Summary of Alternatives to Methyl Bromide for Logs

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Methyl Bromide Quarantine and Pre-shipment (QPS) for logs

- 168 metric tons annually for U.S. log exports from 2009-2012 monitored by USDA. This does not include fumigations performed by state and local operators.

- MB on logs for export remaining one of the largest QPS uses in the United States.

- Increasing EPA (i.e. Clean Air Act) and site-specific usage restrictions provide additional incentive to develop efficacious and cost effective alternatives for log exports.

Current Status of Log Treatments

- Heavily dependent on fumigants, particularly methyl bromide
- Questionable fumigation schedules, penetration
- Extended time for effective fumigation

ISPM-15 vs whole log treatments

- methyl bromide fumigation
- conventional heat
- dielectric heat
- sulfuryl fluoride fumigation

Potential MB alternatives for logs

- Vacuum steam
- EDN
- Sulfuryl fluoride
- Phosphine
- Joule heating

Vacuum and steam treatment

Hardwood Log Export

- Generally more valuable than softwoods
- HT not typically done due to issues with degrade, quality
- Vacuum steam can satisfy HT requirement without negatively impacting quality

Current MB schedule for oak logs and oak wilt

T312-a

Oak logs

Pest: Oak Wilt Disease

Treatment T312-a—MB ("Q" label only) at NAP

Temperature	Dosage Rate (lb/1,000 ft^3)	Minimum Concentration Readings (ounces) At[1]:						
		0.5 hr[2]	2 hrs[3]	12 hrs	24[4] hrs	36 hrs	48 hrs	72 hrs
40 °F or above	15 lbs	240	240	200	240	160	120	80

1 Refer to **Table 5-4-2** for adding gas at each reading.

2 If the fumigation is conducted in a closed-door container, take the first reading at 1 hour instead of 0.5 hours.

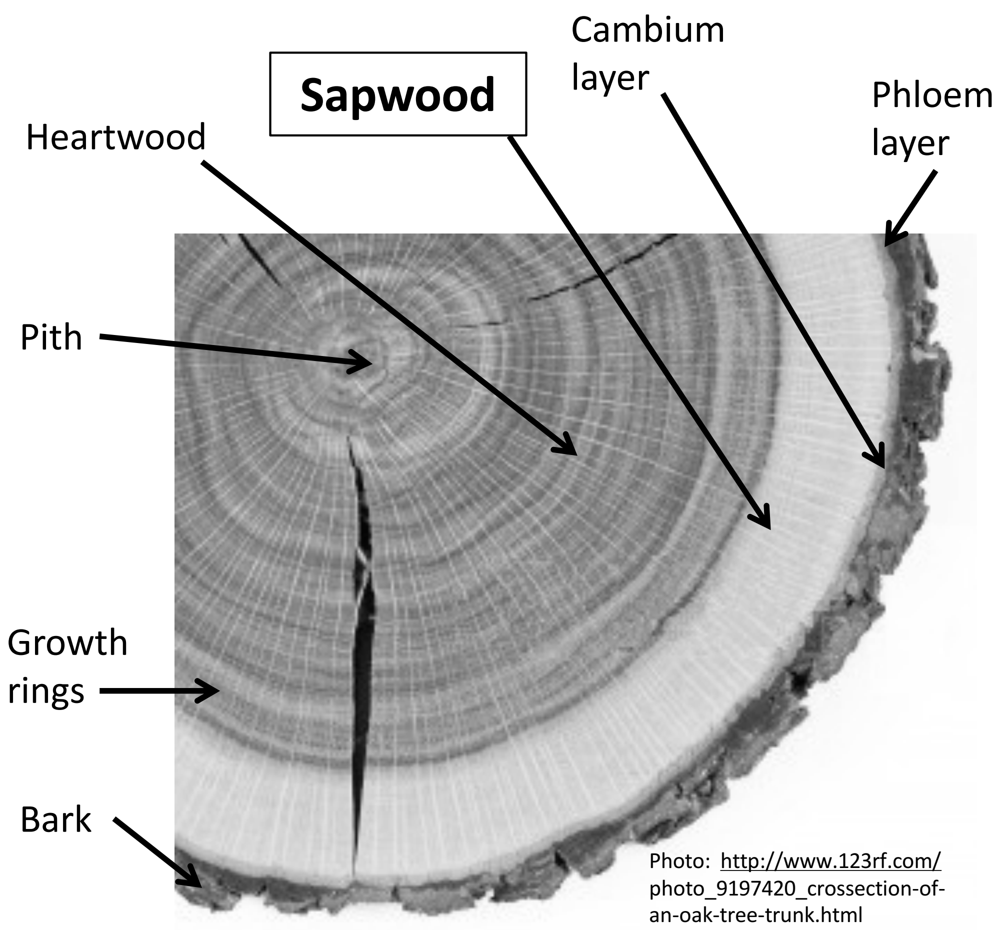
3 If the fumigation is conducted in a closed-door container, take the second reading at 2.5 hour instead of 2 hours.

