

# DEPLETION OF COPPER-BASED PRESERVATIVES FROM PINE DECKING AND IMPACTS ON SOIL-DWELLING INVERTEBRATES

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## ABSTRACT

*Radiata pine decking was treated with CCA or Copper Azole wood preservative to Australian Standard H3 retention using conventional and modified Bethel schedules, and air-dried. Treated and durable hardwood (kwila) control decking boards were subjected to natural leaching in weather-exposed decks in Brisbane, Queensland. Analysis of collected deck runoff water revealed losses up to 700mg Cu, 175mg Cr, 600mg As, 750mg B, 10 mg tebuconazole or 18000 mg tannin per square meter of deck after 10 months, but flux rates had not yet reached zero for any component.*

*Deck runoff water was applied to three soils using an OECD soil leaching column procedure. Although boron was more mobile than others, components tended to be retained in the topmost (first contacted) layer. Deck runoff water was also applied to mown lawn soil. Soil samples were collected before and twice after the first application, and three times after the second. Soil arthropods were dominated by mites (84%), which were identified to family level. No differences in total mite densities were detected between the treatments, except for a significant increase associated with the kwila deck runoff water. However, there were detectable differences in mite community structure between all treatments, indicating differential effects of the treatments on the soil arthropod community.*

Keywords: natural leaching, copper-based preservatives, decks, soil mobility, soil microarthropods

## INTRODUCTION

Laboratory tests have been developed to estimate depletion of wood preservative components in service, and many 'standard' tests exist. These tests have been useful for relative comparisons of preservative formulations, but until recently, little absolute data had been published on natural depletion rates in service [1]. One study [2, 3] compared the loss of boron, copper, chromium and arsenic from timber treated with several wood preservatives, including a CCA and an ACQ preservative during 6 months outdoor exposure to urban rain. Natural depletion rates varied inversely with specimen size, and decreased with end-sealing - results quite predictable from the varying ratio of exposed surface area to volume. But as full-dimensioned material was not exposed, the study did not generate absolute depletion data.

This paper reports absolute depletion (flux) rates of two copper-based wood preservatives from above-ground decks exposed to the weather. Results of accelerated laboratory leaching tests on matched material are reported elsewhere [4]. Because of the impracticality of collecting and containing the runoff from a complete deck in such a manner as to avoid loss or enhancement of preservative components, it was necessary to reduce the deck size considerably, but this was done without compromises in realism. Although the deck boards were cut to a short length, most board ends were sealed to leave only one unsealed end per 1.2 m of deck board. This simulated an average deck board length of 2.4 m, for a realistic average number of cut ends per square metre of deck.

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To assist in interpreting the environmental significance of leached preservative components in the deck runoff water, we also conducted a series of soil mobility studies using the draft OECD soil leaching column protocol [5]. But while flux rate and water and soil concentration data may be useful, their environmental significance needs to be interpreted. What are the impacts of wood preservative or natural hardwood extractive contaminated deck runoff water on soil biota? For an initial study, we monitored the effect on soil and litter non-target microarthropods, especially mites (Acarina), because they are numerically predominant in soils and are important components of below-ground food webs of soils in temperate forest ecosystems. A detailed justification of this choice may be found elsewhere [6].

## MATERIALS AND METHODS

### Preparation Of Treated Specimens

End-sealed seasoned sapwood radiata pine (*Pinus radiata*) decking boards 450 x 90 x 22 mm, with mean air-dry density 488 kg/m<sup>3</sup>, reeded one side, were treated with two preservatives; Tanalith<sup>®</sup> O (Oxide type C CCA wood preservative: Cu 86g/kg, Cr 147.9 g/kg, As 132.7 g/kg) or Tanalith<sup>®</sup> E (Copper-Azole wood preservative: Cu 166 g/L, boric acid 64 g/L, tebuconazole 6.4 g/L). The treatments were performed in a laboratory impregnation plant using conventional vacuum-pressure techniques and typical Australian commercial schedules, without accelerated fixation. Two processes were used for each preservative - a full-cell (Bethel) process achieving 600 L/m<sup>3</sup> and a modified Bethel process achieving 250 L/m<sup>3</sup>. Concentrations of preservative in the treatment fluid were adjusted so that both processes achieved the Australian/New Zealand Standard H3 (above ground) retention in the cross-section, ie 0.38% m/m Cu+Cr+As or 0.27% m/m Cu+tebuconazole. The boards from each treatment, still end-sealed, were immediately wrapped in polythene sheeting and stored under mid-summer ambient conditions (mean daily max. 30°C, mean daily min. 21°C) for one week. After unwrapping they were strip-stacked to air dry under similar conditions until reaching equilibrium moisture content (approximately four to six weeks). 75 mm was removed from each end of each board, and from these pieces were cut cross-sections for chemical analysis. Boards for use in the test decks were selected from the remaining 300 mm lengths closest to the required preservative retention, and end-sealed as required to leave 8.8 unsealed ends per square metre of deck.

### Construction of, and Sampling of Water from, Decks

Decks were constructed and designated CF, CR (CCA: Bethel and modified Bethel respectively) EF, ER (Copper Azole: Bethel and modified Bethel respectively), K and X. The K decks were constructed from untreated heartwood of the naturally-durable hardwood kwila (*Intsia bijuga*) in the same dimensions, as preservative-free controls. The X decks were unpopulated by boards, to act as control rainwater collectors. Decks consisted of four 300 mm boards, parallel and 5 mm apart, attached to two stainless steel angle supports running perpendicular to the board direction.



Attachment was by a single stainless steel screw through the support into the under (reeded) side of the board at each board-support junction (8 per deck). Each deck was suspended within a stainless steel runoff director device so that there was a gap of 3-5 mm between the deck boards and the inside walls of the device, and the top surface of the deck boards was 15 mm below the upper rim of the director. A large glass storage bottle positioned below the director contained the runoff water until it was collected after each rain event. The 'X deck' (runoff director without deck boards) accumulated a corresponding volume of 'pure' rainwater. The use of only stainless steel and glass in the deck supports, runoff director and containment system ensured that the runoff water was not contaminated with compounds that could interfere with or erroneously enhance the chemical analysis. Decks were first exposed to the weather

three months after the treated deck boards reached equilibrium moisture content. Exposure took place in a clean urban location in Brisbane, Australia (27.50 S, 153.03 E), for 300 days.

