OFF-SITE AQUATIC IMPACTS FROM LAND CONTAMINATED BY HISTORICAL PESTICIDE USE

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1 INTRODUCTION

Historical use of pesticides may continue to pose a risk to off-site aquatic ecosystems long after their use has stopped. Persistent pesticides such as copper and DDT build up in soils and can be transported by runoff into streams and estuaries, where they can accumulate in sediments. Aquatic life could be adversely affected if pesticides accumulate to high enough levels. The studies outlined in this paper aim to improve our understanding of the risks to stream aquatic life associated with off-site transport of pesticides from horticultural soils.

Our studies were undertaken in two parts:

1. An initial desk-top assessment of the potential off-site impacts of horticultural pesticides in streams and estuaries in the Auckland region was undertaken to estimate the risk that the key historically-used pesticides copper (Cu), lead (Pb), arsenic (As), and organochlorine pesticides (e.g. DDTs, dieldrin) posed to streams draining horticultural land, and

2. The concentrations of these pesticides in a small stream system receiving runoff from an area with a long history of horticulture and viticulture were measured to check that the predicted potential impacts really would occur.

2 METHODS

2.1 Assessing risks to aquatic life

The potential adverse effects to aquatic life due to pesticide contamination were assessed by comparing predicted and measured concentrations with environmental guidelines (ANZECC 2000, MacDonald et al. 2000). The pesticides of key concern (e.g. organochlorines) are of low water solubility, and accumulate in soils and aquatic sediments. The primary tool for assessing aquatic ecosystem risks is therefore sediment quality guidelines (SQGs).

Sediment quality guidelines provide two values, each reflecting different levels of risk to aquatic biota. The lower values, termed “threshold effects concentration” (TEC) or “Interim Sediment Quality Guideline-Low” (ISQG-low), indicate a concentration below which contaminants should have little adverse effects. The higher values, termed “probable effects concentration” (PEC) or “Interim Sediment Quality Guideline-High” (ISQG-high), represent concentrations above which adverse effects should frequently occur. Between the two values lies an area where effects may occur and should increase in frequency or severity with increasing concentration.

It must be noted that these guidelines are just that – they provide an indication of potential risk to aquatic life (based on overseas studies), and signal the need for further studies aimed at determining whether, or not, adverse effects are really occurring in the system under investigation. In the absence of NZ ecotoxicology data, these guidelines represent the most appropriate method for initial risk assessment.
A key point about the SQGs for protecting aquatic life is that they are lower than soil quality guidelines (or “soil acceptance trigger levels”; ARC/ADHB 2001, ARC 2002) aimed at protecting human health. Therefore, a site may have soils that are acceptable for various human uses (e.g. residential development), but if transported off-site into streams, the soils could cause adverse in-stream effects. This difference is greatest for organochlorines, where guidelines for aquatic life are more than a hundred-fold lower than for human uses. Relevant guidelines are summarized in Table 1, which indicates that organochlorines represent a significant risk factor to aquatic life because of their low guideline values (indicating aquatic organisms are very sensitive to these contaminants).

**Table 1.** Soil acceptance guidelines for protection of human health (ARC/ADHB 2001, ARC 2002) and freshwater sediment quality guidelines for the protection of aquatic life (ANZECC 2000; MacDonald et al. 2000)

<table>
<thead>
<tr>
<th>Pesticide (units)</th>
<th>Freshwater sediment quality guidelines</th>
<th>Soil Acceptance Trigger Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (mg/kg)</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>Copper (mg/kg)</td>
<td>65</td>
<td>270</td>
</tr>
<tr>
<td>Lead (mg/kg)</td>
<td>50</td>
<td>220</td>
</tr>
<tr>
<td>DDT, total (µg/kg)</td>
<td>1.6</td>
<td>46</td>
</tr>
<tr>
<td>Dieldrin (µg/kg)</td>
<td>0.02</td>
<td>8</td>
</tr>
</tbody>
</table>

Notes:

a. ISQG = Interim Sediment Quality Guideline. ANZECC (2000) ISQG-low values are the “trigger values” that prompt further investigations; TEC = Threshold Effect Concentration, PEC = Probable Effect Concentration (MacDonald et al. 2000).

b. ANZECC (2000) guidelines for organics (e.g. organochlorines) are for sediment with 1% organic carbon.

