FROGS IN AN EFFLUENT SOCIETY

Risks, Remedies and Responsibilities

by Dr Sara Broomhall

First published in June 2004 by WWF Australia

ISBN: 1 875941 67 3

Author: Dr Sara Broomhall

WWF Australia
GPO Box 528
Sydney NSW Australia
Tel: +612 9281 5515
Fax: +612 9281 1060
www.wwf.org.au

For copies of this booklet or a full list of WWF Australia publications on a wide range of conservation issues, please contact us on publications@wwf.org.au or call 1800 032 551.

Special thanks to Craig Cleeland for supplying the photographs for this booklet.

CONTENTS

The aim of this booklet is to help you understand:

- What pollutants are
- How frogs interact with their environment
- Why water pollution affects frogs
- Where pollutants come from and how they enter the environment
- How you may be polluting water
- Categories of pollutants (such as pesticides) and their effects on frogs
- Where you can go for further information
- What alternatives there are and what products you can substitute

What is a pollutant?

Pollutants are potentially harmful, and sometimes lethal. It's easy to think of chemicals such as pesticides, detergents, industrial chemicals and so forth as pollutants. Less obvious examples might be extremely high nitrogen or phosphorus levels in water due to fertiliser runoff and sewerage discharges, or sediment from cleared lands. Salinity and litter also cause pollution problems.

For the purposes of this booklet, our main emphasis is water-borne pollutants - those readily identifiable culprits such as pesticides, household detergents, assorted chemicals, and fertilisers.

Pesticides are substances (or mixtures of substances) that are intended to prevent, kill, or repel a particular pest. 'Pests' are species that we want to get rid of, for any number of reasons. Pests can include insects, mice and other animals, unwanted plants (weeds), fungi, or microorganisms like bacteria and viruses. The term 'pesticide' therefore also includes herbicides and fungicides. Unfortunately, most pesticides have some risk of harm to non-pest species precisely because they are designed to be harmful. Of course, many things can be toxic in high enough amounts, even caffeine and parsley, but such high amounts are very unlikely to occur. Problems arise when the amounts we use regularly are directly harmful, or accumulate to harmful concentrations in nature.

Australian frogs

Australia really is a lucky country – we have more than 210 species of frogs! What is more, because Australia has been isolated from other land-masses for so long, our frog species are quite different from the species found in other countries. In Australia, we have three main native frog families. They are the *Myobatrachidae* (or ground frogs), the *Hylidae* (tree frogs), and the tropical *Microhylidae*.




How do frogs interact with their environment?

Life stages

Frogs generally start their life cycle as eggs encased in jelly capsules. Depending on the species, the eggs develop on land or in water. They gradually turn into tadpoles, hatch, and become free-swimming. Tadpoles breathe via gills, like fish. They continue to grow until they reach a certain stage, when a complex hormonal process kicks in that changes them into frogs. This is called 'metamorphosis', and it is really quite remarkable. When they crawl out onto land, the frogs are then mostly terrestrial and breathe via their skin and the back of their throat. Frogs have an essentially "naked" egg (it doesn't have a shell) and, along with other amphibians such as salamanders and caecilians (neither of which are native to Australia), are the only vertebrate group that has both an aquatic and terrestrial phase.

Habitat requirements

Frogs need an environment that is moist, because they 'drink' and breathe through their skin. Most species lay their eggs in water, so the availability of water is essential. Some frogs have evolved to take advantage of temporary pools of water that are created by heavy rain. Others lay their eggs in rivers, and yet others congregate around permanent ponds and streams.

Ecological position

Frogs are important components of many ecological communities, consuming vast amounts of invertebrates and, in turn, providing an abundant food source for many other predators, such as birds and snakes.

Frogs and pollutants in the food chain

If pollutants affect frogs, this can then have carry-on effects on the ecological community. Pollutants that may not be easily excreted or broken down by the body, can accumulate in body tissues. This is known as 'bioaccumulation'. When these animals or insects are then consumed by another animal, the toxins in the prey can then accumulate in the predator's body. This process is called 'biomagnification'. After eating a few contaminated prey items, the concentrations of toxins in the body of top predators can become extremely high. Frogs can bioaccumulate toxins by ingesting contaminated insects and also through direct exposure to pollutants, particularly in the water. When frogs are killed by these pollutants, either directly, or because the pollutants make them very sick and unable to escape a predator, then this causes problems all the way up the food chain. Frogs, with their toxic payload, may make the animals that eat them very sick. With fewer frogs to eat insects, there are ecological problems down the food chain as well.

Why is environmental pollution a frog issue?

The skin of a frog is very permeable. The tadpole stage also relies on gills for breathing. Both of these physiological characteristics make frogs and tadpoles very susceptible to a number of contaminants, which often easily penetrate exposed surfaces such as gills and skin.

Consequently, because frogs inhabit water and land, they may have more opportunities to be exposed to environmental contaminants than many other animals. Frogs also have more ways of being exposed than other animals, because they have gills as tadpoles and a very permeable skin as an adult.

Frog limb abnormalities have been proposed as a possible indicator of environmental abnormalities, particularly in agricultural areas. However, deformed frogs are rare in Australia.

Are frogs more sensitive to environmental pollutants than other species?

Yes and no. In some situations, and for some toxins, frogs may be particularly susceptible to contamination. For example, the insecticide endosulfan is ten times more toxic to *Rana* tadpoles than to catfish or damselfly nymphs. We rarely test the effects various contaminants have on adult frogs so in many cases, we simply don't know how sensitive they are. Unfortunately, there is not enough research to provide a definitive answer to this question for most frog species.

WHAT WE DO AND DON'T KNOW

Why don't we have all the answers?

