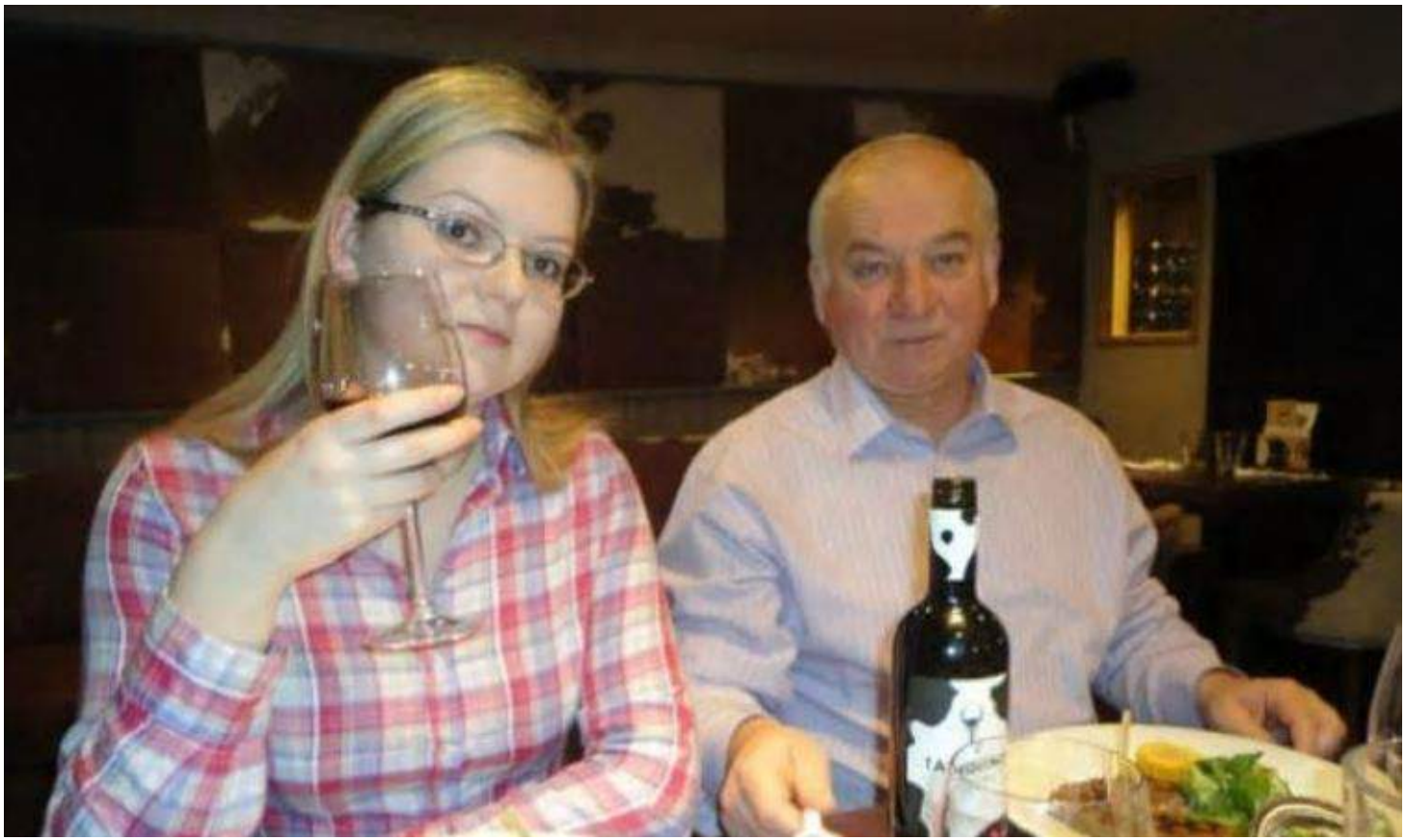
A tale of two chemicals -a neurotoxin and a fire-fighting foam

Barrie M Peake

4 March 2018 Sudden illness of Sergei Skripal (ex. Russian double agent) and his daughter Yuila in Salisbury, England



Military personnel investigating the poisoning of Sergei Skripal on 11 March in Salisbury
Chris J Ratcliffe/Getty

Alexander Litvinenko

- a critic of Putin who died in London in 2006 after drinking green tea laced with radioactive polonium 210

- just hours before he slipped into unconsciousness, Mr Litvinenko whispered: "The bastards got me, but they won't get everybody"

- the symptoms exhibited by the Skripals (comatosed etc.) suggested that they had been poisoned by a **neurotoxin**

- a London court gave permission for blood samples to be taken from the Skripals for examination by chemical weapons inspectors at the UK Porton Downs laboratory

- confirmed that a military-grade neurotoxin of Russian origin had been left on the front door of their home

- Britain immediately expelled 30 Russian diplomats

- Russia denied all these allegations and retaliated by expelling 30 British diplomats