### 2.2 Modelling

We used a simple predictive model to estimate whether contaminated soil runoff is likely to impact on stream sediments under various land-use scenarios. This model can be represented schematically as:
In the model, we add the appropriate amount of suspended sediment and contaminant from each land use, according to the scenario conditions, and mix them together.

The calculation can be represented by:

\[
\begin{align*}
\text{Horticulture Contaminant mass (mg)} &+ \text{Pasture Contaminant mass (mg)} &+ \text{Earthworks ex-pasture Contaminant mass (mg)} &+ \text{Earthworks ex-horticulture Contaminant mass (mg)} \\
\text{DIVIDED BY} &+ &+ &+
\text{Horticulture SS mass (kg)} &+ \text{Pasture SS mass (kg)} &+ \text{Earthworks ex-pasture SS mass (kg)} &+ \text{Earthworks ex-horticulture SS mass (kg)}
\end{align*}
\]

\[= \frac{[\text{Contaminant}]}{(\text{mg/kg or parts per million})}\]

Using this model, we explored the area of horticulture in a catchment that would be needed to exceed relevant in-stream SQGs.

2.3 Pesticide survey

The area we chose to check the modeling predictions is located in north-west Auckland, and has a long history of horticulture and viticulture, dating back to the early 1920s. Pesticide levels in the soils of the properties had been assessed previously, and found to be elevated above soil acceptance trigger levels in many areas. Copper, Pb, DDT, and dieldrin were all found above trigger levels in some locations, with Cu and DDT having the most frequent and widespread exceedances.

We used the data provided by these earlier assessments to locate sampling sites aimed at determining how much soil-bound pesticide was moving off the land, and how it was accumulating in the receiving streams and wetlands.

The area is physically quite complex, with 4–5 small headwater streams emerging from small, fairly steep, upper catchments. Old orchards are sited at the head of some of the sub-catchments, while extensive plots of vineyards and orchards fill some of the lower areas. Much of one stream catchment is now pastoral land. Because of this complexity, we chose to sample in several places using techniques aimed at obtaining samples of recently mobilized or deposited soils and sediments.

The areas we chose to sample were:

- Vineyard runoff soils: These were taken from the bottom of two blocks in areas where fine sediments running off the lots would have accumulated before being transported into the stream and wetland.
• Vineyard wetland sediments: These were taken from a wetland surrounded by vineyards. The sediment built up in this wetland reflects accumulated inputs of soils lost from the adjacent vineyards.

• Hill slope soils: These were taken on a pastoral hillside below an old orchard, to assess the movement of pesticides down slope into the stream below.

• Streamside floodplains: These were soils/sediments from depositional areas beside the stream where sediment carried by the stream would be deposited following storm flows.

• Stream bed sediments: We targeted pool areas where fine sediments transported from the headwaters were most likely to accumulate.

In such small headwater streams it is very difficult to differentiate stream sediments that have been transported by the stream from the soil that forms the banks and bed of the stream. The latter material may be old soils deposited in pre-European times and be recently exposed by stream erosion, i.e., the top soils in banks and the bed are playing the role of bedrock in larger streams. Therefore, we took samples where fine sediments transported by the stream accumulated, both in and beside the stream. Fine sediment deposits occurred in the stream as loose sediments in pools where flows were restricted by vegetation. We also sampled obvious depositional areas beside the stream where sediment carried by the stream would be deposited following storm flows. These included stream wetlands, and also “streamside deposition zones” (small floodplains adjacent to the stream channel).

Soil samples were composites made up from >10 sub-samples of surface soil (top 2–3 cm) taken from each area, the aim being to obtain a robust average measure from each sampling site. Stream sediments were composites of several surficial samples taken from 2–5 m reaches at each site.

Five water samples were also taken. Four of these were visually clear, with only very small amounts of suspended flocculated solids, and these were analysed for total Cu only. One site, from a headwater wetland, was rich in orange Fe-floc, indicating oxidation of Fe-rich, anaerobic, shallow ground water on emergence from the hillside. This was analysed for iron (Fe), arsenic (As), Pb, and Cu.