4 After 24 hours, add enough fumigant to bring the concentration up to 240 oz.

Vacuum steam targeted log treatment objectives

- Complete mortality of oak wilt fungus (*Ceratocystis fagacearum*) in the sapwood zone of red oak logs;

- Complete mortality of WTB and *Geosmithia morbida* fungus in phloem region of Eastern black walnut logs.



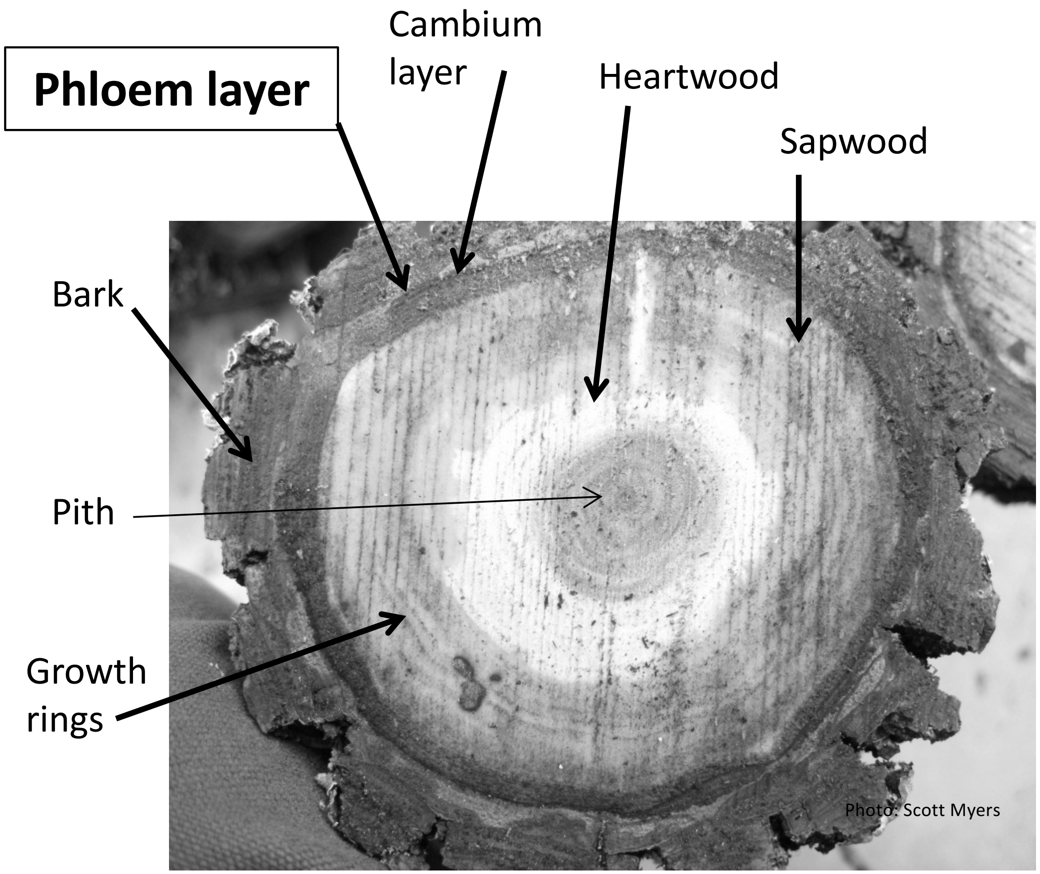
Oak cross section

Proposed draft schedule for oak logs

Pest: Oak Wilt Disease

Temperature and Vacuum	Exposure Period
90ºC, 100mm HG	6 hrs projected

Vacuum steam as a proposed phytosanitary treatment for oak logs for export



Walnut cross section

Proposed draft schedule for walnut logs

Pest: Thousand Canker Disease (Walnut twig beetle and *Geosmithia* fungus)

Temperature and vacuum	Exposure Period
90^{o}C, 100mm HG	4-6 hrs projected

Vacuum steam as a proposed phytosanitary treatment for walnut logs for export.

Vacuum steam advantages

- high reliability with heat degradation of protein the mode of action;
- increased treatment flexibility when compared to fumigants. Depth can be adjusted if/when new pests of concern emerge.
- effective at lower log temperatures than fumigants

An ideal fumigant

- Highly toxic to target pests stages but not toxic to plants and vertebrates
- Harmless to foods and commodities/equipment, does not react to metals
- Easily generated, inexpensive, economical in relation to required dosage ,
- Non-explosive, non-flammable, insoluble in water, not easily absorbed
- Easily diffuses, and rapidly penetrates the commodity
- Stable in the gaseous state, easily detected by human senses
- Efficacy not seriously affected by temperature or atmosphere
- Efficacy not dependent on pests actively breathing
- Not persistent, no residual effect, should off-gas quickly after use
- Should not affect the ozone layer, should not be a greenhouse gas