We are blessed with lots of frog species, but environmental toxicology is a relatively new field here in Australia. The majority of aquatic toxicological testing usually focuses on species such as fish, shrimp, and invertebrates.

How applicable are studies on fish and invertebrates to frogs? Good question!! Generalisations are hard to make because a frog's sensitivity also varies according to the specific toxin tested. For example, we know that frogs do not react to mercury the same way fish do. Consequently, we cannot assume that frogs will react the same way as other animals – or even that all species of frogs will react the same. However, frogs are more similar to fish in many ways than they are to birds and mammals.

At least 80% of the available research on environmental contaminants and frogs uses American and European species. Unfortunately, these studies may have little direct relevance to the unique frog species and environmental conditions in Australia.

In many cases, we don't know what chemicals are, or might be, in our waterways. We also don't know if or how they may combine to form new toxins. Nor do we know what they may break down into.

How relevant are these toxicity tests to real world situations anyway?

One of the most widespread protocols for assessing the toxicity of a chemical to an aquatic species is the acute toxicity test, which provides information about what sort of concentrations are overtly harmful to the test animals. However, even though animals may not die, they may get sick, or their growth may be stunted. Such chronic effects appear only after weeks, months or years, and are much more difficult, and costly, to assess. Bacteria and light can break down some chemicals into other substances and these may be more or less harmful than the original compound.

Where do pollutants come from?

Outside of natural disasters, almost all pollutants are the result of human activities, whether created directly, or as by-products of production processes.

How many chemicals do we use here in Australia?

For a start, there are over 40,000 industrial chemicals listed by regulatory authorities, and over 4,500 agricultural and 3,000 veterinary products registered for use in Australia. Do we know the effects that each of these chemicals have? Frogs are not a standard test species, so in most cases we don't know what they do to frogs. In addition, many chemical formulations are based on other, older formulations. These formulations have generally been originally tested a long time ago and so may not meet contemporary standards. The Australian Pesticides & Veterinary Medicines Authority (APVMA) assesses existing chemicals in response to concerns about their health, trade or environmental effects.

Due to the huge number of chemicals in use, only a small proportion have been assessed and so we often don't know the effects that all these chemicals have on frogs.

Unfortunately, information on agricultural and veterinary chemical usage is not formally collected across Australia. We do know that herbicides, insecticides and fungicides have been regularly used in Australian farming for at least 40 years. We also know that all forms of pesticide use have increased over the past two decades and that we spend around a billion dollars on them annually.

Who produces pollutants?

The list of who produces pollutants is enormous because many things that we use in day to day life either cause pollution while being manufactured, or become a pollutant when we finish with them.

Take, for example, most peoples' morning routine.

You get out of bed. If it's a wooden bed, the wood has usually been treated with preservatives and anti-fungal agents, perhaps sealed with a varnish. Many of these treatment processes discharge waste water, not to mention the initial process to produce the preservatives and varnishes, all of which are likely to be toxic to frogs in variable amounts. Chlorinated phenols are used as wood preservatives and pesticides, and are often the by-products of paper pulp milling. All these chemicals are toxic in high doses.

If the sheets on the bed are cotton, they have usually undergone a bleaching and dying process. Chlorine based bleaches can be dangerous to frogs. The cotton industry uses thousands of tonnes of insecticides every year to control pests. Pesticides, and their effects on frogs, are discussed in much greater detail later on in this booklet. Your sheets are partially polyester? Many plastics industries are again highly polluting. Bisphenol A, a high-volume chemical used to make polycarbonate plastic, epoxy resins, and other chemicals, has been shown to be weakly estrogenic to fish. Estrogen is an important hormone that regulates many bodily functions in many animals, including frogs.

Polychlorinated biphenyls (PCBs), which are widespread contaminants in industrialized nations, were used to manufacture paints, plastics, adhesives and electrical goods (such as transformers and capacitors), non-carbon copying paper and are used as hydraulic and cooling fluids. PCBs have been shown to cause reproductive failure in birds, cause liver, stomach and thyroid gland injuries and affect the immune system in other animals. PCBs are so persistent and mobile in the environment that almost everyone has been exposed to them.

You grab your towel (again it is likely to be cotton) and walk across to the bathroom. Think about the preserved and sealed wood of the floor, and how logging industries can also cause problems with erosion and sediment into rivers. The rug on the floor and the paint on the wall may be a source of acrylic acid. This acid is used to produce acrylic esters and resins, and used in detergent intermediates and oil treatment chemicals. It is also emitted in the production of acrylate, and from polishes, paints, coatings, rug backings, adhesives, plastics, textiles and paper finishes. According to the National Pollutant Inventory database (collated by the Department of Environment and Heritage DEH), about 90% of acrylic acid in the environment is expected to end up in water. It has slight toxicity to aquatic organisms such as fish and has high toxicity to birds.

In the bathroom, you step into the shower. Your shampoo bottle is usually made from plastic. Its label is usually bleached paper (as is most toilet paper). Pulp and paper mills discharge dioxins to air and billions of liters of liquid effluent each year. In fish, this effluent can cause delays in sexual maturity and reduced egg production, depress sex steroids, cause masculinisation of female fish, and suppress immune functions.

Your shampoo may contain up to 50 ingredients. A number of them are foaming agents, or 'surfactants'. Surfactants have been shown to be harmful to frogs and are discussed more extensively later on in this booklet, on page 10. Some anti-dandruff shampoos contain selenium. Excess selenium is associated with reproductive effects and mortality in wild birds, although we don't have a good understanding of what it does to frogs. However, sodium selenite has been shown to cause severe developmental abnormalities in the African clawed frog (*Xenopus laevis)* at concentrations of 2 mg/L. One teaspoon of salt is 5,000 mg, so 2mg is a very tiny amount.