Samples of surficial sediments from two stormwater ponds from adjacent urbanising catchments were also taken to obtain additional information of the likely impacts of urban development. One was developed from historical orchard land, while the other was developed from pastureland.

Samples were analysed by R.J. Hill laboratories (Hamilton). A full suite of organochlorine pesticides1 were analysed in the soils and sediments, but only DDTs and dieldrin were found above detection limits (0.5 μg/kg, ppb). Copper and Pb were measured in the soils and sediments as “total recoverable” extracts (strong acid digestion of the whole soil or sediment sample after drying and 2 mm sieving).

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1 Organochlorines analysed were: DDE, DDD, and DDT (o,p’- and p,p’- isomers); dieldrin, aldrin, endrin, endrin aldehyde, hexachlorobenzene; α-, β-, and γ-HCH; heptachlor, heptachlor epoxide; endosulfan I & II; endosulfan sulphate, cis- & trans-chlordane, and methoxychlor.
3 RESULTS

3.1 Predicting off-site effects from simple modelling

Preliminary assessments using the modeling approach outlined in section 2.2 found that for Cu there needs to be a substantial proportion of the catchment in horticulture for stream sediments to exceed the SQG – approximately 40%. This is because the SQG of 31.6 mg/kg (TEC) is only about half the average concentration of ~75 mg/kg typically found in horticultural soils (ARC 2002). This was qualitatively borne out by the concentrations measured in the stream system, which were lower than the SQG (typically <20 mg/kg Cu).

For DDT and dieldrin, SQG are much lower than the concentrations found in horticultural soils, and therefore only a small proportion of the catchment needs to be in horticulture before SQGs are predicted to be exceeded. The freshwater SQG (TEC) is 5.3 µg/kg for total DDT and 1.9 µg/kg for dieldrin, whereas average Auckland horticultural soil concentrations are 1060 µg/kg and ~100 µg/kg respectively (ARC 2002). The proportion of catchment needed to be in horticulture to exceed SQGs is predicted to be less than 1%.

The levels of DDT encountered in the horticultural stream system we studied qualitatively confirm this prediction, with soil and sediment concentrations of total DDT ranging from 40–238 µg/kg for the branch with the highest proportion of horticultural land, to 43–83 µg/kg further downstream where the proportion of horticultural land is lower. These concentrations are all well above threshold effect SQGs.

There was insufficient data for source concentrations of dieldrin in the area we studied to provide reliable links with our off-site stream data. The concentrations of dieldrin in the stream and wetland sediments were variable, but were generally near to, or below, SQGs in the stream system, and were above SQGs in the vineyard system.

The simple model described in section 2.2 provided a way of predicting which pesticides would be of greatest concern for off-site impacts. The qualitative predictions were tested (and as described in the following sections, confirmed) in the field study.

3.2 Contamination levels compared with in-stream guidelines

The field study of the small headwater streams showed the following key results:

1. Copper levels were only elevated above SQGs in vineyard soils and headwater wetlands. A small amount (approximately 2–4 times) of dilution with uncontaminated stream sediment would be sufficient to bring concentrations to below threshold effect levels. It seems, therefore, that Cu poses relatively little risk to in-stream aquatic communities.

2. Copper levels in stream waters were low, except in the highly contaminated wetland containing high amounts of flocculated iron, and (to a lesser degree) in the vineyard wetland. In both these sites, Cu levels in the sediments were high. The data indicate that widespread adverse effects due to Cu in the water column are unlikely to occur.

3. Lead levels were below SQGs in all samples except in the contaminated headwater wetland draining the historical orchard. Lead does not therefore appear to be a significant risk factor for these streams.

4. DDT levels were elevated in most samples, in particular in the surface runoff soils, vineyard wetland sediments, and wetland(s). Concentrations of DDT in the soils and
floodplain sediments were high enough to cause adverse effects on aquatic life, requiring substantial in-stream dilution by clean sediment to bring concentrations below SQGs. Streambed sediments had DDT levels above threshold effects levels, but below probable effects levels (after accounting for effects of organic carbon). Concentrations of DDT in the streamside deposition zone soils (median = 75 µg/kg) were similar to those in the streambed sediments (median = 61 µg/kg), suggesting that in-stream dilution may not be effective at reducing DDT.