Alternative fumigants in forestry Armstrong *et al.* 2014 - literature review

- Reviewed in detail over 30 fumigants (15 major and 18 minor) and potential to be used for wood products (logs), pros and cons, economics, environmental and safety issues
- **Major** (used worldwide and produced in large quantities or having potential to be used for wood products) : **Phosphine (PH_3), Sulfuryl fluoride (SF) , Ethanedinitrile (EDN)**, Carbonyl sulphide, chloropicrin, dichlorofos, dimethyl disulphide, ethyl formate, ethylene oxide, hydrogen cyanide, methyl iodide, methyl isothiocyanate (metam-sodium, metam-potassium), nitric oxide and ozone
- **Minor** -obscure, not commercial, not available any more, no data on forest pests etc.
- Recommends research focus on EDN, followed by SF.
- New Zealand research on EDN continues and on reduced rates and recapture of MB

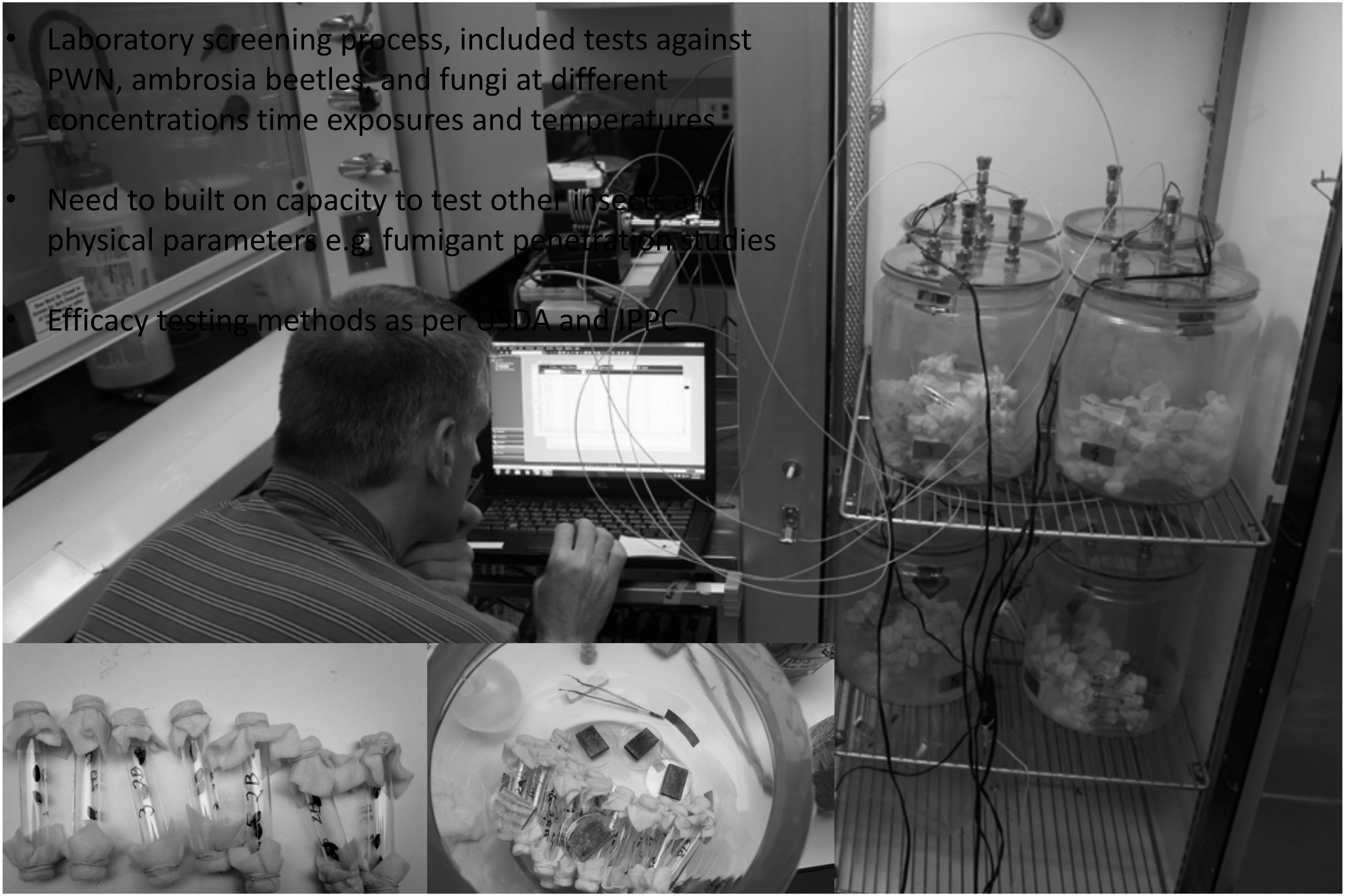



FPInnovations: Test method development and evaluations: PH_3, SF, a fluorine based fumigant, and recently EDN

- Laboratory screening process, included tests against PWN, ambrosia beetles, and fungi at different concentrations time exposures and temperatures

- Need to built on capacity to test other insects and physical parameters e.g. fumigant penetration studies

- Efficacy testing methods as per USDA and IPPC



What is EDN?