After each rain event all runoff water was collected, volume recorded, a sample taken in a glass container for analysis and a further portion (a constant 11% of the total amount collected) frozen in a stainless steel container for later use in soil column studies. After small rain events (< 2 mm) that did not produce sufficient water for analysis the analytical sample was reserved and pooled with the sample from the following event. Analyses were conducted for total Cu, Cr and As (CCA decks), Cu, B and tebuconazole (copper azole decks) and tannin (kwila deck). Analysis for Cu and Cr used atomic absorption spectrophotometry (AAS), As was determined by inductively-coupled plasma atomic emission spectrometry (ICP\_AES), B by ICP\_AES or colorimetry using azomethine-H reagent, tebuconazole by gas chromatography with nitrogen-phosphorus detector after extraction onto a C18 solid phase extraction (SPE) cartridge, and tannin by UV-visible spectrophotometry using Folin-Denis reagent. No attempt was made to distinguish between valence states of metals.

### Soil leaching column studies

The OECD procedure [5] was followed, except that we were evaluating the soil mobility of preservative components already dissolved in deck runoff water, rather than the individual compounds for which the method was written. This necessitated minor changes to the methodology, but the principle of the OECD test was strictly observed. Three soils were selected to give the required spread of properties, which are given in Table 1

**Table 1:** Properties of soil used in leaching columns

Soil property	Units	Soil			
		S1	S2	S3	
CEC	meq/100g	5	27.1	21.5	
Organic C	%	1.7	4	3.3	
pH	units	5.1	5.1	5.9	
Clay	%	10	20	23	
Silt	%	14	47	32	
Sand	%	76	33	45	
Sand fractions:	Coarse	38	6	14	
	Fine	38	27	31	
Exchangable cations:					
	Ca	mg/kg	198	104	616
	Mg	mg/kg	75.5	234	470
	Na	mg/kg	22.6	34	137
	K	mg/kg	10	120	90
	Cu	mg/kg	<1	1.7	1.4

Runoff water composites for each deck were prepared by blending a constant proportion of each of the water samples collected from that deck at the first 14 rain events (during the first 10 weeks of exposure). The total amount of rainfall in these 14 events was 123 mm. Runoff from later events, which generally contained less of each component, was not included in these composites, as the 1300 mL minimum volume required for the soil column experiments had been reached. It was recognised that the amount of deck runoff resulting from a rain event varied from deck to deck, because of variations in the amount of water retained by or deflected from the deck – the ‘hold-up’ factor. A very light shower which produced a measurable sample below the unpopulated deck could be completely absorbed by the boards in another deck, and differences in absorption between timber species and treatments resulted in variations in the amount of runoff. This variation was reflected proportionately in the volumes of runoff water applied to the soil columns.

Soils were packed into 40 mm i.d. glass columns, saturated with deionised water, and allowed to drain under gravity. Portions of composite were added dropwise to soil columns over a period of

48 hours, using a multi-channel peristaltic pump. For the control columns (to which was added composite from the unpopulated deck), 154 mL of composite was added, corresponding to 123 mm of rainfall on the surface area of the soil. The volume of composite added to other columns was reduced in proportion to the hold-up factor for the relevant deck. An additional equal volume of deionised water was then added to the column at the same rate. Column effluent solution was collected on four occasions – after 50% and 100% of the leachate composite had been added (CE1 and CE2), and after 50% and 100% of the additional deionised water had been added (CE3 and CE4). The soil in the column was removed and sectioned into five equal layers, coded (from topmost to lowest layer) as SL1 to SL5. Each column effluent sample and each soil layer sample was analysed for the preservative components of the relevant deck.

## Microarthropod study

### Site

The experiment was conducted in an area of mown lawn within the Queensland Government Science campus at Indooroopilly (in Brisbane, which has an annual average rainfall of 1158 mm with a summer maximum). There was a sparse cover of *Eucalyptus propinqua* and other native Australian trees over an even sward of lawn grasses. Soil characteristics are in Table 2. The study site was divided into 4 application areas (Figure 1), which corresponded to each deck (C, E, K) and to a wet control zone (U) (rainwater from the unpopulated X deck only). The surface of each area was 61 x 38 cm, exactly twice the surface area of the deck collector, and was marked off with a welded steel frame 6 cm high. Each application area was protected from natural rainfall events by a raised clear polyethylene cover. Application zones were separated from each other by 80 cm, within which we established a dry control (O).

**Table 2:** Soil characteristics of the experimental area (n = 9 samples).

Characteristic	Mean	Range
pH	5.2	4.8-5.7
Conductivity (mS/m)	118	81-155
Organic carbon (%)	10.9	9.3-12.7
CEC (meq/100g)	49.8	46-53
Clay (%)	36.7	30-39
Silt (%)	23.9	16-26
Fine sand (%)	23.3	21-25
Coarse sand (%)	16.2	11-32



**Figure 1:** Layout of treatments. C = CCA; E = Copper Azole; K = kwila; U = rainwater only, from the X (unpopulated) deck; O = unwatered “dry” controls between each area.

### Leachate application and soil sampling

Two applications of each treatment were made in order to simulate natural rainfall events: the first equivalent to 29.5 mm of rain and the second two weeks later (10 mm rain). At each application, water from duplicate decks was applied to each area using watering cans. Immediately adjacent to each frame, an equivalent amount of standard artificial rain was applied in order to avoid gradients in soil moisture between the treatment areas and the surrounding soil.

Soil samples were taken with a metal cylinder 6 cm in diameter, to a depth of 5 cm. Samples were taken twice (3 days and 12 days) after the first treatment and three times (3 days, 8 days and 12

days) after the second. At each sampling time, 15 soil cores were taken (4 areas x 3 replicates + 3 dry control samples), and the sampling holes were backfilled with sterile sand. The 3 replicate cores from each treatment were <10 cm apart. Cores were placed in plastic bags and transported to the laboratory on the day of collection for immediate extraction of organisms. Soil organisms were extracted using Tullgren funnels (heat extraction process) and collected into 70% ethanol. Samples were randomly arranged in the Tullgren funnels, powered by light globes, and organisms extracted for 4 days. The light intensity was increased each exposure day from 15W to 60W to progressively dry the sample and force animals out. Tullgren funnels were an appropriate extraction technique because they extract only live animals.