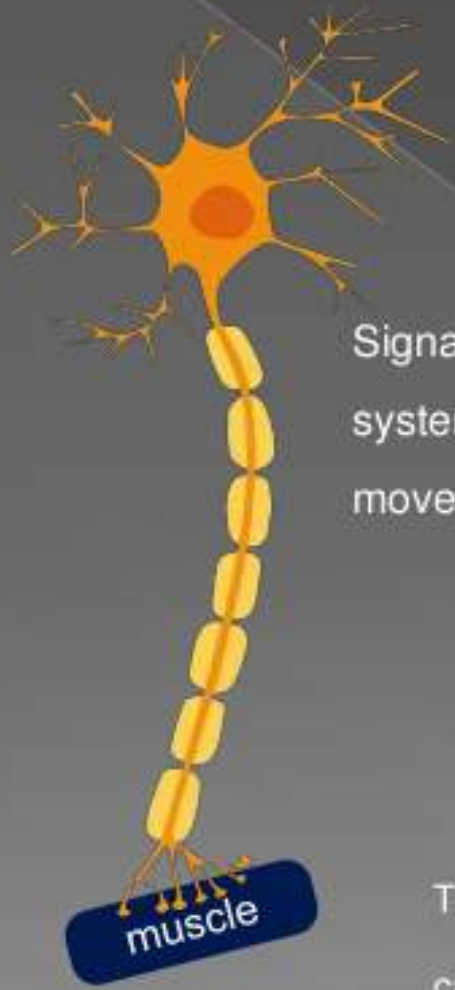
What is a neurotoxin ?

A substance that alters the structure or function of the nervous system

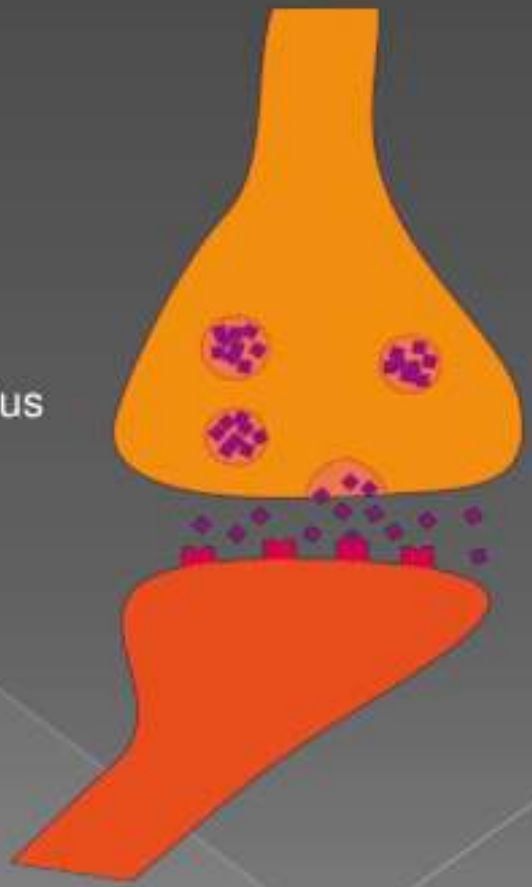
How does a neurotoxin work ?

- each of our 100 million nerve cells (***neurons***) are connected to 10,000 other neurons
- however, these neurons are ***not*** in direct contact with each other
- instead, they communicate using highly specialized chemicals called ***neurotransmitters***
- these chemicals interact with target sites called ***receptors*** located throughout the brain (and body)

The point where your muscles and nervous system meet is called the neuromuscular junction (NMJ)