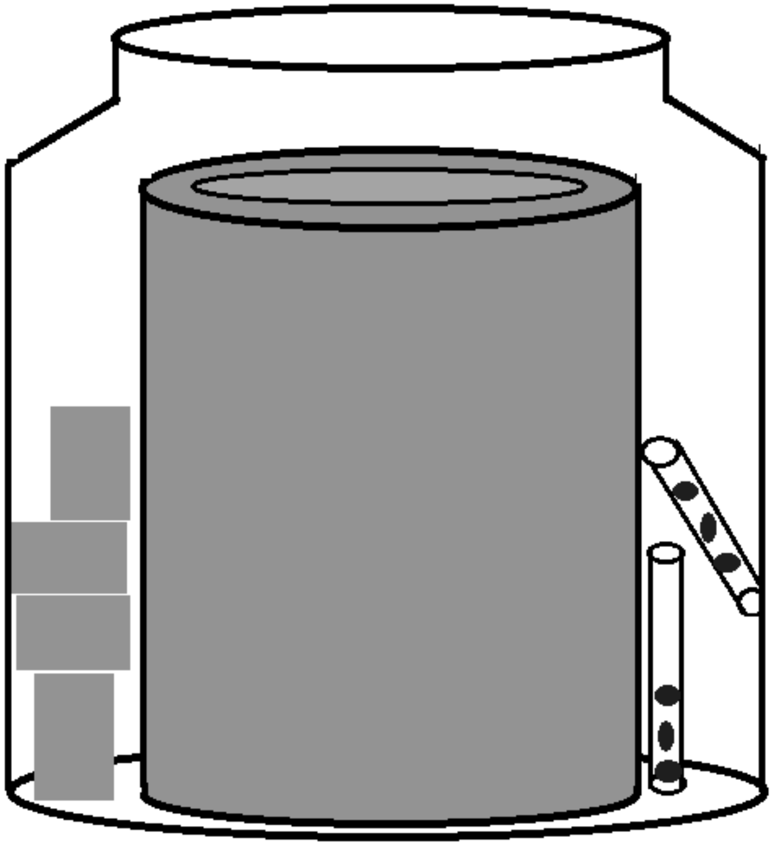
Cyanogen, ethanedinitrile, carbon nitride, dicyan, dicyanogen and oxalonitrile with chemical formula C_2N_2. Started with BOC/Linde, now Draslovska.

Properties	EDN™	Methyl Bromide	EDN™ Advantages for timber application
Boiling point	-21 ° C	3.6 ° C	EDN™ can be applied as a gas and is effective against target pests at very low temperatures.
Vapour Pressure	515 kPa (21°C)	214 kPa (21°C)	EDN™ has a high vapour pressure hence it will penetrate quickly and distribute easier than methyl bromide.
Density in Air	2.2	3.27	Both fumigants are heavier than air but EDN is lighter than methyl bromide hence ventilation can be quicker than methyl bromide
Specific Volume (@ 25°C and 1 atm)	462L/kg	256L/kg	This is the comparative volume of each product – EDN™ creates much more gas per kg.
Molecular weight	52.04	94.94	EDN™ has a low molecular weight which means it can move quickly from areas of high concentration to low concentration and achieve equilibrium faster.
Exposure limits	10 ppm	5 ppm	EDN™ has a twice higher TLV exposure limit than methyl bromide
Van der Waals radii	160 pm	185 pm	Smaller molecule hence greater penetration into timber and logs

EDN registration update

- Approved :
  - Australia (Full registration)
  - Czech Republic (Critical Use Permit)
  - South Korea
- In progress
  - New Zealand, Malaysia, Israel, Russia, USA, European Union, Turkey, South Africa, Egypt, Sri Lanka, …