Cores were wet-weighed before extraction. After invertebrates were extracted, samples were sieved to separate the material into rock and coarse organic matter (>2 mm) and soil (<2 mm), and weighed. Organism density was expressed as number per 100 g dry sample weight. Organisms extracted from cores were identified [7, 8, 9] to family for mites (except Euoribatida which were taken to cohort level) and order level for other groups, and counted. Immature animals that could not be recognized were sorted to order.

### Data analyses

Mite community data and the effects of treatments over time were analysed using multivariate techniques within the PRIMER package [10]. Non-metric multidimensional scaling (MDS) based on a Bray-Curtis similarity matrix was used to investigate patterns of community structure. Two-dimensional solutions with lowest stress were used for interpretation. ANOSIM (a multivariate non-parametric equivalent of analysis of variance) with 5000 permutations was used to test for differences between treatment effects and time periods, and similarity percentages (SIMPER) was used to elucidate which taxa were contributing most to similarities between samples within each treatment, and to dissimilarity between treatments. For MDS ordinations and ANOSIM all taxa were included: for SIMPER juveniles and unidentified “others” were omitted, but immature Mesostigmata were retained. All data were square-root transformed before analysis.

## RESULTS AND DISCUSSION

### Depletion from Decks:

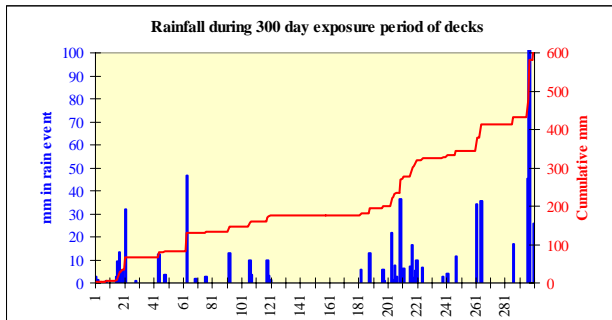
During the weather exposure period, total rainfall of 600 mm occurred in 48 rain events as depicted in Figure 2. The central dry period is typical of the Brisbane spring. During the exposure period, mean air temperature minima and maxima during autumn, winter, spring and summer were 15°&25°C; 8°&19°C; 14°&23°C and 19°&28°C respectively. Concentration data of each component in the collected runoff water from each deck type is given in Table 3. Initial retention and 300 day depletion of each component in the deck boards is given in Table 4.

**Table 3:** Deck runoff water concentration (mg/L) data. \*Teb = tebuconazole

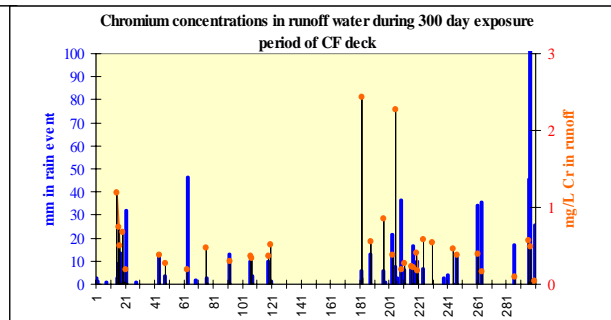
Deck:	CF			CR			EF			ER			K
Component:	Cu	Cr	As	Cu	Cr	As	Cu	B	Teb*	Cu	B	Teb*	Tannin
Minimum	0.013	0.039	0.100	0.013	0.042	0.108	0.136	0.138	0.0006	0.094	0.178	0.0007	2.91
Mean	0.453	0.561	1.97	0.554	0.554	1.11	3.29	2.87	0.0263	2.52	2.61	0.0284	78.7
Maximum	2.53	2.43	5.69	2.19	2.72	3.77	20.1	13.4	0.137	13.0	10.6	0.113	853
Std. Dev.	0.543	0.534	0.992	0.451	0.472	0.705	4.13	2.69	0.0391	2.68	2.28	0.0312	154

**Table 4:** Retention and depletion of preservative components from decks. \*Teb = tebuconazole

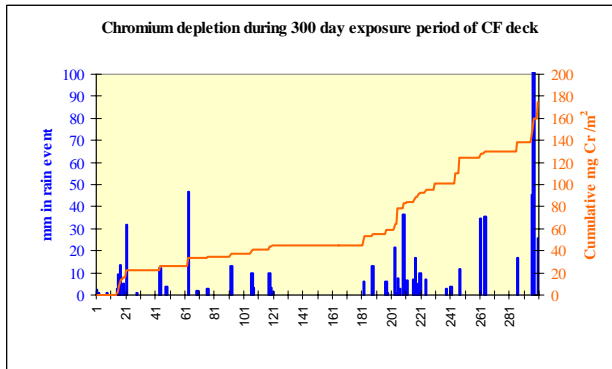
Deck:		CF	CR	EF	ER
Mean retention (%m/m) in deck boards (before exposure)	Cu	0.0838	0.120	0.266	0.269
	Cr or B	0.157	0.147	0.0182	0.0184
	As or Teb*	0.137	0.107	0.0124	0.0077
	TAE	0.378	0.374	0.278	0.277
Amount of component in deck (g/m <sup>2</sup> ) (before exposure)	Cu	8.58	11.7	23.3	26.1
	Cr or B	16.1	14.4	1.60	1.78
	As or Teb*	14.0	10.5	1.08	0.747
Amount (mg/m <sup>2</sup> ) depleted in 300 days	Cu	100	153	708	607
	Cr or B	149	171	744	769
	As or Teb*	623	414	8.62	10.4
% of component depleted in 300 days	Cu	1.17	1.31	3.03	2.33
	Cr or B	0.924	1.18	46.5	43.2
	As or Teb*	4.44	3.95	0.795	1.39



