Mytilus edulis* was gradually inactivated. At 10 mg/l. *Mytilus edulis* was unable to form byssal threads, and within 36 hrs the ability to close the valve was inhibited. At 0.5 mg/l juvenile *Mytilus edules* had reduced and irregular heart beats. At 4 mg/l the burrowing activity of *Cardium edule*, *Astarte montagui*, and *Astarte sulcata* ceased.

The behaviour of fish and snails in microcosms containing natural lake water and algae containing 0.5mg/l. NP were also studied. (Weinsberger and Rea, 1981) Guppies reacted immediately with an initial startle reaction followed by slightly disoriented swimming behavior and reduced feeding. Two of the six guppies died within 24 hrs and the others recovered after 36 hours. The snails dropped from the inner surface of the tank and did not emerge for 8 hours. Following this, five of six snails returned to their normal feeding behavior. At a concentration of 0.056 mg/l. NP, *Mytilus edulis* showed decreased byssal strength and a change of scope for growth (energy available above that needed for maintenance) .

During a flow-through toxicity test with *Pimephales promelas*, exposure to less than LC_{50} of NP (0.135 mg/l.) resulted in lethargic but stimuli- reactive behavior in surviving fish. (Holcombe et al, 1984) At concentrations as low as 0.098 mg/l., some loss of equilibrium was observed.

4. Surfactants can act synergistically with other more toxic pollutants.

LAS significantly increased the toxicity of parathion and certain parathion- related pesticides but had no effect on endrin or dieldrin toxicity. Studies with DDT were inconclusive. Toxicity of No. 2 and No. 4 fuel oils were also significantly increased in the presence of LAS. These studies show a possible synergism between LAS and pesticides or petroleum products. However, no substantial experimental evidence has been located to prove that LAS actually enhances the uptake of the agents. (National Technical Information Service, 1991, V49-V54.)

Equal ratios of LAS and chloramines were slightly synergistic at low concentrations but additive at higher concentrations. For unequal ratios, the two chemicals were strongly synergistic. Likewise, for copper and LAS mixtures, an additive effect was reported at equal ratios or at high concentrations of unequal ratios, while a synergistic effect was reported at low concentrations of unequal ratios. One study reported an antagonistic effect between LAS and copper and LAS and zinc in the developing cod embryo. No synergistic effects were observed when LAS was mixed with other surfactants.

Several studies have been conducted to investigate the possible interactions of LAS with pesticides and other potential aquatic contaminants, to determine whether some synergistic or antagonistic effects occur. One such study assessed the effects of chronic surfactant exposure on pesticide toxicity in goldfish. (Dugan, 1967) The single reported study with LAS (4 mg/l. for 37 days) indicated that the chronic toxicity of 50 ng/ml. of DDT was substantially enhanced by prior exposure to LAS. The effects of LAS on the acute toxicity of several insecticides to the fathead minnow (*Pimephales promelas*) have been examined. (Solon et al, 1970). LAS at 1 mg/l. increased the toxicity of parathion by 100% and LAS at 0.5 mg/l. gave a significant increase. In contrast, no synergism was observed with endrin. The results with DDT were too inconsistent to discern any synergism with LAS.

The interaction of LAS with several organophosphate pesticides related to parathion was also reported. (Solon and Nair, 1970) Of the eight pesticides tested, five (parathion, methyl parathion, ronnel, trithion, and trichloronat) exhibited synergism of acute toxicity with LAS at 1.0 mg/l. No synergism was found with dicapthon, guthion and EPN (Ethyl para-Nitrophenyl Phenylphosphonothioate). No synergism was found between LAS and dieldrin toxicity in the bluegill (*Lepomis macrochirus*) and no correlation was found between the uptake of dieldrin into fish tissue and LAS concentration. (Hill, 1970)

Since surfactants may be used to aid in the cleaning of oil spills in aquatic environments, the question has arisen as to whether the presence of surfactants may enhance the toxicity of the petroleum products to fish. The addition of 1 mg/l. LAS to No. 4 grade fuel oil increased the toxicity from 91 mg/l. for the oil alone, to 51 mg/l. with oil and LAS. (Hokanson and Smith, 1971)

In a study of fresh water fish indigenous to the Hudson River of New York, the acute toxicity of No. 2 and No. 4 fuel oils was significantly increased by performing the tests in the presence of l.5 ml/l. LAS. (Rehwoldt et al, 1974)

In a study of the effects of metal ions at concentrations as low as 10 ppm in combination with a nonionic surfactant at sub-toxic concentrations, it was demonstrated that metal ions are significantly more toxic to *C. elegans* when combined with a non-ionic surfactant. (Dennis et al,

1997) Due to problems with evaluating the data, it is unclear whether any of the above studies has shown synergistic effects, or merely additive effects.