Your shaving cream may contain octylphenol, which is also a breakdown product of a chemical widely used in the pulp and paper industry and is found in many common household cleaners. Octylphenol adversely affects both the growth of snapping turtle hatchlings, and development in tadpoles. Your antiperspirant contains aluminium, which may have effects on the nervous system, and is toxic to frogs at concentrations of 0.86 - 1.6 mg/L.

Your toothpaste can contain carrageenen as a thickener, triclosan as an antibacterial, and fluoride. The first can cause intestinal ulcerations, the second has been shown to accumulate in wild fish, and there is some evidence that fluoride-contaminated water can cause frog eggs to hatch prematurely. We don't know what effects these things have on Australian frogs.

All of these products are washed down the drain. Many trillions of litres of contaminated water flows through sewerage systems in Australia every day. Although sewerage is partially treated, treatment plants often do not capture all the solids we rountinely flush down toilets, such as wrappers, cigarette butts, dental floss, nappies, and toilet paper, let alone treat things like chemicals, cleaning products and detergents.

At least 80% of water samples taken from rivers and catchments in the USA in 1999 and 2000 contained chemicals such as disinfectants, antibiotics, antioxidants, caffeine, fire-retardants, and fragrances. Surfactants and platicizers (such as 4-nonylphenol and bisphenol-A) were also found in over 50% of samples. The potential toxicological effects of most of these compounds are relatively unknown. This means that many possible contaminants are entering our waterways, and we simply do not know what effects they may have on our frogs. Research has shown that caffeine is teratogenic (i.e. causes birth defects) to the African clawed frog (*Xenopus laevis)* and causes malformations of embryos at concentrations of 0.12 mg/L. One cup of coffee contains 100mg caffeine. Interestingly, caffeine spray is now being used as a slug and snail killer; and may also be used to control pest frogs in Hawaii, by causing then to go into cardiac failure.

We haven't even gotten to electricity, or your morning coffee, or breakfast, or cars, or roads yet! This is meant to illustrate how things that are either directly polluting, or are the result of an industry that pollutes, permeate our daily lives.

So how am I polluting?

Potential sources of pollution in a city or town include:

i. domestic pesticide use
ii. domestic fertiliser use
iii. discharge from sewerage treatment plants (both domestic and industrial sources)
iv. transport of pollutants and sediments via stormwater
v. irrigation drainage and runoff from roads
vi. groundwater contamination from land fills.

i. & ii. Domestic pesticide and fertiliser use:

Many household products are classified as pesticides. Did you know that insect repellents; flea and tick sprays, powders, and pet collars; cockroach sprays and baits; rat and mice poisons; some kitchen, laundry and bath disinfectants and sanitizers; mold and mildew killers; some lawn and garden products (such as weed killers); and some swimming pool chemicals are classified as pesticides?

Did you know that some flea powders, collars, and sprays may include carbamates, pyrethrins, chlorpyrifos, and organophosphates? If you have never heard of these chemicals, then perhaps now is a great chance to start learning about them. I will define pesticides and their effects further on. Fertilisers can contain heavy metals or change soil pH, or cause excess nutrients in waterways that may lead to algal blooms.

iii. Discharge from sewerage treatment plants:

Many people flush things down the drain because its an easy way to get rid of them. In 2000-2001 Sydney Water collected 1,348 cubic metres of litter from the litter booms, trash racks and gross pollutant traps. Sediment capture was almost 40,000 tonnes. This, however, is less than 70% of the solids that flow through the system.

A Sydney Water media release titled "Household Sinks Put Environment at Risk" on 02 May 2002 cautioned that increasing amounts of paints, solvents, paint strippers, fuel, oil, food scraps, milk, cooking oil, small rubbish items such as cigarette butts, bandage wrappers and cotton tips (which slip through traps and filters), pesticides, and poisons are being tipped down the drain. When compared to 1994, an additional 2,174 tonnes of grease and oil entered the system in 2001. The Minister responsible for Sydney Water cautioned that many of these items may cause blockages in pipes, causing them to overflow, and smaller items slip through screens and can end up directly in waterways. Chemicals and poisons can't be screened and are difficult to treat, they too can end up in our waterways.

The responsibility lies with all of us.
We cannot rely on the sewerage system to take care of the household items we put down the drain. Everything we do may directly affect our waterways and the frogs that live in them. ***We need to be mindful of what we do – in some cases it may be easy to change a behaviour.*** For example, one could pour old milk onto a garden bed, not down the drain (milk can clog up the treatment system). And old paints and garden sprays can be taken to chemical disposals. There are suggestions and details on where one can safely dispose of old chemicals at the end of this booklet.

Let's take a ride through the wastewater system…

Sewerage:

Sydney Water provides sewerage services to collect, transport and treat wastewater from households and industry, for more than 3.9 million people. This equates to around 1,300 megalitres (a megalitre is one million litres) of wastewater every day! I mention Sydney Water only in order to illustrate how sewerage systems operate in Australia, and because so many Australians live in Sydney. Sydney Water also provides good information services, so we can get a better picture of what happens.

We already know that sewerage treatment plants do not eliminate all harmful contaminants flowing through the system. For example, many plants exhibit leaf damage when irrigated with 'reuse' water, which is sewerage water that has had partial treatment but is not yet drinkable. What we don't know is exactly what things are passing through, nor what effects they might have. The presence of many potential contaminants are not routinely monitored. For example, domestic inputs to sewerage works contain natural and synthetic estrogens from human excretion, such as estradiol. Very small concentrations of estradiol have been shown to cause many developing African clawed frog *(Xenopus laevis)* embryos to become female. Estrogens in the environment, or chemicals that mimic oestrogens, are thought to disrupt many hormonal processes in aquatic animals. Chemicals that do this are known as 'Endocrine Disrupting Chemicals' (EDCs), and are discussed more comprehensively later on.