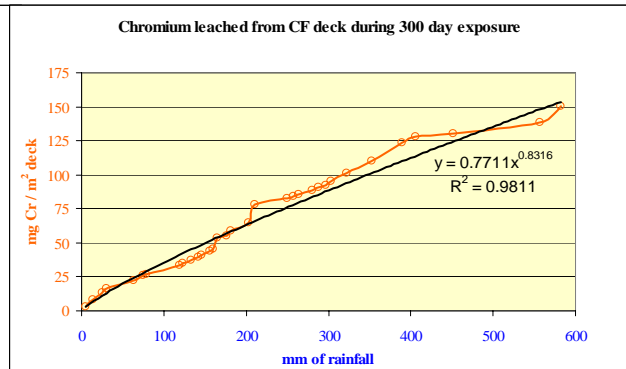
**Figure 2:** Rainfall distribution



**Figure 3:** Chromium concentration in runoff



**Figure 4:** Chromium depletion vs exposure time



**Figure 5:** Chromium depletion vs rainfall

Figures 3 to 5 show the chromium depletion data from the CF deck plotted in different ways. Against time, the rate of depletion appears quite erratic, reflecting the erratic rainfall pattern. When the amount of rain is used as the independent variable, the plot becomes more regular and better correlated to a smooth trendline. The goodness of fit is still not perfect, because the rate of depletion depends not only upon the amount of rain but also upon the way in which it falls. It became obvious during the work that short heavy showers did not produce as much depletion as an equivalent number of mm of steady rain, probably because the latter kept the wood wet for longer and also wet deeper into the interior zones, thus mobilising additional leachable species. Data relating to depletion of the other components has therefore been presented as function of rainfall rather than time (Figures 6 - 8).

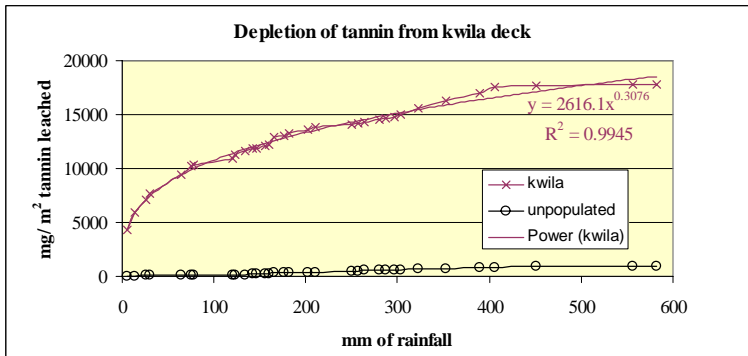


Figure 6: Depletion of tannins from natural kwila (K) and unpopulated (X) deck

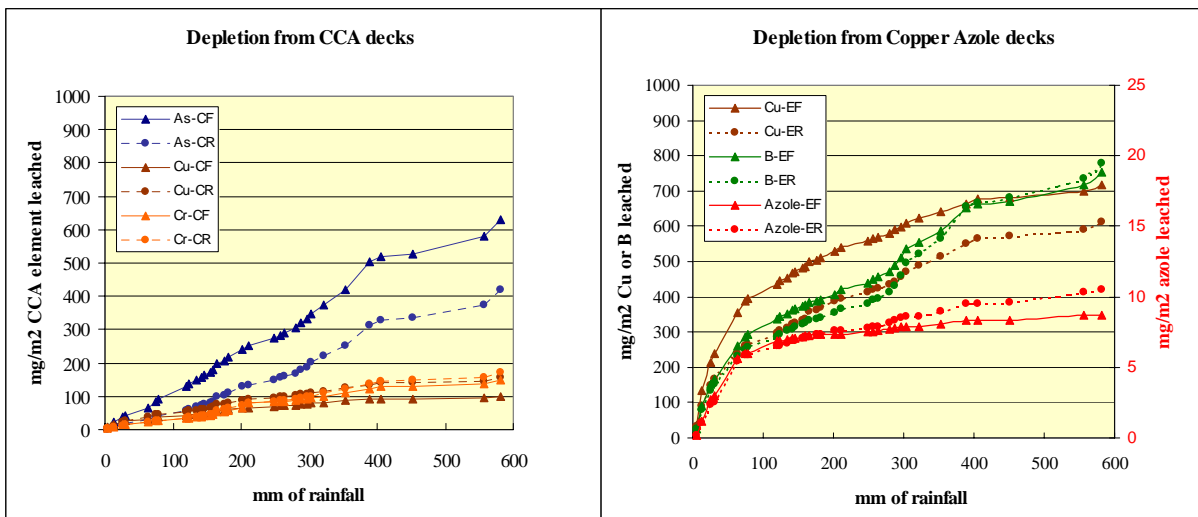


Figure 7: Cu, Cr and As depletion from C decks

Figure 8: Cu, B and azole depletion from E decks

The model equations (Table 5) gave the best fit to the deck component depletion. These models should be more useful than simple flux rates (Table 6), as they should be applicable to all locations with comparable environmental conditions.

Table 5: Depletion models:  $y = \text{mg of component lost per m}^2 \text{ of deck per } x \text{ mm of rainfall since first exposed.}$

Component	Bethel process (CF or EF)	Modified Bethel (CR or ER)
<b>CCA treated radiata pine:</b>		
Cu	$y = 3.265x^{0.5540}$ $R^2=0.982$	$y = 2.152x^{0.6873}$ $R^2=0.990$
Cr	$y = 0.771x^{0.8316}$ $R^2=0.981$	$y = 0.5846x^{0.8955}$ $R^2=0.986$
As	$y = 1.529x^{0.9467}$ $R^2=0.994$	$y = 0.326x^{1.118}$ $R^2=0.992$
<b>Copper Azole treated radiata pine:</b>		
Cu	$y = 151.1\ln(x) - 265.9$ $R^2=0.988$	$y = 20.634x^{0.5507}$ $R^2=0.960$
B	$y = 16.84x^{0.6091}$ $R^2=0.949$	$y = 14.32x^{0.621}$ $R^2=0.959$
Tebuconazole	$y = 1.899\ln(x) - 2.809$ $R^2=0.956$	$y = 2.292\ln(x) - 4.508$ $R^2=0.981$
<b>Untreated kwila:</b>		
Tannin	$y = 2616x^{0.3076}$ $R^2=0.995$	

Changing from a full Bethell process (CF) to the low uptake process (CR) appeared to markedly reduce the depletion of As from CCA-treated decks, at the expense of somewhat increased depletion of Cu and Cr, but the lack of replication prevents forming a firm conclusion. In the case of the Copper

Azole decks, the lower uptake process (ER) may have produced some decrease in Cu depletion but a similar increase in tebuconazole depletion, with B unaffected.