EDN research at FPInnovations

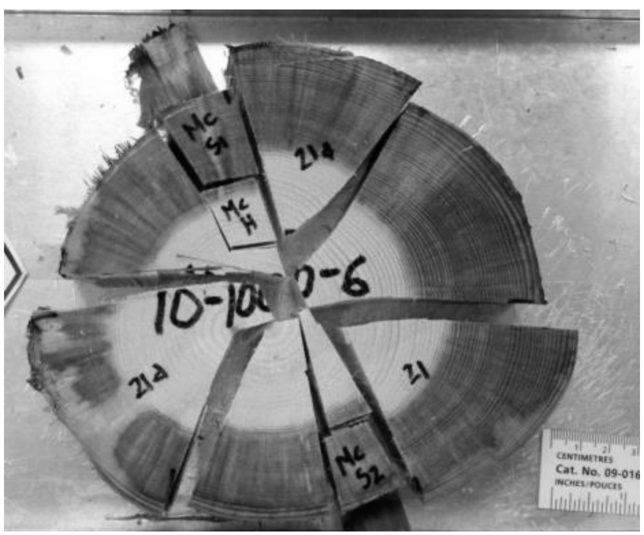


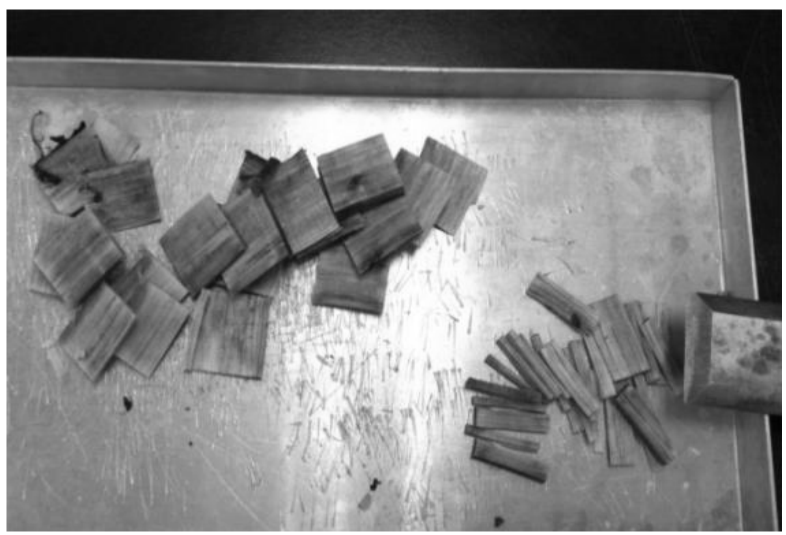
Code	Pathogen	Isolate ID
A	*Ceratocystis fagacearum*	C660
B	*Ceratocystis fagacearum*	C460
C	*Ceratocystis fagacearum*	C465
D	*Heterobasidion annosum*	X66C1
E	*Heterobasidion annosum*	Deck 3-3B-aB
F	*Heterobasidion annosum*	Ha MKRF-4
G	*Phytophora ramorum*	EU1 (SOD 03-002)
H	*Phytophora ramorum*	NA2 (04-38813)
I	*Phytophora ramorum*	NA1 (1295)
J	*Geosmithis morbida*	CCF3879
K	*Geosmithis morbida*	1259
L	*Geosmithis morbida*	1223

- 10 L jars (USDA method)
- 10 and 20˚C
- 50 and 100 g/m^3
- 1, 3, 6, 12, 18 and 24 hours
- Green lodgepole pine and grain infested with fungi
- Aiming high load factor, close to 40%