Effluent and receiving waters around Sydney sewerage treatment plants (STPs) have been found to contain significant amounts of metals such as boron, cadmium, cobalt, copper (which causes gastrointestinal, liver and kidney problems in humans, and disrupts gill function in fish), silver, iron, lead (which can delay mental development in humans and cause kidney problems), mercury, manganese and nickel. Many heavy metals are acutely toxic to fish and frogs. For example, cadmium causes mortality in a salamander, *Ambystoma opacum*, at concentrations above 10.2 µg/L. A teaspoon of salt is about 5 million µg (not including the spoon, of course!), so 10 µg (called "micrograms"), is about as much as a single grain of salt in a litre of water. Metals are heavier than salt, so the amount we are talking about here is very, very, very tiny.

The maximum concentrations of aluminium in effluent and receiving waters at Blackheath, NSW over the past six years ranged between 110 µg/L and 1,420 µg/L. These are 2 to 25 times the trigger value of the Australian and New Zealand Water Quality Guidelines, and therefore likely to be harmful to organisms such as tadpoles that inhabit these waters. Aluminium is toxic to the American toad *(Bufo americanus)* at concentrations between 860-1,660 µg/L. Remember that a teaspoon of salt is about 5 million µg, so this is less than 1/3,000 of a teaspoon!

STP discharges have also been found to contain cyanide (which disrupts respiratory functions in animals), chlorpyrifos (an organophosphate insecticide), dieldrin (an organochlorine

The in's and out's of waste water

solids
milk
detergents
paint
cleaning products
pesticides
etc.

No tests for some contaminants

High Volumes (eg. 1,300,000,000 L per day in Sydney)

input to drains, toilets etc.

incinerators
- dioxins

ash & soil conditioners
- heavy metals
- pH

ground water

Solid Output

Sewerage Treatment Plants

changes in vegetation

irrigation

by-pass

Liquid Output

ground water

storm water

heavy metals
- aluminium
- chromium
- boron
- mercury
- lead

pesticides
caffeine
painkillers
benzene
surfactants
urea
hormones
chlorine
nitrate

to streams etc.

road debris
oil
detergents
weedkillers
petrol
etc.

insecticide), chloramines, and nonyl phenol ethoxylates (surfactants).

Residual chlorine (used to disinfect drinking water and sewerage, also contained in many home disinfectants) has been detected in the effluent and receiving waters of Sydney STPs for several years. The observed maximum concentration in the effluent and receiving waters at Castle Hill, NSW during 1999/2000 was 2,230 mg/L – a total load of 1,829.28 kg in one year. This value is double or triple the concentration that kills fish, because chlorine is toxic to freshwater fish at concentrations of 70-840 µg/L. Many sewerage treatment places such as Sydney water are committed to improving water quality around discharge sites. But it is a big and expensive job.

It is highly unlikely that discharges will ever be harmless. Therefore, it is up to all of us to be mindful of what we add to this toxic burden on our waterways. We can all help frogs by not putting harmful things down the drain.

iv. Transport of pollutants and sediments via stormwater

The litter you throw in the streets, the oil your car drips onto the road, and the soap suds you wash off your car can all make it through the stormwater drains and into your local river.

A secondary consequence of stormwater is that at times of higher flows (such as during intense rainfall) the capacity of STPs to treat and manage wastewater becomes weakened, and thus flows bypass some treatment processes. Consequently, partially treated sewerage can be discharged directly into rivers. Such discharges can generate an acute pollution episode. An example of this is the 300 tonnes of dead fish removed from a river in France after a storm event in 1992.

v. Irrigation drainage

'Spray-drift' and 'run-off' are terms that describe when contaminants move away from the place where they were intended. Chemical sprays, particularly fine ones, can be blown a long distance by the wind. This can cause serious problems in agricultural operations where spray is released from aeroplanes or big machinery, but it can also be a problem in your own backyard if you spray on a windy day.

Run-off occurs when chemicals have been applied to plants and then water (either rain or irrigation) washes these chemicals off the plants, and either into the soil or off into dams, creeks and rivers.

vi. Groundwater contamination from landfills and industrial activities:

'Groundwater' is the underground reservoir that supplies wells, springs, and creeks. It provides around 20% of Australia's total water requirements; this figure increases to 100% in some remote mining settlements.

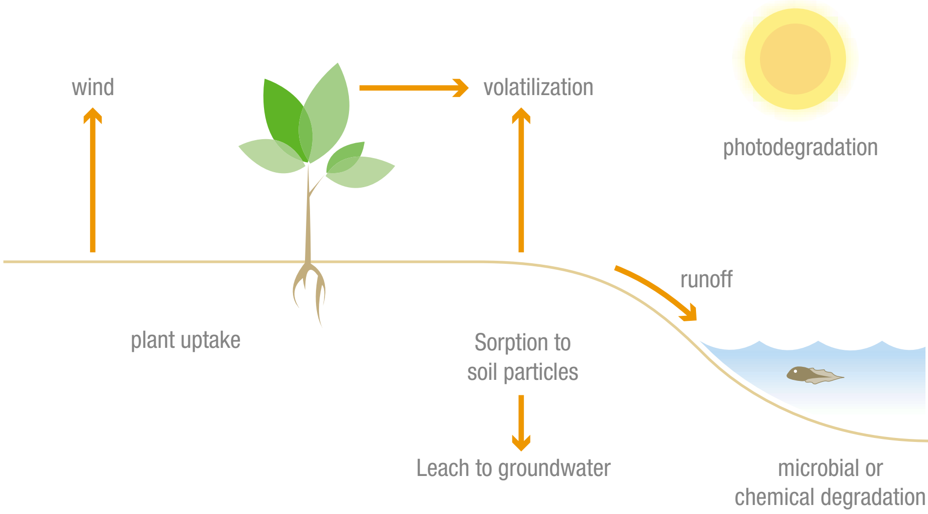
Deep below ground, it may still become contaminated by agricultural and industrial activities. Even your own backyard has the potential to affect groundwater in surrounding areas. Agricultural dip-sites (especially where arsenic and organochlorine products were used), old metal smelting sites (such as copper and lead), closed tips, gas plants and works, garages, power stations (where buried hydrocarbons and heavy metals occur), manufacturing spills, broken pipelines, and mining-related activities and bores are all sites where contaminants can leach through the soil to groundwater unless responsibly managed.