**Table 6:** Flux rates ( $\text{mg m}^{-2} \text{d}^{-1}$ ) of components from decks during various periods since first exposed

Component	Bethel process (CF or EF)			Modified Bethel (CR or ER)		
	21	90	300	21	90	300
<b>CCA treated radiata pine:</b>						
Cu	1.54	0.508	0.341	1.88	0.642	0.521
Cr	1.05	0.411	0.495	1.12	0.433	0.580
As	3.14	1.64	2.10	1.47	0.749	1.402
<b>Copper Azole treated radiata pine:</b>						
Cu	16.9	3.47	2.39	11.3	5.04	2.05
B	12.5	3.92	2.51	11.0	3.36	2.59
Tebuconazole	0.269	0.074	0.029	0.257	0.077	0.035
<b>Untreated kwila:</b>						
Tannin	448		129		59.4	

### Soil leaching studies

Concentration of each preservative component present in the composite runoff water sample applied to the soil columns, as determined by chemical analysis, is given in Table 7.

**Table 7:** Concentration of components in 10 week composite runoff water samples of stated volume

Deck	Volume mL	As mg/L	Cr mg/L	Cu mg/L	B mg/L	tebuconazole mg/L	tannin mg/L
CF	1360	1.198	0.315	0.393	0.047		
CR	1430	0.539	0.267	0.428	0.035		
EF	1340	0.030		3.810	3.209	0.033	
ER	1390	0.054		2.654	2.759	0.039	
K	1450						86.1
X	1700	0.015	0.013	0.011	0.008	<0.001	<1

Detectable concentrations of As in the EF and ER runoff water and of B in the CF and CR runoff water could be taken to indicate a small but measurable extent of cross-contamination between these decks, which could be due to rain droplet bounce or splashing. But the fact that considerably smaller concentrations of As were detected in the U deck, which was immediately adjacent to the CF deck, than in the more distant E decks tends to suggest that these elements may have been present at low concentrations in the preservative solutions used to treat the boards, and that removal of components from the system by droplet bounce was minimal – probably 1-5%.

After conducting the soil column experiments, chemical analysis of soil layers and column effluent fractions was able to distinguish differences between the unpopulated deck and decks EF and ER only, and then only for the Cu and B components. For all other components except tebuconazole and for all other decks, the amount of component present in the aliquot added to the column was too small when compared with the amounts of that component naturally present in the soil. In the case of tebuconazole, the aliquot contained only about 4  $\mu\text{g}$ , and state-of-the-art instrumentation was unable to detect the resultant concentrations in each fraction. So generally, analytical results of fractions from columns spiked with composites from test decks were not significantly different from those obtained from the corresponding columns spiked with composites from the unpopulated deck. In short, the deck leachates contained insufficient of all components to make a measurable difference to the soil, except for Cu and B from the Copper Azole decks (Tables 8 & 9).

**Table 8:** Distribution of copper from EF and ER composites in soil column and column effluent

Deck:	EF deck			ER deck		
mg Cu added in aliquot:	0.457			0.346		
Soil in column:	S1	S2	S3	S1	S2	S3
mg Cu found in fractions						
SL1	<b>0.530</b>	<b>0.466</b>	<b>0.380</b>	<b>0.330</b>	<b>0.307</b>	<b>0.244</b>
SL2	<0.025	<b>0.04</b>	<0.025	<b>0.026</b>	<b>0.02</b>	<0.025
SL3	<0.025	<b>0.04</b>	<0.025	<0.025	<0.025	<0.025
SL4	<0.025	<b>0.03</b>	<0.025	<0.025	<0.025	<0.025
SL5	<0.025	<0.025	<0.025	<0.025	<b>0.03</b>	<0.025
CE1	<0.01	<0.01	<0.01	<0.01	<b>0.02</b>	<0.01
CE2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CE3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CE4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Found as % of added:	116%	126%	83%	103%	109%	71%

**Table 9:** Distribution of boron from EF and ER composites in soil column and column effluent

Deck:	EF deck			ER deck		
mg B added in aliquot:	0.386			0.328		
Soil in column:	S1	S2	S3	S1	S2	S3
mg B found in fractions						
SL1	<b>0.033</b>	<b>0.016</b>	<b>0.040</b>	<b>0.031</b>	<b>0.019</b>	<b>0.036</b>
SL2	<b>0.067</b>	<b>0.093</b>	<b>0.129</b>	<b>0.051</b>	<b>0.046</b>	<b>0.144</b>
SL3	<b>0.096</b>	<b>0.120</b>	<b>0.181</b>	<b>0.075</b>	<b>0.083</b>	<b>0.118</b>
SL4	<b>0.072</b>	<b>0.059</b>	<0.020	<b>0.060</b>	<b>0.103</b>	<0.020
SL5	<b>0.027</b>	<b>0.023</b>	<0.020	<b>0.032</b>	<b>0.020</b>	<0.020
CE1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CE2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CE3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CE4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Found as % of added:	76%	81%	91%	76%	83%	91%

Recoveries of copper were variable, possibly reflecting the variability between the soils in terms of their absorptivity for cations and their native copper content. Generally the applied copper did not migrate far, with a possible exception in S2, but the high recoveries from this soil indicate considerable native copper content which may have contributed to the apparent movement. Boron recoveries were more reproducible. Boron migrated more readily than copper, in accordance with general perceptions of the mobility of this element. Although boron did not break through the lowermost soil layer, it would probably do so (at least with soils S1 and S2) if given additional leaching water.

In order to generate soil leaching column data for the remaining components (Cu, Cr As from CCA decks and tebuconazole from copper azole decks) spiking the relevant runoff waer composites with these components was undertaken. All components thus enhanced tended to remain in the surface layers; mainly SL1 but sometimes also in SL2. However, we refrain from reporting these data as the lack of information about the form in which the components are present in the runoff water makes it impossible to be sure that our component spikes were in the same form (oxidation state, ionic species, etc) and thus behaved the same as equivalent concentrations of naturally-present components.

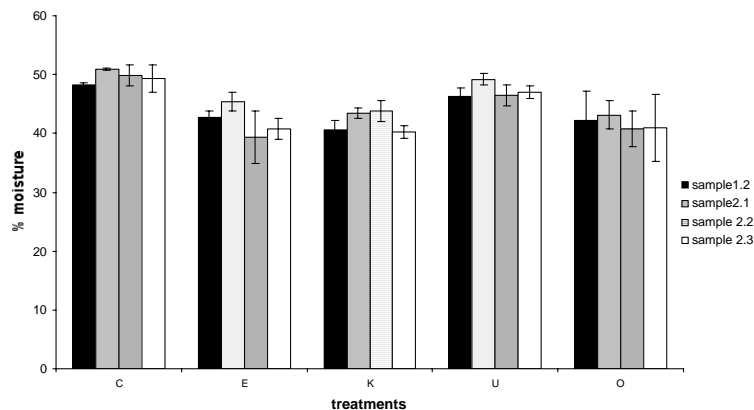
## Soil invertebrate studies

Compositions of the deck runoff composites applied to the field soil at application are given in Table 10. Predictably, the second application contained lower concentrations of most preservative components.