Other studies have looked at such interactions somewhat more rigorously. (Tsai and McKee, 1978) and (Lewis and Perry, 1981) One investigated the effects on goldfish (*Carassius auratus*) of various chemical interactions that might occur in a stream receiving chlorinated sewage effluents. (Tsai and McKee, 1978) Utilizing mixtures of chloramines, LAS and copper as representative of possible interactions, it was found that equal ratios of LAS and chloramines were slightly synergistic at lower concentrations, but additive at higher concentrations. LAS concentrations ranged from 1.8 to 6.5 mg/l. For unequal ratios, the two chemicals were strongly synergistic. When LAS was combined with copper, the toxicity was additive at equal concentrations and at a ratio of 2:1 (LAS:copper). However, when the ratio was 1:2, the effects were additive at high concentrations and synergistic at low concentrations. The ternary mixtures of chloramine, copper and LAS in various ratios were all additive at high concentrations and synergistic at low concentrations.

The effects of LAS alone and in combination with the heavy metals, zinc and copper on the development of cod (*Gadus morhua L.*) were also tested. (Swedmark and Granmo, 1981) Results indicate an interaction between the metals and LAS, giving a weak antagonistic effect for zinc and a strong antagonistic effect for copper. LAS significantly increased the accumulation of zinc in young goby (*Proterorhinus marmoratus)*. (Topcuoglu and Birol, 1982)

Surfactants are known to alter the permeability of biological membranes to water and ions and may modify the uptake of heavy metals in fish. Since cadmium (Cd) is taken up primarily through the gills of freshwater fish, Cadmium uptake was studied in freshwater trout (*Salmo gairdneri*) exposed to LAS. (Part et al, 1985) Results showed that 0.14 µg/l. LAS more than doubled the cadmium transfer into the gill, while 100 µg/l. LAS markedly reduced cadmium transfer. Results showed that fish exposed to low levels of LAS and cadmium (well below LC_{50} values) take up lethal concentrations of Cadmium. This increased uptake of cadmium is due to the destructive effects of LAS on the gill, increasing the permeability to cadmium. Modification of cadmium transfer in both “low dose” and “high dose” LAS experiments suggests that LAS affects cadmium transfer by a specific mechanism, most likely the result of LAS interacting with proteins involved in cadmium transport in the gills.

The results of these studies with pesticides and petroleum products show the possibility for synergism between LAS and other potential aquatic toxicants at doses of LAS not of themselves toxic to aquatic species. The hypothesis has been offered that LAS may enhance the uptake of these agents, but there is not substantial experimental evidence as yet for this view.

Conclusions:

The available literature supports the following conclusions:

- Environmental concentrations of surfactant in the inland waters range between .005 mg/l. and 2mg/l.
- Surfactants can be toxic to aquatic life at concentrations as low as 0.025 mg/l. for LAS, 0.37 mg/l. for alcohol ethoxylates and 0.5 mg./l. for quaternary ammonium compounds.
- Sublethal concentrations which have demonstrated adverse effects on aquatic species are: nonylphenol at 0.098 mg/l. and LAS at 0.005 mg/l. (Misra et al 1987).
- Surfactants have demonstrated synergy with many chemical compounds and may interact with other toxic pollutants to make chemical mixtures with unknown toxicological properties.

- Reducing surfactants in aquatic environments may reduce direct aquatic toxicity as well as limit the extent of synergistic reactions that would otherwise amplify the harmful effects of other pollutants.

Action:

After researching the effects of detergents on the aquatic environment, Cogent Environmental Solutions Ltd., a Canadian company whose principal has pioneered other low-odour and zero-V.O.C.-emission cleaning products, concluded that cleaners would have to be redesigned with a new group of ingredients in order to reduce the environmental impact on our ecosystem. For further information on their new cleaning technology see Process Cleaning solutions or ECOgent at either processcleaningsolutions.com or Ecogent.ca.

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