What do we know about agricultural pesticides and where they go?

Although agriculture is the largest user of pesticides, significant quantities of herbicides are also used by local councils and road and rail authorities for weed control.

We do not know the total contaminant load in Australia - how much is used and where it is used -we can only make estimates based on the amount of money spent per year. The problem with estimates is their uncertainty. Chemicals may break down or degrade, and these degradation products may act in many different and unpredictable ways. Chemicals can also move off-target. Refer to diagram below. For example, 1) those which are sprayed can move through the air, 2) those applied directly to the soil may be washed off into nearby surface water, or 3) they may percolate through the soil to groundwater, 4) groundwater can also transport chemicals into surface water bodies or irrigation water sources elsewhere, and 5) sediment can be an additional potential source of exposure. Lastly, the potential effects of exposure to multiple pesticides applied in a given area cannot be assessed.

So now that I have talked about the numbers and volumes of chemicals we use ourselves, how can we tell what effects these may have on frogs?



THE USUAL SUSPECTS

What can we really say about the effects that all the chemicals we use have on Australian frogs?

Unfortunately, the answer is: we can say very little. Existing research suggests that many products have the potential to be harmful, but in most cases we simply don't know. We are forced to make educated guesses.

I have listed three main categories of contaminants:

- ***Pesticides,***
- ***Surfactants (detergents, soaps, wetting agents, and their metabolites) and adhesives***
- ***Fertilisers and heavy metals.***

This list is by no means comprehensive, and many compounds and their effects simply cannot be included here (unless you really want to read a tome the size of the Sydney telephone directory!). The idea here is to introduce you to the sorts of things that are commonly used and some of the possible effects they can have.

Pesticides:

There are currently over 4,500 agricultural pesticide products registered for use in Australia. These products are used extensively in both urban and rural environments. Any given active ingredient can be used in many different brands and formulations. For example, the herbicide 2,4-D has over 100 trade names and formulations.

When used according to label directions, many pesticides should be relatively safe for humans, However, again, we are generally unsure what effects they have on frogs. Moreover, when they move off target, breakdown or accumulate in water bodies, then their effects may be much worse.

Since the term 'pesticide' incorporates many products such as insecticides and herbicides, I have split the topic into six sub-sections which can be read in any order. Three subsections discuss some of the major types of insecticides: the organochlorines; the organophosphates; and the carbamates. The next three subsections will briefly outline herbicides, then additives, and the final section is a special case of compounds that have particular action. These are the endocrine disrupting chemicals.

Organochlorines

Organochlorines were the first synthetic chemical pest control agents, and include DDT, chlordane, lindane, endosulfan, metolachlor, pronamide and heptachlor. DDT was used extensively in developed nations until it was banned from use in the USA in 1972 and Australia in the mid 1980's, although it is still widely used in much of the rest of the world.

DDT, and most other organochlorines, have very high environmental persistence. For example, a recent study found that the average residue levels of DDT in the stomach contents of birds in Australia in 1990 were 179.21 µg/L (a µg is one millionth of a gram) despite not being used for 20 years. Harmful effects have been reported in one frog species at concentrations as low as 2 µg/L DDT. This amount is equivalent to two pinches of salt in ten tons of potato chips.

Organochlorine residues continue to be detected in fish from the Mississippi River Basin.

Organochlorine pesticides such as endosulfan are still being used in Australia. Endosulfan attacks the central nervous system in mammals, but we don't know what it does to frogs.

Organochlorines such as dieldrin, endosulfan, toxaphene, and chlordane are also weakly estrogenic (they act as hormone mimics). Endocrine disrupting chemicals have been shown to cause extensive limb malformations in the frogs *Rana clamitans* and *Rana catesbeiana*. Despite widespread contamination, very few studies have measured organochlorine residues in native Australian frogs.

Organophosphates

Today, organophosphates have partially replaced organochlorines because of their lower environmental persistence. Organophosphates tend to inhibit cholinesterase, disrupt enzyme processes and nerve impulses, or denature proteins. In Australia, we use them extensively in agriculture and within urban areas.

The organophosphate pesticides diazinon and chlorpyrifos are active ingredients in a number of domestic garden pesticides and both have been detected in effluent and receiving waters in most Sydney STPs. The observed maximum concentration of diazinon was 1.71 µg/L. Little information is available on the effects of diazinon on frogs. As an illustration, a search of a scientific journal database produced 1,553 papers that mentioned diazinon. Only one of these was on frogs. This paper, a Canadian study, found that the lethal concentration of diazinon to green frogs *(Rana clamitans)* was 2.8 to 5 µg/L.

Therefore, we don't know their potential risks to Australian frogs.

Carbamates

Like organophosphates, the low persistence of carbamate insecticides has led to their widespread acceptance. Carbamates often disrupt the movement of nerve impulses. Despite their acceptance, carbamate based insecticides have been found to produce developmental malformations in skeletal tissue and musculature of *Rana* species. Exposure of *Xenopus laevis* and *Hyla* tadpoles to carbaryl caused mortality at some concentrations and changed swimming behaviour at others. In addition, its toxicity increased tenfold in the presence of ultraviolet-B radiation.