EDN effective against pine wood nematodes within 24 hours

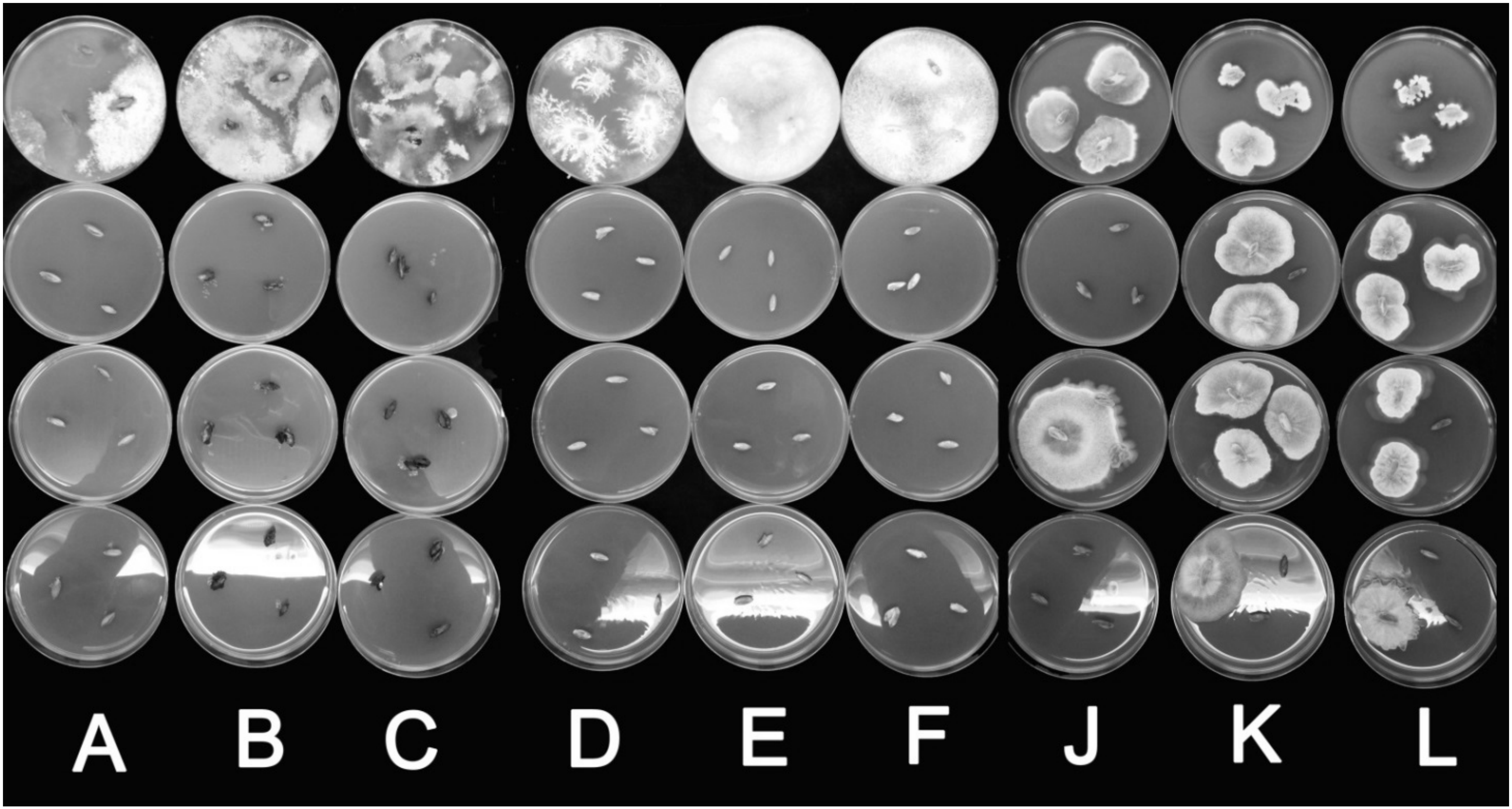
- In small test blocks killed in all parameter combinations even at 1 hour at both 50 and 100 g/m^3. at 10C an 20C
- In logs there were few survivors at 1, 3 and 6 hours exposures.
- No survivors at 100 g/m^3 exposed to 12, 18 or 24 hour exposures
- But - few survivors at 50 g/m^3 for 18 hours at 20C (dead at 12 and 24h)
- Lower temperature does not significantly affect the efficacy of EDN, which often is an issue for other fumigants.





EDN efficaceous against fungi

Even at a low dose and very short exposure time (1-3 hours) at 10 and 20°C



Ethanedinitrile (EDN): Previous research

Chung et al 2007

Table 2. Ethanedinitrile efficacy to PWN, *Bursapelenchus xylophilus*

Fumigant	Dose (g/m3)	No. of Sample tested	Mean No. of Nematode per 100g of wood chips(SD)	95.0% CI	Mean Mortality (%) (SD)
EDN	48	10	190.5(±81.9)	(131.9, 249.1)	88.43(±4.96)
	69	10	363.2((±265.6)	(173.2, 553.2)	77.94((±16.14)
	97	25	59.9((±45.5)	(41.9, 78.7)	96.36((±2.77)
	148	25	32.6((±23.5)	(22.9, 42.3)	98.02((±1.43)
MS	1000ml	25	38.8((±44.2)	(20.6, 57.1)	97.43((±2.68)
Untreated	-	60	1646((±1984)	(1133, 2159)	-

Mean Mortality: based on untreated sample

SD (Standard Deviation).

United States Department of Agriculture

Ethanedinitrile (EDN): Previous research

Lee et al 2016: 6 hr treatments, range of temps, unreplicated

Table 3. Toxicity of C_2N_2 to *B. xylophilus* nematodes and larvae of *M. alternatus* in naturally infested *P. koraiensis* logs in three different temperature ranges

Temperature (°C)	Dose (g m^{-3})	Load factor (%)	Volume of chamber (m^3)	Infested pine logs	*Ct* products (g h m^{-3})	*M. alternatus* larvae		*B. xylophilus* nematodes[a]	
						Dead/total	Mortality (%)	Dead/total	Mortality (%)
21–33	100	46	107	95	398.68	801/801	100.0	1500/1500	100.0
6–12	120	46	50	57	547.22	563/563	100.0	2100/2100	100.0
−1–3	150	30	108	73	595.95	583/583	100.0	1700/1700	100.0

[a] Mean number of nematodes per 100 g of wood sample.