**Table 10:** Concentration (mg/L) of components in deck runoff for the two field soil applications.

Application:	1				2			
Source deck:	C	E	K	X	C	E	K	X
As	1.05	-	-	<0.02	1.37	-	-	<0.02
Cr	0.58	<0.05	-	<0.05	0.47	<0.05	-	<0.05
Cu	0.85	5.68	-	0.025	0.73	2.93	-	0.029
B	-	4.24	-	0.05	-	2.16	-	0.07
Tebuconazole	-	0.038	-	<0.001	-	0.016	-	<0.001
Tannin	-	-	170	3.3	-	-	98	4.3

Minimal variability in soil moisture developed during the application period, as shown in Figure 9, for the last four sampling periods. The changes between the periods are principally the result of applying the treatments. The level of soil moisture was naturally very high in the study area



(between 40% and 50%), but there were significant differences between each treatment area: soil moisture for the C area was higher than for the E and K areas. The changes between each treatment zone may partially explain variability in the invertebrate communities. Moisture can have a significant impact on the abundance of soil fauna [11]. The rapid response of the mites to change in soil moisture seems to be the result of vertical movement of the animals.

**Figure 9:** Field soil moisture in latter half of trial- mean (n=3)  $\pm$  two standard deviations. The second runoff water application occurred before sampling period 2.1.

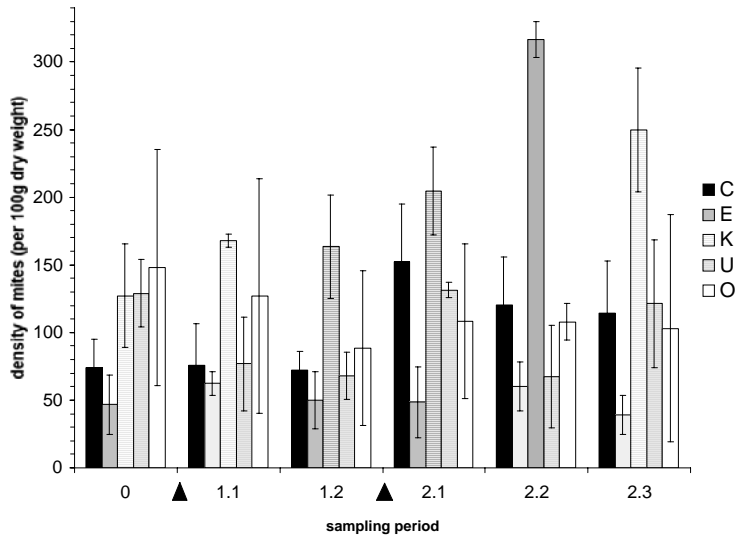
## Invertebrate order, mite families and densities

More than 13 000 invertebrates were collected during the study. Overall, samples were dominated by mites (84%) and springtails (8%). The most dominant groups were the oribatid (7815 individuals) and mesostigmatid (2589) mites. Because of the domination of mites in this area, we decided to focus analysis on mite taxa, and identified eighteen families. The Euoribatida (Oribatida) were not identified to family level because of the complexity of this cohort (more than 100 families).

Total mite densities are presented in Figure 10. There are differences in sampling times between the two controls (U and O), with a higher density of mites in the U control after the second application, probably due to changes in soil moisture. The O control has The very large standard deviations in the O controls are probably due to their spread over the whole site (width 2.4 m).

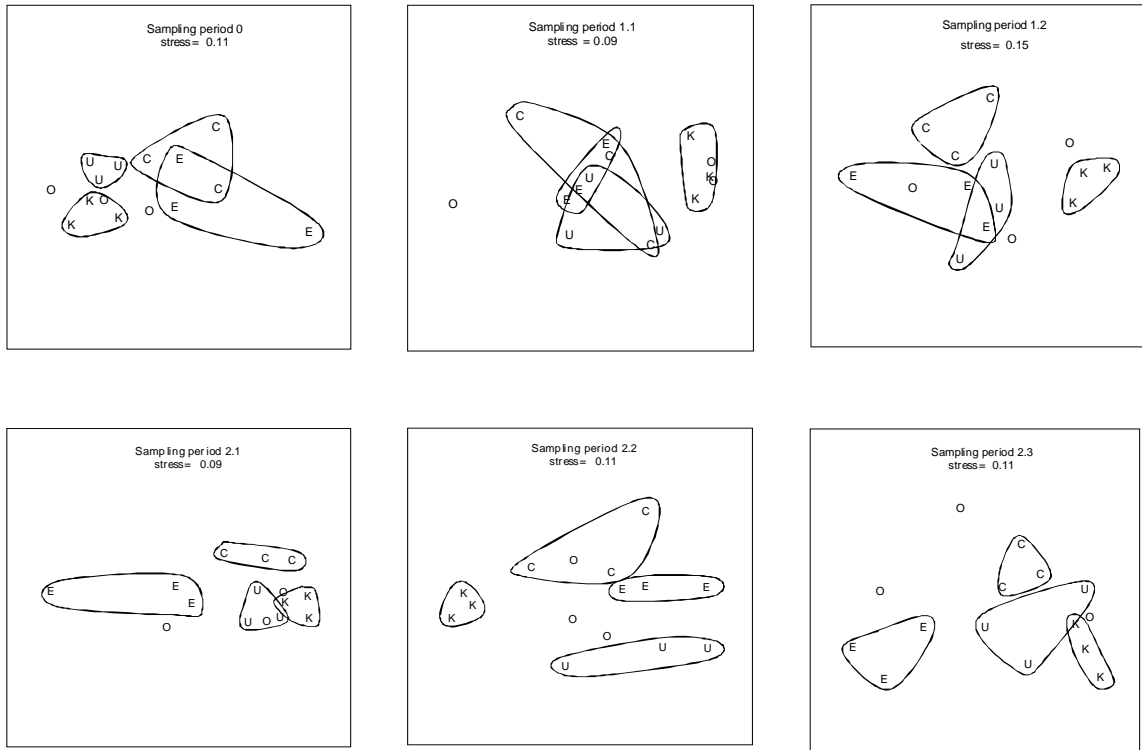
There appeared to be no significant effect of CCA and copper-azole-contaminated runoff water, whereas the kwila-contaminated runoff had a positive impact on the density of soil-dwelling mites. This increasing density of mites (mainly oribatids) may be due to an increase in microbial activity caused by elevated tannins in the soil and consequent greater food availability for mites

(oribatid are known to feed primarily on fungal spores [9]); or through an indirect impact by removal of tannin-sensitive predators or pathogens of the mites.