We can assume the effects on Australian species are likely to be similar, but until formal studies are conducted, the real dangers remain virtually unknown.

Herbicides and fungicides:

Atrazine is the most commonly used herbicide in the U.S. In Australia, atrazine has been found to contaminate as much as 50% of groundwater samples in some areas, although the extent of groundwater testing is extremely limited.

Recent research has found that male African clawed frogs *(Xenopus laevis)* suffered a tenfold decrease in testosterone levels when exposed to 25 ppb (parts per billion) atrazine. One part per billion is the equivalent of one drop of impurity in 500 barrels of water. Paraquat has been found to cause malformations to *Xenopus laevis* embryos at concentrations of 0.2 mg/L. The fungicide Vinclozolin alters sex differentiation of male rats. Again, we do not know the effects of atrazine, or many other herbicides, on Australia frogs.




Surfactants:

Synthetic surfactants can also contribute to water pollution, as around 7 million tons are produced worldwide every year. Surfactants are used in many compounds to break down the surface tension in water, and help them disperse. Alkylphenols and alkylphenol ethoxylates (APEs) are commonly used in many industrial, agricultural and domestic applications. Both of the surfactants alcohol ethoxylate and alcohol ethoxy sulfate were found to have toxic effects on *Xenopus laevis* embryos and tadpoles. In particular, embryos had malformed gills. These two surfactants are used extensively in consumer products.

It appears that alkylphenols were not tested for in effluent of STPs here in Australia until last year. Nevertheless, nonyl phenol ethoxylates were detected in effluent and receiving waters at Blackheath in 2000/2001. Although sewerage works treat effluent, they are not yet effective at removing many contaminants.

Additives:

We tend to know formulations only by their active ingredient, with little regard to the many other additives that are not listed on the label.

Here in Australia, Dr. Reinier Mann undertook research on glyphosate. Glyphosate is supposed to be one of the most non-toxic herbicides available. Dr. Mann found that the surfactant, not the active ingredient, had serious impacts on frogs and tadpoles; therefore, compounds considered safe may not be safe at all. These sorts of findings can lead to companies changing the formulations of their products, however, such harmful effects are simply unknown until someone does research on it. Unfortunately, the amount of money spent on such research is vanishingly small.

Endocrine disrupting chemicals:

Many environmental contaminants, such as plasticizers and pharmaceuticals, are known to have estrogenic effects, or behave as hormone mimics or disruptors. These ultimately affect basic life functions such as growth, reproduction and development, and maintenance of the body. Without killing individuals, they can seriously jeopardise whole populations.

While DDT is one such compound, the alkylphenolic surfactants used in items such as detergents, paints and pesticides may be of greater concern. These chemicals are also used in industries including pulp and paper, textiles, pesticides, metals and plastics, and institutional and household cleansers. For example, a concentration of 16 µg/L Bisphenol A (a high-volume chemical used to make polycarbonate plastic, epoxy resins, and other chemicals), altered the proportion of sex cell types in the testis of male fish, while higher concentrations inhibited gonadal growth in both sexes of fish. Remember than a microgram is one millionth of a gram. Bisphenol A also bioconcentrates in freshwater clams and lower water temperatures causes it to persist even longer in tissues.

A high incidence of intersexuality has been observed in wild populations of riverine fish in many parts of the United Kingdom – this sexual disruption is associated with exposure to effluents from sewerage treatment works.

Again, the effect of endocrine disrupting chemicals has not yet been studied in Australian frogs.

Fertilisers:

Fertilisers have only recently been proposed as a potential threat to frogs, but it is one of the most serious problems at a local level. Researchers in the northern hemisphere noted a correlation between amphibian declines and environmental increases in nitrates and ammonia.

Sublethal concentrations of nitrite in water caused both physical and behavioural changes in the Cascades frog in the USA. Urea fertiliser decreased survival in two American amphibian species.

Australian frogs have evolved in an environment that is comparatively low in nitrate and phosphate, so it is possible that Australian frogs may have a greater sensitivity to these chemicals. Nitrates are becoming a larger concern among environmental monitoring agencies in Australia because nitrate contamination is considered the most significant and widespread contaminant of groundwater. The main problem with increased nitrate concentrations is the potential to stimulate algal growth and blooms. At high enough concentrations, nitrate is toxic to aquatic life.

In temperate areas in south eastern South Australia, dairies, piggery feedlots, cheese factories, abattoirs, and spreading of wastes, nitrogenous fertilisers and natural leaching of leguminous fertilisers can greatly increase concentrations of nitrate in groundwater. Sugarcane growing is a major source of nitrate contamination in groundwater in coastal Queensland. Indeed, increased nutrient load is already affecting the Great Barrier Reef.

Fertilisers can also dramatically change soil chemistry, such as pH, and heavy metal content. Acidity can also lead to mobilisation of metals such as aluminium & iron and can increase chemical demand for dissolved oxygen in waterways, leading to lower oxygen availability for fish and tadpoles. pH also alters how tadpoles react to fungal attack, bacterial infection, or how they are affected by heavy metals or UV-B radiation, and so on.

Many fertilisers contain impurities such as cadmium, lead and mercury. Most heavy metals such as mercury, boron, cadmium and cobolt are harmful to frogs. Mercury, for example, is one of the most toxic compounds to frogs yet found. This means that fertilisers may have considerable long-term impacts on our frog species; either directly, or through modifying other variables such as pH and metal impurities.

Combinations:

Commercial preparations are often a combination of two or more pesticides or they incorporate various solvents, carriers or surfactants. Biological testing is generally only done on the active ingredients.

Some chemical combinations may have additive or synergistic effects, that is, the combined effect is much greater than just the sum of the effects that each compound has by itself. They may also combine with other environmental parameters such as pH.