Dilution factors required to bring Cu and DDT levels to threshold effects levels (TEC) are summarised in Table 2.

Table 2. Dilution required to bring average concentrations of Cu and DDT from various sources to threshold effects levels (TEC; Cu = 31.6 mg/kg, Total DDT = 5.28 µg/kg)

<table>
<thead>
<tr>
<th>Source</th>
<th>Cu</th>
<th>DDT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Dilution</td>
</tr>
<tr>
<td></td>
<td>(mg/kg)</td>
<td>required</td>
</tr>
<tr>
<td>Hill slope soils</td>
<td>14.4</td>
<td>0.46</td>
</tr>
<tr>
<td>Vineyard soils</td>
<td>121</td>
<td>3.8</td>
</tr>
<tr>
<td>Vineyard wetland sediments</td>
<td>91</td>
<td>2.9</td>
</tr>
<tr>
<td>Streamside floodplain soils</td>
<td>14.0</td>
<td>0.44</td>
</tr>
<tr>
<td>Stormwater pond sediments</td>
<td>24.0</td>
<td>0.76</td>
</tr>
</tbody>
</table>

The average concentrations of Cu, Pb, and total DDT found in the various environments examined in this study are summarised in Figure 1. Based on comparisons with SQGs, the study has confirmed that DDT represents the greatest threat to in-stream aquatic life. DDT-contaminated soils are finding their way into the streams at concentrations that may have adverse effects (note that probable effects SQGs are plotted in Figure 1 for DDT, while for Cu and Pb the SQGs are the much lower threshold effects levels).

3.3 Longitudinal variations in contaminant concentrations

3.3.1 Vineyard system

The vineyard stream is very short. It emerges from an underground culvert, intercepts several shallow drains from the vineyard and then flows directly into a large wetland, which it traverses via a shallow incised low flow channel, before discharging through a culvert to a local stream. Small increases in flow would result in the stream overflowing its bank and flooding across the wetland, which would act as a good settling and filtering basin.

Concentrations of Cu in vineyard soils, runoff soils, and vineyard wetland sediments were similar (Figure 2), suggesting that Cu is fairly mobile.

In contrast, DDT concentrations dropped off between the vineyard soils and the receiving wetland (Figure 2), possibly indicating that degradation is occurring. This is supported by changes in the DDT composition between vineyard soils, runoff soils, and the wetland (Figure 3).
Copper levels in soils and sediments

Lead levels in soils and sediments

Total DDT levels in soils and sediments

Note: threshold effects levels are too low to show on this plot
(TEC = 5.28 µg/kg, ISQG-low = 1.6 µg/kg)

Figure 1. Average (± S.E.) levels of Cu, Pb and DDT in soils and sediments
Figure 2. Average concentrations of copper and total DDT in vineyard soils, runoff soils (i.e. surface soils sampled in this study from runoff deposition areas), and the vineyard wetland. Error bars are ± SE in mean (n=3 for vineyard and wetland soils, n=2 for runoff soils).

Total DDT in the vineyard soils was dominated by DDE and DDT, with little DDD. Composition was highly variable. The runoff soils had relatively less DDT, and more DDD than the parent vineyard soil. This suggests some anaerobic transformation is occurring, either during transport or (more likely) after deposition in the settling areas we sampled. This trend appears to continue in the wetland, where DDD is present in even greater proportions.

Figure 3. Changes in the composition of total DDT in vineyard soils, runoff soils (i.e. surface soils sampled in this study from runoff deposition areas), and the vineyard wetland. Error bars are ±SE in mean (n=3 for vineyard and wetland soils, n=2 for runoff soils).
### 3.3.2 Orchard stream system

The “orchard stream” system is a more typical headwater stream system. Land use is dominantly pasture, with land in the headwaters being orchards or vineyards at present or in the past. However, there are vineyards in the lower catchment as well. Longitudinal changes in pesticide concentrations are summarised in Figures 5a & b.