Ethanedinitrile fumigation of pinewood nematode in wood blocks

24 hour treatment @ 20 °C

	PWN per gram dry weight	
EDN initial dose	pre treatment	21 days post treatment
40 g/m3	208.6 ± 101.1	0
60 g/m3	170.3 ± 42.6	0
80 g/m3	259.2 ± 81.4	0

Mean % WMC = 151.9 ± 47.4

White pine logs inoculated with fungi – then pinewood nematodes

Fumigations of *P. strobus* logs with ethanedinitrile (EDN) for 24 hours at 20 °C

EDN Concentration (g/m^3)	Pre-treatment			Post-treatment (21 days)		
	Mean No. PWN	Mean No. PWN/g	No. Logs with PWN/No. Total Logs	Mean No. PWN	Mean No. PWN/g	No. Logs with PWN/No. Total Logs
Control	10.00	1.99	12/22	19.2	1.93	19/22
40	5.60	1.01	15/20	0.00	0.00	0/20
60	7.36	1.79	12/22	0.00	0.00	0/22
100	8.75	1.88	13/20	0.00	0.00	0/20

Further work

- Coordinate research efforts, generate new data if required, assist with registration process
- Support registration within USA and Canada (efficacy on North American wood species and some specific wood pests
- Support registration within IPPC (ISPM 28 then ISPM15)
- Specific concentrations and time, commodities and scenarios (suggested schedules) need to be confirmed using larger replication and in scaled up tests. Hydrolysis.
- Address health and safety issues. Methyl iodide.

Sulfuryl fluoride review

- long history as a structural fumigant for termites and other wood boring insects;
- accepted as an official MB alternative in ISPM-15 for SWPM;
- gaining favor as a log fumigant in current discussions with China;
- concerns with efficacy at lower temperatures and on egg stage of insects. Increased dosage may be required at lower temperatures, and efficacy against particular pathogens questionable (oak wilt).

Yang, A., et al. (2018). "Survival of the oak wilt fungus in logs fumigated with sulfuryl fluoride and methyl bromide." Forest Products Journal.

- SF fumigations for 72 hours with 240, 280, and 320 g/m3 or 96 hours at 128 and 240 m3.
- MB fumigations were conducted using the current treatment schedule for oak logs destined for export (240 g/m3).
- Frequencies of successful pathogen isolation before treatment were higher for AI logs than for NI logs based on isolation rates from wood chips sampled from the sapwood.
- Treatments greatly reduced frequencies of viable pathogen presence, but **neither treatment** was successful in eradicating the pathogen.
- Small block *Quercus* penetration studies simulating penetration and diffusion of SF and MB into oak logs resulted in slow, variable fumigant diffusion that never reached CT combinstions lethal to *B. fagacearum*.

Phosphine (PH3) review

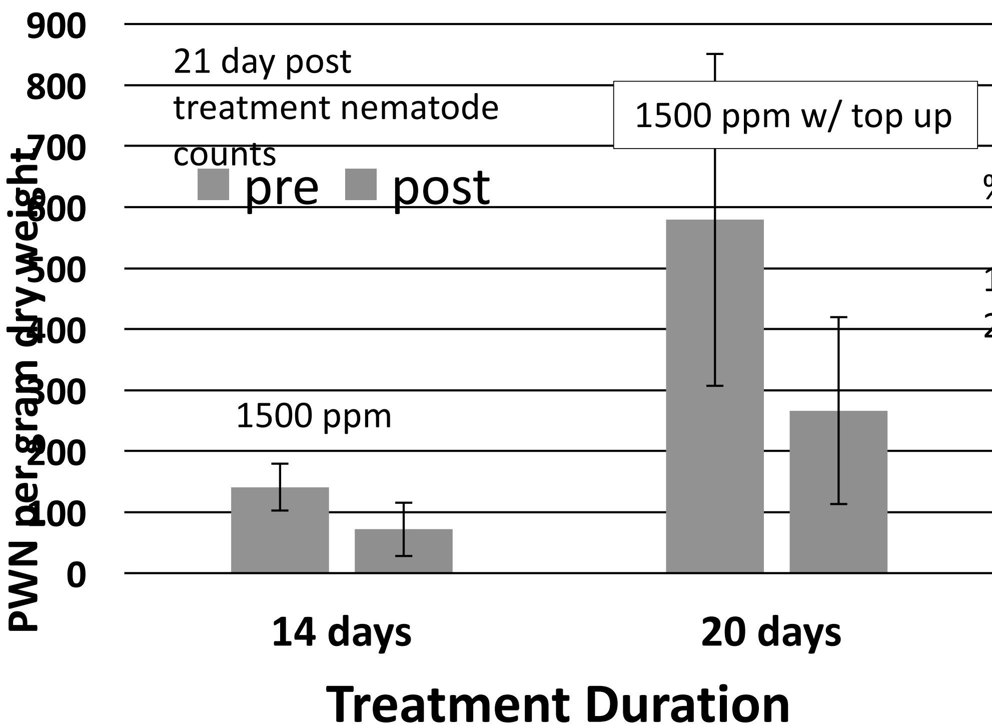
- New Zealand uses PH3 for shipboard fumigations of long transit *P. radiata* logs (10 days) to China;

- PH3 found to be generally inefficient against nematodes and fungi. Poor penetration an issue;

- Safety issues surrounding use (eg. flammability).