Although little is known about interactive effects, the potential implications of contaminant mixtures are serious.

Metabolites:

We also need to consider that chemicals break down in the natural environment. Methoprene, used for controlling mosquitoes and fire ants, is considered comparatively safe and inert. Its an insect growth regulator that interferes with insect development. Such biologically-based pesticides, or others that utilise pheromones and microorganisms, are becoming increasingly popular because they are often considered safer than traditional chemical pesticides.

However, the photoproducts and metabolites of methoprene, which form as it breaks down in sunlight, have been found to cause developmental deformities in the African frog *Xenopus laevis*. Although the concentrations used were much higher than would be expected if the product was used according to directions, they still indicate cause for concern, especially in cases where the amounts used do not comply with the label directions.

So, products previously considered safe for frogs may not be so safe after all. Here are some other questions for you. What do we really know about the products used in the home and garden? Many chemicals are labelled as “Readily Biodegradable”, but what do they degrade to? Its not specified on the label. In fact, many ingredients are not listed on the label at all, or simply generalised to: “sudsing agent”, “thickener”, “cleaning agent” and the like. Of course, many products really are safe to use - but which ones? for how long? and safe for what animals? I mention all this in order to raise questions in your mind about the products we use everyday.

Where can I find out about these chemicals?

There are a number of handbooks available, such as “The Pesticide Manual”, edited by CDS Tomlin and published by the British Crop Protection Council (2000), and “The Agrochemicals Handbook”, edited by Kidd & James (1991), and published by The Royal Society of Chemistry, Information Services, Cambridge, England. It lists many pesticides, their chemical composition, and toxicology data on various test species, but such technical handbooks are big and heavy and sometimes expensive.

Or you can contact agencies such as the Environmental Protection Agency and the APVMA.

Probably your best bet is the world-wide-web. Quite a lot of information is readily accessible on various toxicology websites. However, be warned that not all of the information on the web is scientifically based and can make unsubstantiated claims.

In Australia:

Regulatory and governmental sites:

- National Industrial Chemicals Notification and Assessment Scheme (NICNAS): www.nicnas.gov.au/australia/NRA.html
- The National River Contaminants Program: www.rivers.gov.au
- The Environmental Protection Agency:
  - NSW: www.epa.nsw.gov.au
  - NSW EPA | What are pesticides? www.epa.nsw.gov.au/envirom/pestwhtr.htm
  - SA: www.environment.sa.gov.au/epa/epa/
- Australian Pesticides & Veterinary Medicines Authority: www.apvma.gov.au

Department of Environment & Heritage:

- Department of Environment and Heritage: www.deh.gov.au
- Inland Waters: www.deh.gov.au/water/
- National Pollutant Inventory: www.npi.gov.au *(this site has thorough reviews, but only includes a limited number of pollutants)*
- Australian Water Resources Assessment 2000: audit.deh.gov.au/ANRA/water/docs/national/Water_Contents.html
- Waterwatch : www.waterwatch.org.au/
  - ACT: www.act.waterwatch.org.au/
  - Vic: www.vic.waterwatch.org.au/
  - QLD: www.qld.waterwatch.org.au/
  - Tas: www.tased.edu.au/tasonline/dorsetww/
  - NT: www.lpe.nt.gov.au/waterwatch/
  - WA: www.wrc.wa.gov.au/ribbons/index.html
- Sydney Water: www.sydneywater.com.au
- Land & Water Australia: www.lwa.gov.au
- Australasian Society for Ecotoxicology: www.ecotox.org.au
- Food Standards Australia New Zealand: www.foodstandards.gov.au/aboutus/

Other:

- Streamwatch: www.streamwatch.org.au/main.jsp
- Cooperative Research Centre for Water Quality and Treatment: www.waterquality.crc.org.au/

International sites:

- Swedish EPA: www.internat.naturvardsverket.se/index.php3
- WWF Canada. Reducing your risk to pesticides: www.wwf.ca/satellite/reduce-risk/index.html
- Agency for Toxic Substances and Disease Registry: www.atsdr.cdc.gov/atsdrhome.html *(Agency of the U.S. Department of Health and Human Services - it provides information on substances and priority lists of the most hazardous ones and includes some very thorough reviews)*
- US EPA: www.epa.gov
- US EPA Office of Pesticide Programs: www.epa.gov/pesticides/ *(Highly recommended site).*
- US EPA Office of Pollution Prevention & Toxics: www.epa.gov/opptintr/index.html
- California Department of Pesticide Regulation: www.cdpr.ca.gov

- United States Department of Agriculture: www.usda.gov/
- Pesticide databases: www.cipm.ncsu.edu/index.html
- The EXtension TOXicology NETwork EXTOXNET: ace.orst.edu/info/extoxnet/ *(Highly recommended site for specific pesticide information - easy to use)*

Environmental, lifestyle and personal sites:

- Burke's Backyard, chemical disposal: www.burkesbackyard.com.au/2002/archives/2002/conservation_&_the_environment/chemical_disposal
- www.rfu.org/AboutPulp.htm *(about the pulp and paper industry)*
- Environmental Media Services: www.ems.org/household_cleaners/information.html *(some great info on alternative cleaners and links to other sites)*
- Reach For Unbleached! - Consumer education about paper and pulp mill monitoring www.rfu.org/index.htm
- WWF: www.wwf.org.au

So what can you do?

Since easy answers are not at our fingertips, we need to employ some basic common sense. Sometimes a non-chemical method of cleaning or pest control is as effective as a chemical alternative. Sometimes we can minimize the chemicals we perhaps need to use, and any reduction is a step in the right direction for our frogs.

My common-sense ideas would be these:

✓ First, don't use chemicals gratuitously. Be reasonable. Ask yourself if your lawn has to be completely free of weeds, can you choose hardier plants, do you need to bleach the bathroom every week, and so on. If its not really necessary, then don't use it.