The left branch has a major contaminant source at the head of the catchment, as reflected by the high level of contamination in the top wetland (site W1 in Figure 5). Concentrations of Cu in the wetland were similar to those in the nearby orchard soils (site LO). Levels of Pb and, more particularly, DDT, were higher in the wetland than in the source soils. This suggests localized, high level contamination in the vicinity of the wetland or transport and accumulation of historically high residues into the wetland, where they have accumulated and remained. Concentrations were lower (and fairly similar) in the rest of the stream system, with no clear longitudinal trends.

Copper concentrations in the water column of the left branch were elevated in the top wetland (where soil contamination was also very high), but levels dropped rapidly with distance downstream (Figure 4). Heavy metals originating from the contaminated wetland are probably bound to iron oxides, and these are removed from the water column by flocculation, adsorption to plants and sediments, and sedimentation.

![Total Copper in Orchard Stream Waters](image)

**Figure 4** Longitudinal trends in total Cu concentrations in the Orchard Stream waters.

In the stream’s right branch, Cu and DDT concentrations were markedly lower in the hill slope and floodplain soils than in the orchard soils (Figure 5). Concentrations of Cu on the hill slope were approximately one-tenth those present in the orchards, while DDT levels were only 1/100th of the orchard soil concentrations. Clearly there is little off-site movement of these contaminants from the orchards to the hill slope sampled, particularly for DDT.
Orchard stream system: Soil and sediment Copper

Orchard stream system: Soil and sediment Lead

Figure 5a  Longitudinal trends in copper and lead concentrations in soils and sediments in the Orchard Stream system.
Figure 5b  Longitudinal trends in total DDT concentrations in soils and sediments in the Orchard Stream system.
3.4 Contaminant transport mechanisms

This study sampled a range of headwater aquatic environments to establish the scale of off-site pesticide impacts and to suggest what transport mechanisms were operating. The results showed that soil-bound pesticides can be washed off directly into streams and wetlands. By contrasting the findings for the different study areas, we can make some observations on likely transport processes.

In the vineyard stream, wetland soil concentrations of Cu were similar to those found in the vineyard soils. Simple wash-off of fine top-soils is the most likely explanation. In the normal course of operation of the vineyard, there are bare soil tracks, wheel damage, occasional earth-disturbing operations (such as discing and replanting) so there is plenty of opportunity for surface runoff to deliver soils to the drains and stream leading to the wetland. DDT concentrations dropped off between the vineyard soils and the wetland, possibly indicating attenuation and degradation. This explanation is supported by changes in the DDT composition between vineyard soils, runoff soils, and the wetland.

While there was evidence for considerable mobility of pesticides into the watercourses in the vineyard, such high mobility is not necessarily found in all runoff situations. The pasture hillslopes below the orchards were not highly contaminated, although it seemed from the topography and soil wetness, that upslope runoff was reaching these soils, probably as both surface and subsurface runoff. Contrasting this to the vineyard stream leads to the conclusion that soils disturbance is an important vector in pesticide mobility.

Once in the stream system, pesticides seem to be readily transported downstream, as evident in the orchard stream system. There is, however, also evidence for removal of Cu from the water column in the stream system, probably by processes such flocculation, sorption, and sedimentation of iron-oxide bound metal.

4 CONCLUSIONS

Our studies of pesticides in Auckland have so far shown that:

- Soil-bound pesticides from horticultural/viticultural land are being washed into streams and wetlands at environmentally significant levels.

- Organochlorines, mainly DDT, are the pesticides most likely to cause adverse effects of aquatic biota in streams. This is because SQGs for organochlorines are much lower than the concentrations of these pesticides in horticultural soils.

- Copper and lead are unlikely to cause widespread adverse impacts. This is because typical soil concentrations are not much higher than SQGs.

The studies indicate that DDT may pose a real threat to small headwater stream ecosystems in horticultural areas. Management of DDT-contaminated soils may therefore be required to minimise the off-site impacts in some situations. Further work is required to improve our understanding of when these impacts will occur. To do this, models that would provide reliable quantitative predictions of pesticide concentrations in streams in a variety of catchment settings are required. Because our current ability to predict adverse effects is based largely upon international SQGs, it is important that we obtain a better understanding of the reliability of these measures, especially for organochlorines. Robust methods to test whether the adverse effects predicted from our studies are really occurring in NZ’s streams are therefore needed.
REFERENCES