United States Department of Agriculture

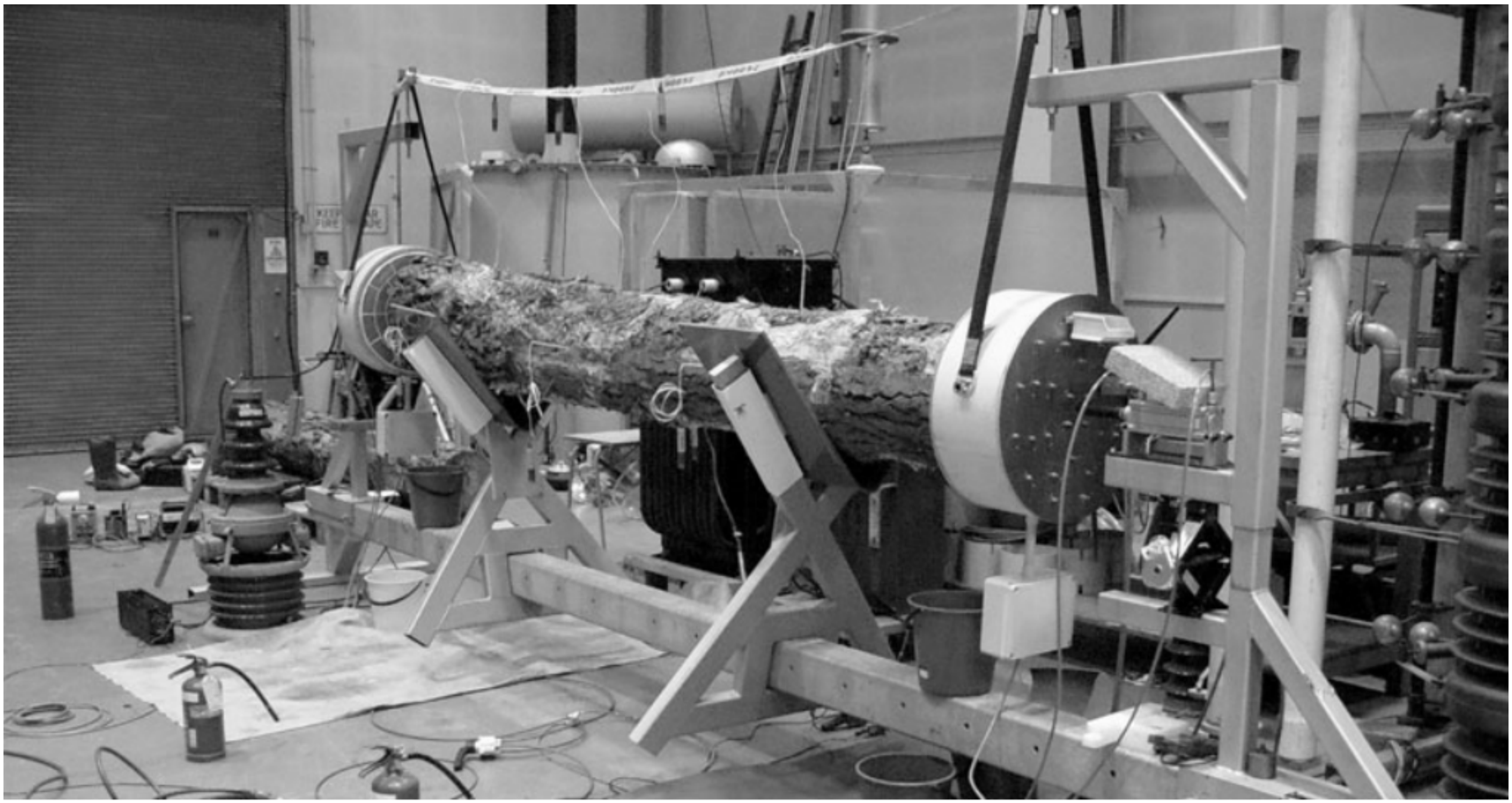
Phosphine fumigation of PWN in pine blocks at 20 ºC



% moisture (dry basis)

14 d – 208.5 ± 10.1
20 d – 214.3 ± 4.3

Joule heating of *Pinus radiata*



Joule heating implementation

- Single log treatment has been worked out based on modeling characteristics of *P. radiata* logs;
- Volume of P. radiata the single largest obstacle to implementation;
- Initial capital cost of equipment and electricity may be prohibitive, though government funding may assist.

Latest references on alternatives for log treatments

- Juzwik, J., et al. (2019). "Vacuum Steam Treatment Eradicates Viable *Bretziella fagacearum* from logs cut from wilted *Quercus rubra*." Plant Dis 103 (2): 276-283.

- Yang, A., et al. (2018). "Survival of the oak wilt fungus in logs fumigated with sulfuryl fluoride and methyl bromide." Forest Products Journal