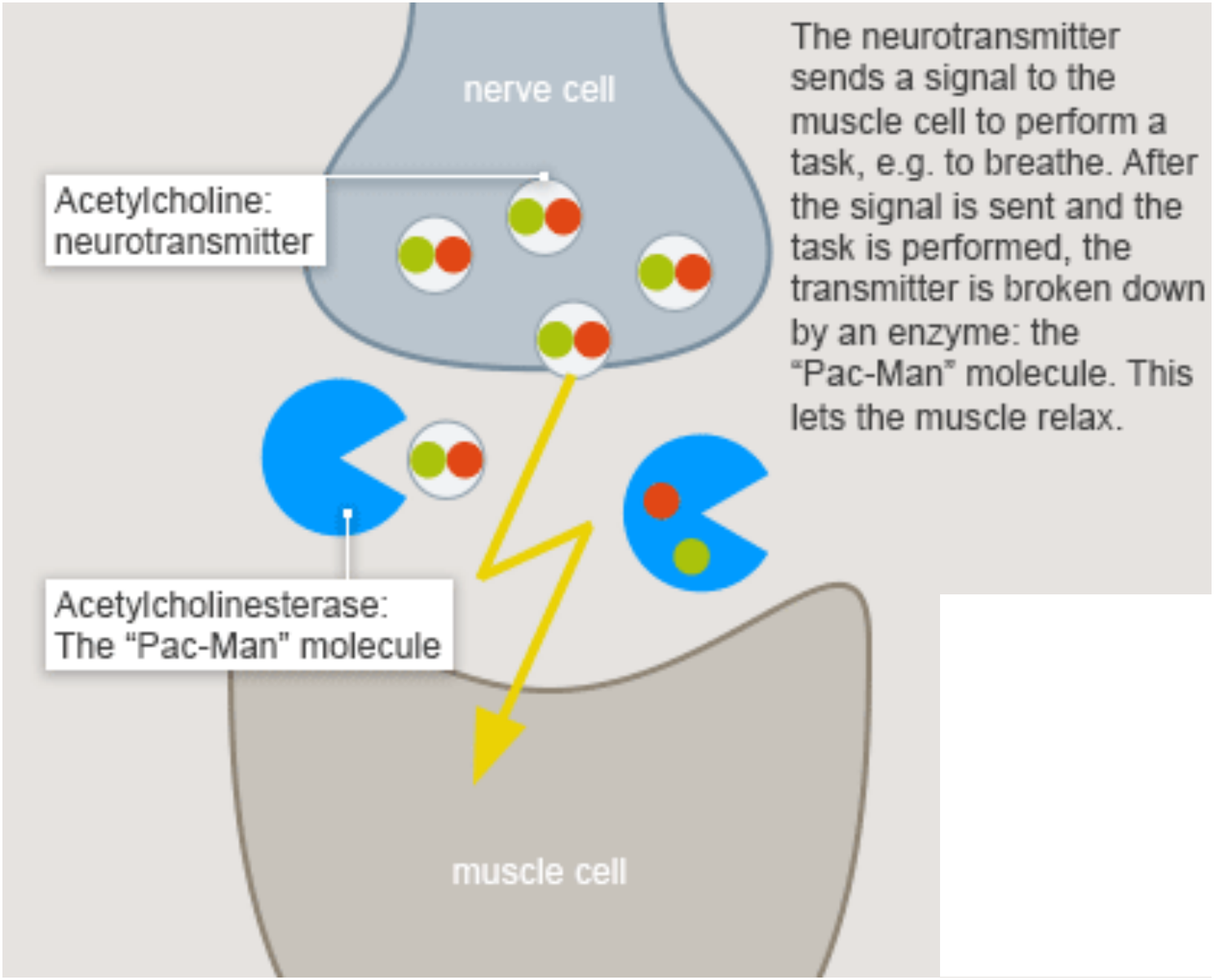


Signals sent from your central nervous system to the NMJ tell muscles to move

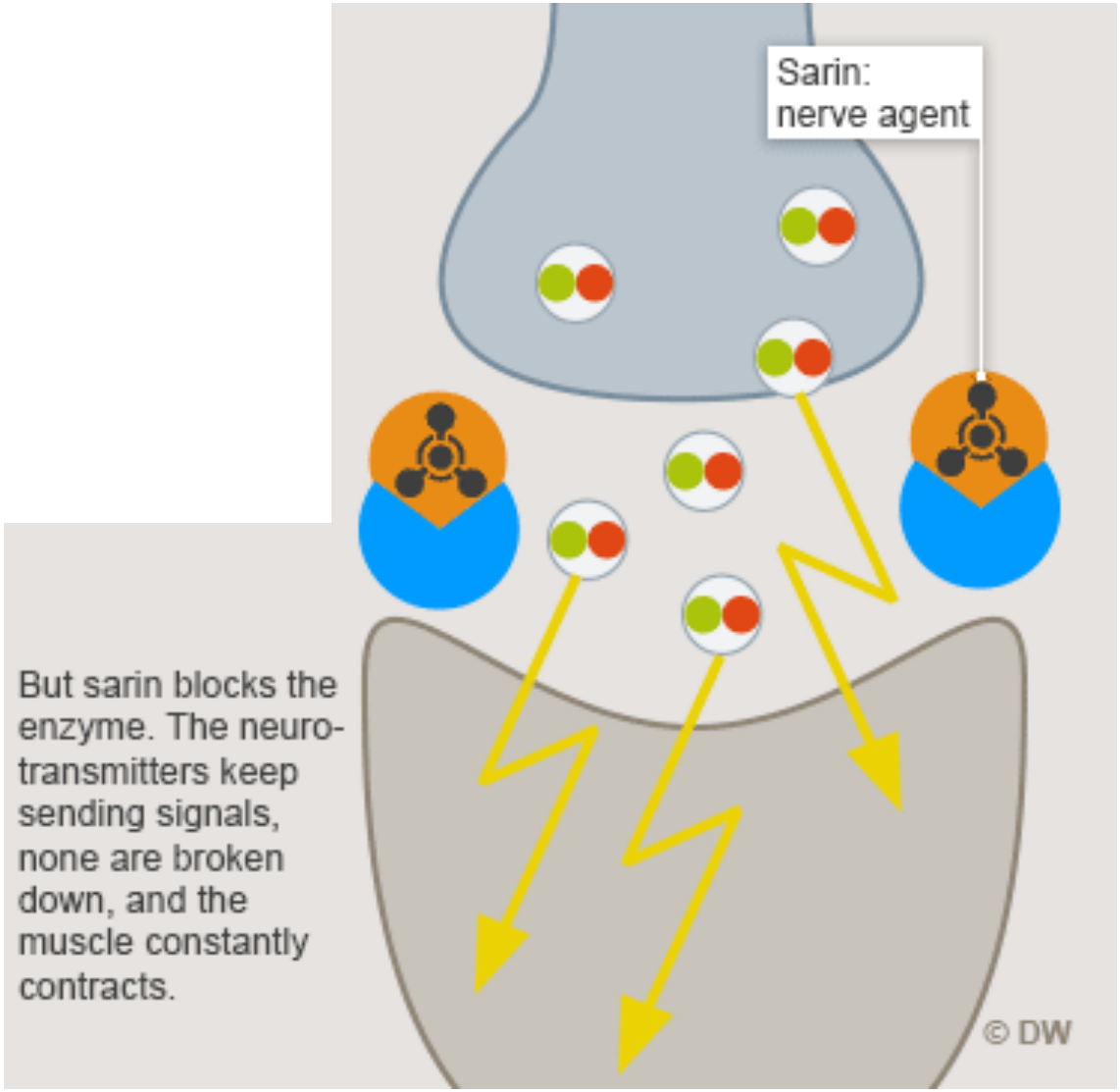


The synapses at the NMJ use a neurotransmitter called acetylcholine

Normal nerve transmission



In the presence of a neurotoxin



Health effects induced by a neurotoxin

Can include:

Limb weakness and numbness
Muscular paralysis
Vomiting
Shortness of breath
Pupil dilation
Drooling and sweating
Diarrhoea
Loss of memory, vision
.
.

DEATH

Antidotes for a neurotoxin

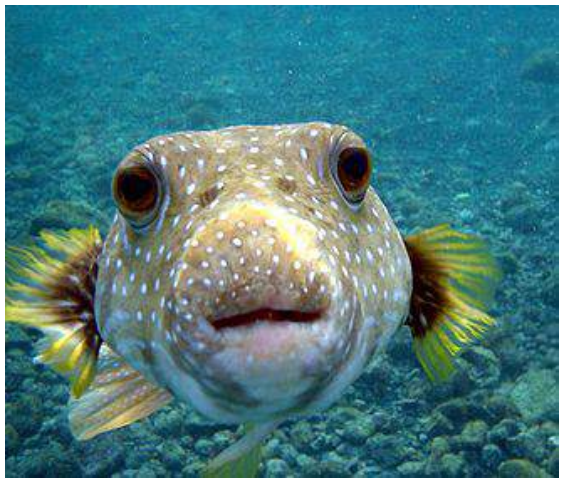
Atropine

- blocks the acetylcholine receptors
- ***but*** needs to be administered within 30-60 mins of exposure

History of neurotoxins

Natural Sources

Include:



- **tetrodotoxin** from puffer fish

- algal toxins eg. **cyanotoxin**

Synthetic neurotoxins

Germany (1930's –early 1940's)

1935 IG Farben chemical conglomerate

Gerhard Schrader in his lab at IG Farben.
Credit: Bayer AG Corporate History & Archives

German neurotoxins

- 1936 tabun (GA) death in 20 mins
- 1938 sarin (GB)- odourless, colourless, volatile liquid
  - 1 mg or 1/50 drop kills in minutes
  - 75 x more lethal than mustard gas
- 1943 soman (GC)