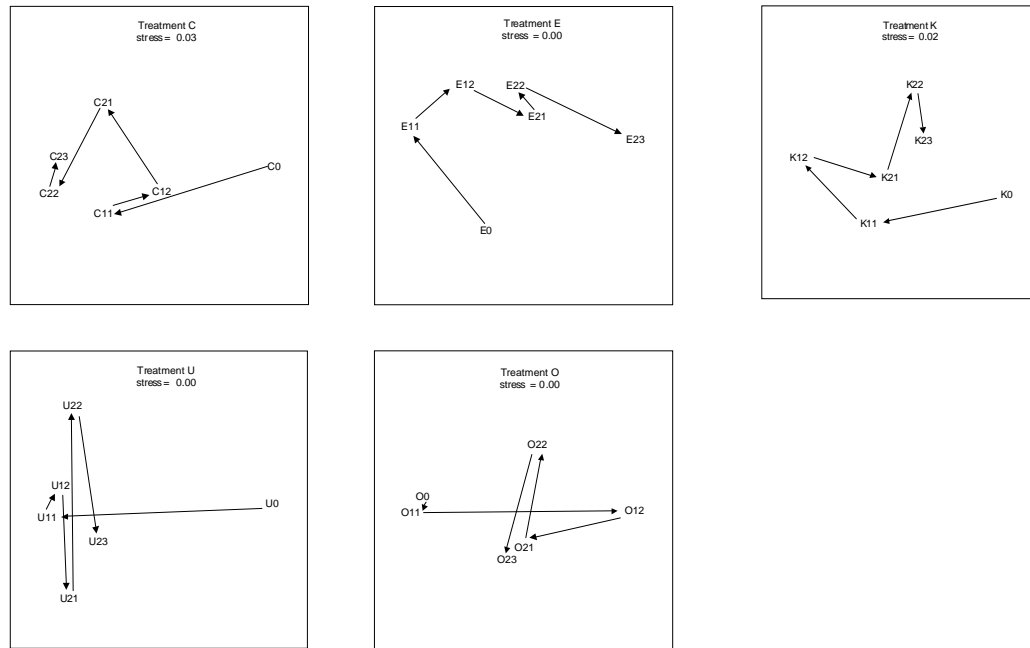
Mite Community structure The 2-dimensional MDS ordinations of samples at the same sampling period are presented in Figure 11. Samples that are closer together in the ordination space are more similar than those further apart. There is substantial overlap of communities at the start of the experiment: after application of the preservative treatments, communities in each tend to drift apart in ordination space, suggesting a community-level effect of these chemicals.

**Figure 10.** Total densities of mites in each treatment at each sampling period  $\pm$  two standard deviations. The triangles indicate the timing of the two runoff water applications.  $n = 3$  for all treatments.



**Figure 11.** MDS ordinations of mite communities at each sampling period. U = watered control; O = unwatered control; C = CCA; E = Copper Azole; K = kwila.

MDS ordinations for each treatment separately are shown in Figure 12. The independent “dry” control (O) shows changes due to natural changes in soil moisture and temperature. The watered U control shows oscillations after an initial shift in composition, again probably due to changes in soil moisture after the first application. The microarthropod communities in the three treatments C, E and K show differing responses to chemical application. The K treatment community appears to be returning towards the initial state after some short-term changes. For the two other treatments (C and E), the points are moving away from the initial state, indicating that the effects of the treatments are on-going.



**Figure 12.** MDS ordinations of mite communities in each treatment. Arrows indicate trajectories of community composition over time.

ANOSIM results are presented in Table 11, and show that there were significant differences in mite community structure between time 0 (before application) and all subsequent sampling periods. However, there was only one significant pairwise difference between post-treatment periods, which suggests that there is no difference between times after runoff water applications. Comparisons between treatments were all significantly different from each other, but none was different from the O control. These differences could reflect the large variation in mite abundance between the treatments, partly explained by differences in soil moisture and natural spatial variation between the widely separated O samples.

The global similarity between the different treatments is quite high, but is decreasing over time after the first runoff water application. The increase of similarity percentage between time 0 and time 1.1 can be explained by an increase in soil moisture, then the decrease could reflect the differential effect of each treatment on the mite community. This result is compatible with the ordination analyses. Moreover, the dissimilarity between time seems to increase between each period, which confirms the differential effect and the increasing “specialisation” of the mite community.

At each sampling time, only three taxa were necessary to explain 50% of similarity between samples (Table 12). These three families are the same in each case, and are all oribatid taxa (Euorobatida, Oppiidae and Nanhermanniidae). The same ratio of dissimilarity was explained by about 4 or 5 different taxa each time, which confirms that the community is complex, with none of the taxa dominant. Taxa responsible for discriminating between treatment effects (all post-treatment

samples combined) are given in Table 13. Eurobatida appear to increase in abundance and Nanhermannidae to decrease in response to all leachate treatments, compared to treatment 0.