✓ Use compost in preference to a commercial fertiliser. If you don't want to compost, at least try more natural alternatives such as manure, seaweed, and fish emulsion fertilisers. The timing and placement of fertilisers can minimise off-site losses through runoff. Placement within the soil is preferable to surface application.

✓ Take advantage of web-based sites and material to check the products you think you will be using often. You may have a choice between a few different products – these sites might help you decide which would be the least damaging.

✓ If you need it for a specific purpose or pest, try to use products with very narrow modes of action rather than broad spectrum ones that have across-the-board effects. For example, a number of insecticides are insect growth regulators, and interfere with specific moulting processes. One example is precor, a flea control liquid. These narrow mode products are less likely to have an impact on vertebrates.

✓ Consider where you are using the product. When it rains will it just wash off into the nearest pond, catchment or drain? What happens then? Can you prevent this runoff?

✓ It's often easier to exclude pests than to control them. You can often prevent cockroaches and household insect pests by removing food scraps and storing food in sealed containers. Block off indoor pest hiding places. Use sticky traps. Remove standing water, such as under indoor plants, and fix leaky pipes, because even pests need water.

✓ Most importantly, always read the label and use according to instructions. Its important to not only read the label before buying the product, but also to read the label every time you want to mix or use the product, and before storing or disposing of it. Many contamination events are because formulations have been used incorrectly: Sometimes people simply don't read the label; or they have used the product for years, without checking to see if the formulation has changed; or people use products just before it rains, so the product washes straight off into the nearest waterway. Formulations for high volume rates might be used with low volume equipment, concentrating it; or people may add just a little more to make sure. I'm sure we have all done this in cooking! When it comes to being frog-friendly, though, its not worth the risk.

✓ If the chemical treatment didn't work, do not assume that using more pesticide than the label recommends will do a better job. It won't. You will need to find an alternative.

What can you do with leftover hazardous household products or pesticides?

DO:

- ✓ Try to use up all of the product.
- ✓ If you simply can't use it anymore, then give useable, leftover products to friends or neighbours.
- ✓ Take unwanted products and potentially dangerous waste to a household hazardous waste disposal program (see below).

Sydney Water runs a tremendous household chemical collection program, where you can drop off most types of chemicals, paints and the like. Phone 1800 814 719.

- National Chemical Collection initiative within Australia
  Phone 1800 008 182
  www.chemclear.com.au
- EcoRecycle Victoria (03) 9639 3322 or Infoline: 1800 353233 (within Victoria).
  www.ecorecycle.vic.gov.au
- DrumMuster (national program for the collection and recycling of empty, cleaned, non-returnable farm chemical containers).
  Phone: (02) 62306712.
  www.drummuster.com.au

DON'T pour leftover products or pesticides:

- ✓ Down storm drains or into creeks, because storm drains often send water directly to our creeks or the ocean without treatment. Toxins can poison fish, plants and tadpoles, and can even end up in drinking water supplies.
- ✓ Down your sink or toilet, because many chemicals may pass through the treatment plant untreated, and poison waterways. They may even interfere with the operation of wastewater treatment systems.
- ✓ On the ground, because they may seep into groundwater or be washed down storm drains.
- ✓ Into your garbage bin, because they could seep into our groundwater from the landfill. However, water-based paints could be left to dry out and then placed in the garbage bin.
- ✓ Lastly, don't burn them, because they often also release toxic fumes when they burn.

Some alternative suggestions (however, I have not personally tested all of them):

- ✓ Degreasers: Use citrus-based or water-based detergents. Avoid products with methylene chloride.
- ✓ Detergents: Avoid products with phosphates. Try laundry soaps. AVOID chlorine bleaches. If you need bleach, use a hydrogen-peroxide based one.
- ✓ Surface cleaners: Try lemon juice and vinegar to cut grease. Borax can be used to soften water in order to prevent soapy deposits. Try to use vegetable oil based soaps.
- ✓ Drain openers: Using a sink strainer eliminates most problems. Pour boiling water down drains once a week to eliminate grease. If a drain is partially clogged, try putting in some baking soda with 1/2 a cup of vinegar, and seal the drain. This produces carbon dioxide bubbles which may dislodge the obstruction. Uncover and follow with boiling water.
- ✓ Oven cleaner: Try a baking soda, salt and water paste.
- ✓ Mildew: Scrub with a mix of borax and water on a scouring sponge. Full strength vinegar is more powerful, but don't forget to rinse. Again, avoid chlorine based mold killers.
- ✓ Toilet: Clean often with baking soda. Let a cup of borax stand in the bowl overnight for a more serious clean.
- ✓ Furniture polish: Use almond, walnut, olive, or linseed oil.
- ✓ Wash your car on the lawn if possible, so that the soap doesn't run into the storm water drains.
- ✓ Fleas: Obviously the first step is to vacuum regularly and washing pet bedding often. Empty the vacuum cleaner bag every time and seal in a bag in the garbage. Steam cleaning carpet may also kill adult and juvenile fleas. Try using an insect growth regulator to prevent larvae from maturing. Pyrethrins are considered the least harmful of the adult flea pesticides, but be careful that the pyrethrin isn't mixed with other more toxic ingredients. Wash pets with a citrus oil shampoo and use a flea comb. Sometimes herbal flea collars with ingredients such as eucalyptus, citronella and cedarwood can work well.
- ✓ Mosquitoes: Screens on windows and doors are the biggest help. Remove standing water near the house. Frogs and spiders are great insect predators so encourage them to hang around! If you must use a repellent, try citronella ones. And avoid wearing strong-smelling products (which seem to attract mosquitoes).

To be frog-friendly, we all need to consider our choices and their potential for harm.