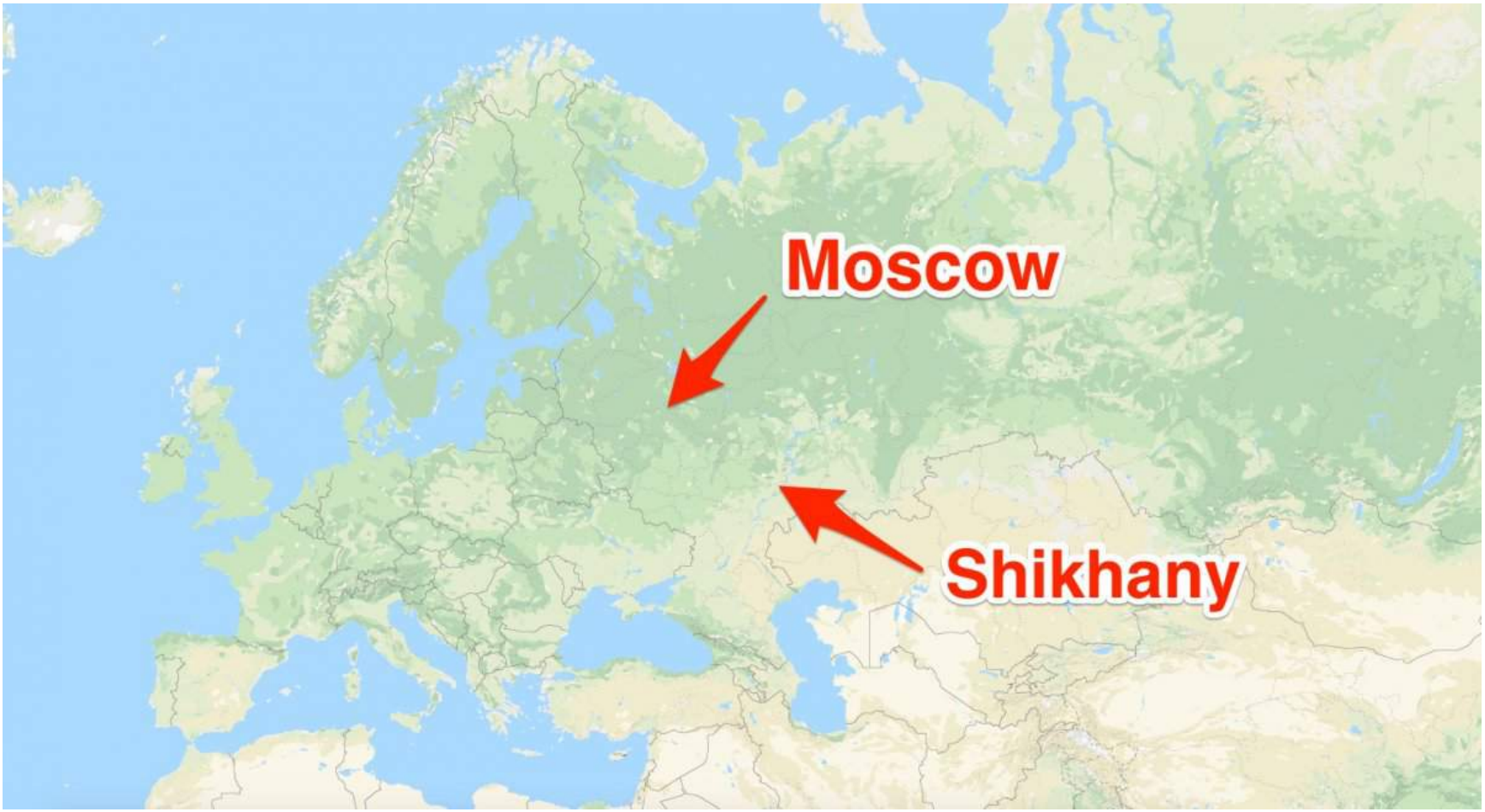
Never used by the Germans in WW II

UK/US/ Candian Neurotoxins

Early 1950's - plant protection laboratories at ICI in UK developed the V series of neurotoxins (**VX**)

- low volatility, and high cutaneous and systemic toxicity
- optimum combination of toxicity and storage stability

Russian neurotoxin programme



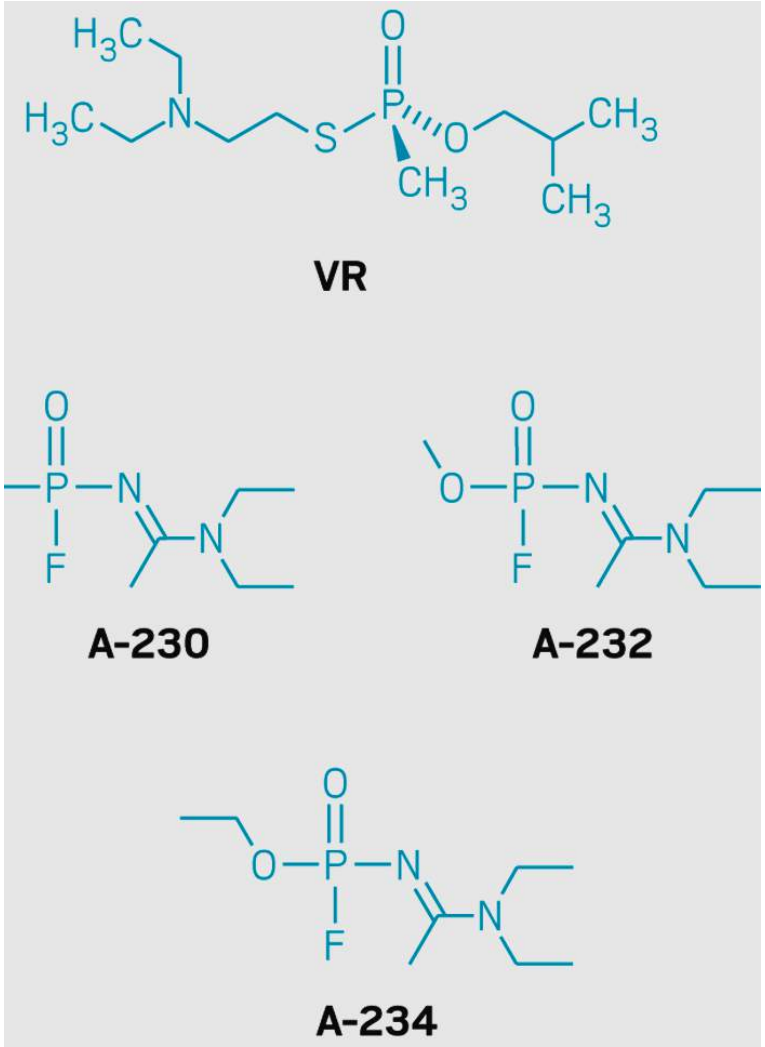
Shikhany chemical weapons research and production site

Russian neurotoxin programme

- beginning in 1987, the former Soviet Union secretly developed at the Shikhan site, the **Novichok** (Russian “newbie”)(“N-series”) nerve agents
- followed the German “G-series” of (1930s) and the UK “V-series” (1950s) of toxins

10 x more deadly than VX neurotoxins

‘Novichok’ toxins



- made from two precursor chemicals that are mixed together just before use

- these precursors could be made at pesticide or fertiliser manufacturers without arousing suspicion

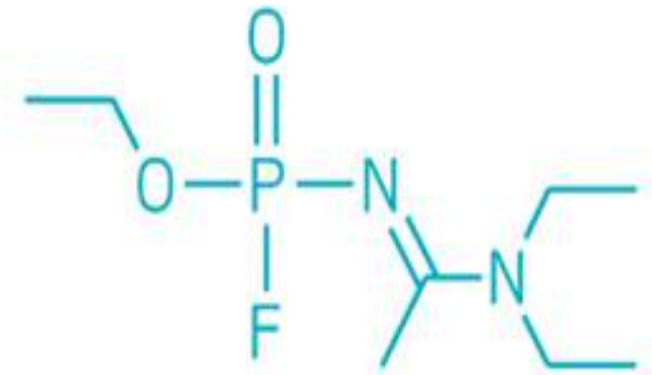
How was a Novichock compound detected in the Skripal case ?