**Table 11.** ANOSIM results for the mite family level data, 5000 permutations. Critical P-value=0.01.

Factor	R-statistic	Significant statistics	P-value	Significant at experiment level
<b>Sampling periods:</b>				
0-1.1	0.356	10	0.002	yes
0-1.2	0.437	6	0.001	yes
0-2.1	0.385	33	0.007	yes
0-2.2	0.481	2	0.001	yes
0-2.3	0.541	2	0.001	yes
1.1-1.2	-0.059	3376	0.675	no
1.1-2.1	0.244	169	0.034	no
1.1-2.2	0.193	192	0.039	no
1.1-2.3	0.215	244	0.049	no
1.2-2.1	0.163	592	0.119	no
1.2-2.2	0.037	1618	0.324	no
1.2-2.3	0.333	48	0.010	yes
2.1-2.2	0.104	869	0.174	no
2.1-2.3	0.089	1248	0.250	no
2.2-2.3	0.022	2080	0.416	no
<b>Treatments:</b>				
C vs E	0.358	3	0.001	yes
C vs K	0.852	0	<0.001	yes
C vs U	0.506	0	<0.001	yes
C vs O	0.123	562	0.113	no
E vs K	0.809	0	<0.001	yes
E vs U	0.432	1	<0.001	yes
E vs O	0.179	201	0.040	no
K vs U	0.784	0	<0.001	yes
K vs O	0.253	62	0.013	no
U vs O	0.117	551	0.110	no

**Table 12.** Degree of similarity of mite communities at each sampling period (from SIMPER).

Sampling period	Average similarity (%)	Number of taxa to explain 50% of similarity
0	76.50	3
1.1	79.28	3
1.2	77.35	3
2.1	75.94	3
2.2	71.97	3
2.3	69.17	3

These statistical results suggest that changes occurred in the mite community structure after runoff (or rain) water application, in each of the four treatments (C, E, K and U). As the dissimilarity between treatments was still increasing at the end of this study, these differential effects are still being manifest, even though the K-contaminated community seems to return to a pre-treatment state.

We identified mites to family level in order to assess the utility of the technique as a relatively rapid method of identifying community change. It is questionable whether family-level determination is sufficient to give statistically meaningful and ecologically interpretable results. Taking the taxonomic resolution to genus or even species level would enable a more accurate assessment of community response to leachates, and allow analysis of species replacements within families. It would also facilitate comparisons of functional group or trophic level changes (herbivores, carnivores, fungivores, detritivores). Further research is necessary before these trade-offs can be analysed and a robust and reproducible method of biomonitoring the impacts of timber preservatives can be devised.

Table 13. Taxa responsible for dissimilarities between treatments: post-treatment samples combined. Top 2 most influential taxa only. From SIMPER analysis.

Treatment comparison (Tmt 1 vs Tmt 2)	Taxon	Average abundance (Tmt 1)	Average abundance (Tmt 2)	Contribution to overall dissimilarity %
C vs E	immature Mesostigmata	65.4	25.9	14.0
	Euoribatida	114.3	61.8	12.7
C vs K	Nanhermanniidae	22.2	179.0	22.9
	Euoribatida	114.3	248.6	14.1
C vs U	Nanhermanniidae	22.2	67.4	13.9
	Euoribatida	114.3	77.6	9.9
C vs O	Nanhermanniidae	22.2	58.88	13.4
	immature Mesostigmata	65.4	44.2	10.0
E vs K	Nanhermanniidae	11.9	179.0	22.9
	Euoribatida	61.8	248.6	18.9
E vs U	Nanhermanniidae	11.9	67.4	19.6
	Phthiracaroida	0.7	7.2	9.3
E vs O	Nanhermanniidae	11.9	58.9	18.4
	Euoribatida	61.8	124.4	14.2
K vs U	Euoribatida	248.6	77.6	20.9
	Nanhermanniidae	179.0	67.4	15.0
K vs O	Nanhermanniidae	179.0	58.9	18.2
	Euoribatida	248.6	124.4	15.8
U vs O	Euoribatida	77.6	124.4	13.9
	Eupodidae	4.5	13.4	10.5

## CONCLUSIONS

Rates of depletion from decks during 300 days service varied widely between preservative components, ranging from 0.029 mg m<sup>-2</sup> d<sup>-1</sup> for tebuconazole to 2.5 mg m<sup>-2</sup> d<sup>-1</sup> for boron, both from copper azole treated decks. Corresponding rates for CCA elemental components varied from 0.34 to 2.1 mg m<sup>-2</sup> d<sup>-1</sup>, while the naturally-durable hardwood kwila lost 59 mg m<sup>-2</sup> d<sup>-1</sup> tannin. Models for depletion behaviour based upon loss vs rainfall were more useful than similar models or calculated rates based upon loss vs time of exposure, as they were less dependent on the specifics of the rainfall pattern during the period. Amounts depleted from decks represented from 0.8% (tebuconazole) to 46% (boron) of the amounts initially present in the deck boards. About 1% of the copper and chromium and 4% of the arsenic initially present was depleted from the CCA-treated decks over the 300 day period.

Deck runoff water generally contained low concentrations of preservative components. When runoff samples from a given area of deck were applied to an equivalent area of soil, concentrations of most components in the soil were not detectably increased over the background. The exceptions to this generalisation were copper and boron from copper azole treated decks, which increased copper

concentrations in the surface layer of soil by about 5 mg/kg, and increased boron concentrations deeper into the profile by about 2 mg/kg.

During the short-term field soil impact study, the global density of invertebrates seemed to be significantly affected only by the kwila-extractive runoff water. While CCA and copper-azole contaminated runoff appear to have had no measurable impact on the density of soil-dwelling mites, the mite community structure seems to have been affected by all treatments. Differential effects of each treatment were recognised but not quantitatively evaluated. A longer-term study is required to determine whether the community structures are permanently altered, or are returning to a natural “equilibrium” state.

The method used, with both independent and dependent controls, was useful for estimating the magnitude and direction of change. The rapid response of soil invertebrates to an addition of water has several important implications. Firstly, it highlights the necessity of sampling at different times, when soil moisture levels are different to estimate species richness of the soil fauna. Second, it suggests that management impacts on soil fauna should be assessed with different soil moisture contents [12].

Although we chose as uniform an environment as possible, natural spatial variation in soil microarthropod populations means that full-cycle shifts in community composition (i.e. away from the initial state on disturbance and back again on recovery) are difficult to track, as initial states themselves vary in space and time, and there may be natural changes irrespective of the treatments applied. Examining communities at a more detailed taxonomic level (species) would provide more accurate data, but requires considerably more technical expertise. As is often the case with using organisms in their natural environment to indicate disturbance and recovery, a compromise between accuracy and efficiency is necessary.

Finally, such studies must be made on different types of organisms to identify species or species groups which could be used as bioindicators in field conditions. These studies should also lead to the standardisation of research and testing procedures. Ultimately, a biotic index of soil quality might be developed to objectively quantify pollution. Single taxon studies and tests are a step towards environmental risk evaluation, but progressively more complicated systems should be designed to analyse interactions between environment and ecology.

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