- check for decreased acetylcholinesterase activity to determine if a nerve agent has bound to the enzyme

- identify the specific nerve agent in body samples either directly and / or indirectly

e.g. unnaturally high blood levels of fluoride, which is used to make the nerve agent

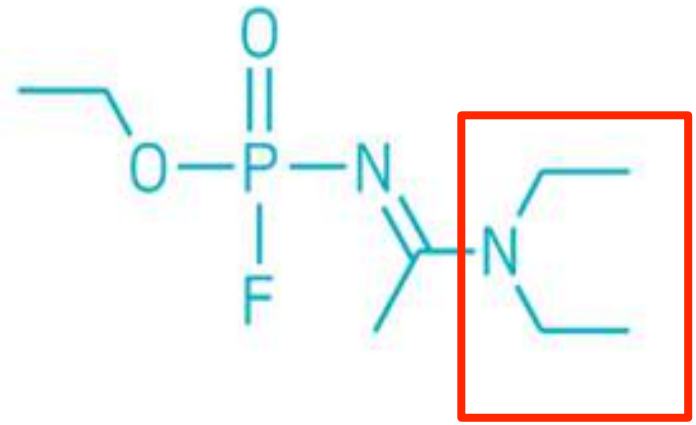
Liquid Chromatography Mass Spectrometry (LC-MS)



A-234

Molar mass

$C_8H_{18}O_2N_2F$ 193



- NC_2H_{10} (-86) 109

How was the Novichok neurotoxin used ?

- most likely in the form of a **gel** as the toxin normally has a low viscosity, only slightly thicker than water
- adding a "thickening agent" would make it adhere longer to a surface -- such as a doorknob, without evaporating
- "The degree of infectiousness is higher in the pure substance than in its gel form *but* the gel form would likely to more fully penetrate the skin”

- "Most likely, the father [Sergei Skripal] touched the door handle first. The daughter [Yulia] probably didn't touch the door handle herself but probably either brushed it lightly or he touched her with his [exposed] hand. It would appear that he was the primary source and the daughter had secondary exposure"

Current status of the Skripal case

Progressively released from Salisbury Hospital :

- 3 affected members of the public
- Detective Sergeant Nick Bailey (26 March)
- Yulia Skripal (10 April)
- Sergei Skripal (18 May)

Russia continues to deny any involvement

Permanent health effects ?

Yulia Skripal May 24 2018

July 1 18 (last Sunday !) Amesbury, Wiltshire UK

Charlie Rowley

Dawn Sturgess

- admitted to Salisbury Hospital exhibiting severe symptoms of neurotoxic poisoning

- July 4 (Wed.) **Novichock** identified as the toxin


onews. euronews. euronews
#GME
euronews. GERMANY
U.S. diplomat tells German car bosses Trump would suspend threats to impose tariffs on cars from EU if it lifts duties on U.S. cars
:01

1.22 pm RNZ Dec. 7 2017

“Government agencies are investigating potential water contamination around Ohakea and Woodbourne airbases “

- “The Environment Minister David Parker said the Defence Force has found levels of two compounds **PFOS** and **PFOA**, above guidelines on groundwater at these sites. “

- "The advice of health officials, based on what we know right now, is that there is no acute human health risk, but it is prudent to test drinking water.“

Testing began in Dec. 2017, even though the Defence Force had been told 6 months earlier in June that the levels of chemicals present at Ohakea airbase exceeded acceptable levels.

6.38 pm 7 December 2017 RNZ Report

“ People living near Ohakea and Woodborne (RNZAF) defence bases are being told not to drink their tap water for at least a month while the supply is tested for contamination “

What makes a fire ?

Fuel + O_2 ⟶ CO_2 + H_2O + **heat**

Different fuels make for different fire classes:

A : combustible materials
(wood, paper, fabric, refuse)

B : flammable liquids

C: flammable gases

D : flammable metals

C: electrical

F: cooking oils & fats

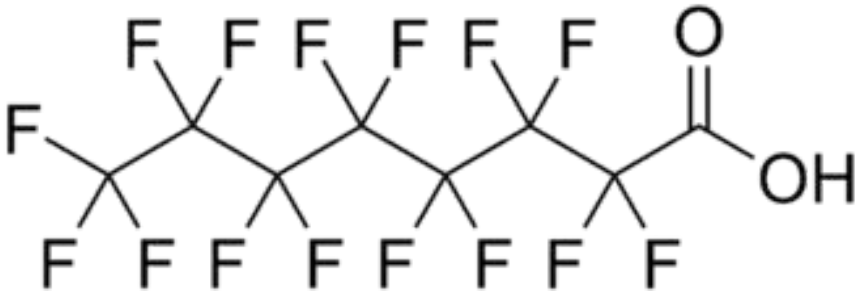
Fire-fighting strategies

Fuel + O_2 

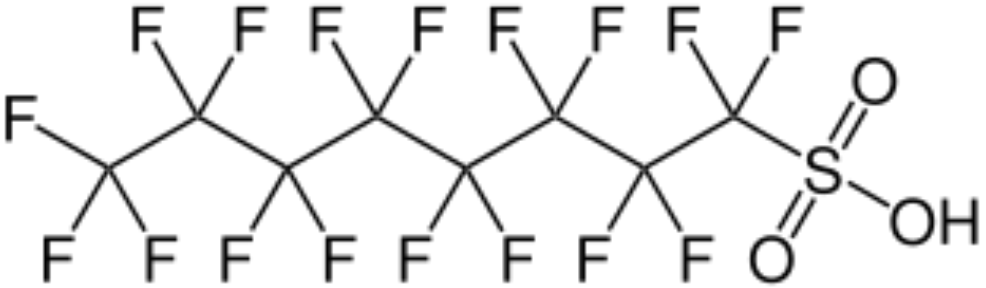
Aqueous film-forming foams (AFFSs) lower the surface tension of water, significantly enhancing its smothering capability

AFFFs used to fight Class B fires include :

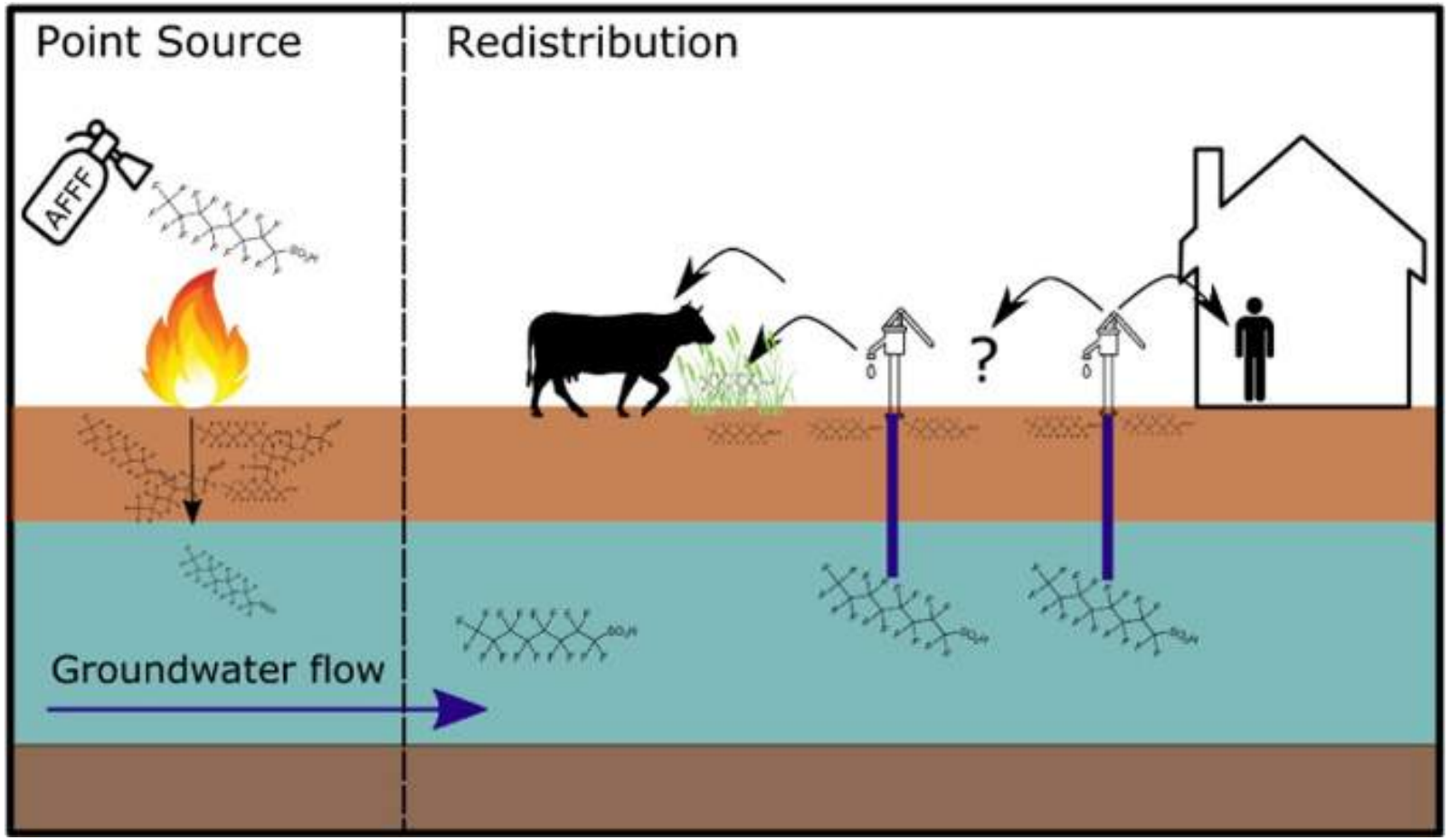
PFOA *perfluorooctanoic acid*



PFOS *perfluorooctanesulfonate*



Entry of PFOA and PFOS into the environment



Environmental Concerns arising from Use of AFFFs

Immediate: increased consumption of oxygen affecting health of surrounding organisms

Long term : Persistent, bioaccumulate and toxic

By 1993, DuPont understood that "PFOA caused cancerous testicular, pancreatic and liver tumors in lab animals"

- long-term consumption linked to increased cancer risk, high cholesterol, a lowered immune system, and issues with babies

Status of PFOA and PFOS usage in NZ

- can no longer be imported or manufactured

- neither the NZ Defence Force or the Fire and Emergency Service routinely used foams containing these compounds since 2006

BUT Auckland Airport was still using them as recently as late 2016, despite having been banned for 10 years in NZ firefighting standards

Otago Daily Times • Tuesday, May 29, 2018

Investigation into contamination from toxic foam expanded

WELLINGTON: The Government is expanding the investigation into water and soil contamination from chemicals commonly found in firefighting foam.

Responsibility for the investigation — which has been led by the defence force until now — will also pass to an across-government group.

the guidelines for drinking water.

Marlborough District Council operations and maintenance engineer Stephen Rooney now says further tests show no toxic foam contamination in Blenheim's town water supply bores.

All nine supply bores were tested, and all came back clear, he said.

Alert over foam chemical levels in water

Otago Daily Times • Saturday, June 23, 2018

AUCKLAND: A study that US officials fought to hold back has been released, showing current levels set for firefighting foam chemicals in water, both in the US and New Zealand, may be much too high.

It says the chemicals, in a group called perfluoroalkyls or PFASs, could be a threat to human health at levels seven to 10 times lower than the current guidelines.

Like the US, New Zealand is investigating mass contamination from firefighting foam residue in water supplies, as is Australia.

The draft report suggested new safe levels in drinking water of seven parts per trillion (ppt) for the chemical PFOS and 11ppt for PFOA.

New Zealand guidelines are 70ppt for PFOS and 560ppt for PFOA.

"Oh, my goodness, that is way too high," said New Hampshire state lawmaker Mindi Messmer, an environmental scientist of three decades who is running for Congress on a clean-water platform.

"Certainly if the 560 is current, that is certainly troubling."

The European Union classifies PFOA as suspected of causing cancer, and that it may damage fertility and unborn children, and damage organs through long or repeated exposure.

New Zealand should lower its levels quickly, Ms Messmer said.

"I hope that happens really soon. If I was a legislator there, I would be very much aggressively fighting for that."

On the same day the CDC report was released, New York Attorney-general Barbara Underwood launched what she called "landmark" legal action against five manufacturers of PFASs, including 3M.

She successfully ran for the New Hampshire state legislature in 2016 after working since 2014 in a task force investigating a cluster of child cancer cases linked to firefighting chemicals.

Her first Bill after her election was to lower PFAS threshold levels in water from an EPA-approved 400ppt for PFOA and half that for PFOS, down to 70ppt for both. But she said she faced stiff opposition.

"That was heavily fought by the regulators, municipal associations, and business and industry associations, and the manufacturers."

> I keep telling people . . . time is your enemy and time costs lots of money

The levels were subsequently lowered both by the state and the EPA, but not low enough, so she put through another Bill, which had just won through, to drop the levels further to 20ppt for both chemicals, she said.

"One of the most important things is to not yield to industry influence. What we saw here was a lot of industry pushback because they realised they were responsible for contaminating.

"You know, they told our Defence Department here it was basically soapsuds, that there was no health effects. And now we've found out . . . that as far back as 1974 the manufacturers knew fully that this caused health problems. So that's been hidden from the public since 1974."

Both PFOS and PFOA have been banned in firefighting foam in New Zealand since 2006, though some airports still stock them, and because they are so long-lasting, they will remain in the water for centuries.

Current foam still contains many PFASs, usually of types that have six rather than eight-chain compounds, so the molecules are smaller.

"The jury is still out on the safety of those," Ms Messmer said.

"They're actually more costly to remove — early indications of that — and there are some early health studies that I've seen that because of the smaller size of the molecules they may actually reside in the organs rather than be excreted."

Ms Messmer's new legislation added two other PFASs to the regulations, PFNA and PFHxS.

Water testing in New Zealand has included tests for PFHxS. But neither it nor PFNA, or other PFASs, are banned or regulated.

"It will be a nasty wake-up call if New Zealand do it badly or wrongly, as it will be very costly to backtrack to fix things," said adjunct professor at Murdoch University in Perth and environmental consultant Jimmy Seow.

"I keep telling people . . . time is your enemy and time costs lots of money."

Over time, PFASs in foam moved easily into water, and over time compounds in them broke down into PFOA, "hence double whammy". — RNZ

“ perfluoroalkyls (PAFSs) could be a threat to human health at levels seven to 10 times lower than current guidelines”

	PFOS	**PFOA**
NZ guidelines (ppt)	70	560
EPA guidelines (ppt)	20	20
Measured NZ levels	?	?

Questions ?

‘War of Nerves – Chemical Warfare from World War I to Al-Qaeda’

Jonathan Tucker (2006)

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