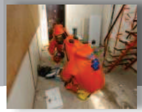


Chemical weapons detection, protection & destruction

Dr. Maarten Nieuwenhuizen - TNO


TNO

The Netherlands Organization for Applied Scientific Research

TNO = Toegepast Natuurwetenschappelijk Onderzoek

≠ The Netherlands Organization

TNO

- founded by law in 1930's
- a not-for-profit organization of 3,800 professionals
- with depth and breadth of multidisciplinary knowledge
- to sustainably:
  - strengthen competitiveness of enterprises
  - well-being of (our) society


TNO – CBRN Protection department

To serve CBRN defence and counterterrorism

- ~ 55 employees + Proqares company
- Only ‘other facility for defensive purposes’ in NL (CWC)
- Designated laboratory for OPCW
- Working for or with:
    - Netherlands Ministry of Defence
    - Netherlands’ Forensic Institute (NFI)
    - National Institute for Public Health and Environment (RIVM)
    - Other defense institutes (USA, GBR, SWE, CAN, NOR, FRA, DEU, …..)
    - Universities (Leiden, Delft, Amsterdam, Strassbourg, NC State University, …..)
    - Industry

Defence against what?

- Against the impact of the presence of a toxic agent

- Defence:
  - Casualties / contamination
  - Impact on military ambitions

- Counterterrorism:
  - Casualties / contamination
  - Societal impact such as psychosocial, economical, political, …


What is toxic?

- Paracelsus: ‘Sola dosis facit venenum’ = the dose makes the poison

Compound	Lethal amount
Kitchen salt	3.700.000
Potassium iodide	300.000
Arsenic oxide	45.000
Potassium cyanide	10.000
Mustard gas	3.000
Strychnine	500
Sarin	20
Tedrodotoxin	5
Ricin	0,02
Tetanus toxin	0,0001
Botulinum toxin	0,00003

Threat

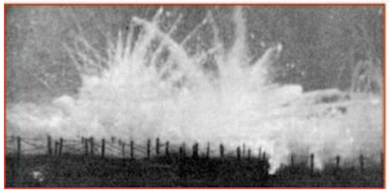
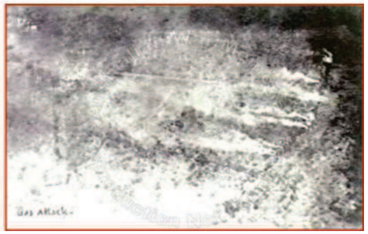
- Classical → non-classical C threat
- Chemical Weapon in the CWC focuses on classical threat

1. "Chemical Weapons" means the following, together or separately:
(a) Toxic chemicals and their precursors, except where intended for purposes not prohibited under this Convention, as long as the types and quantities are consistent with such purposes;
(b) Munitions and devices, specifically designed to cause death or other harm through the toxic properties of those toxic chemicals specified in subparagraph (a), which would be released as a result of the employment of such munitions and devices;
(c) Any equipment specifically designed for use directly in connection with the employment of munitions and devices specified in subparagraph (b).

- This talk:
  - Aspects Chemical Defence: detection, protection & destruction
  - With the wider threat (and terrorism) in mind

The beginning …….







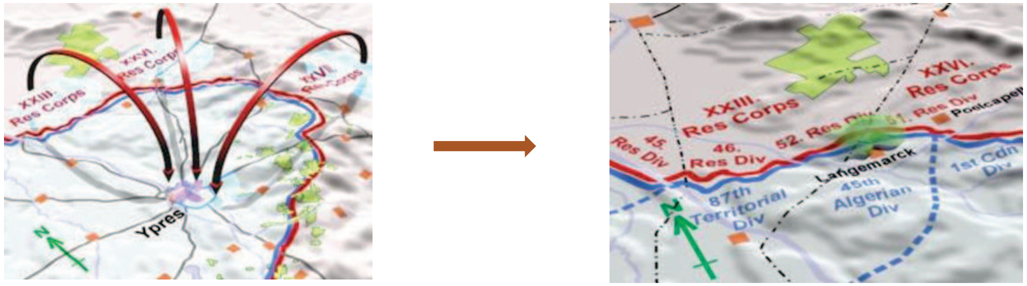


TNO innovation for life

First World War

- Trench warfare came to a hold
- Trying to force extra manoeuvring space
- Germany (Haber): chlorine in Ypres (5730 cylinders)



Langemarck on 22 April 1915 (17.00)

Later on……

- Gas → C (up till 4 generations of chemical warfare agents)
- C → NBC
- NBC → CBRN
- Warfare → Warfare and/or Terrorism

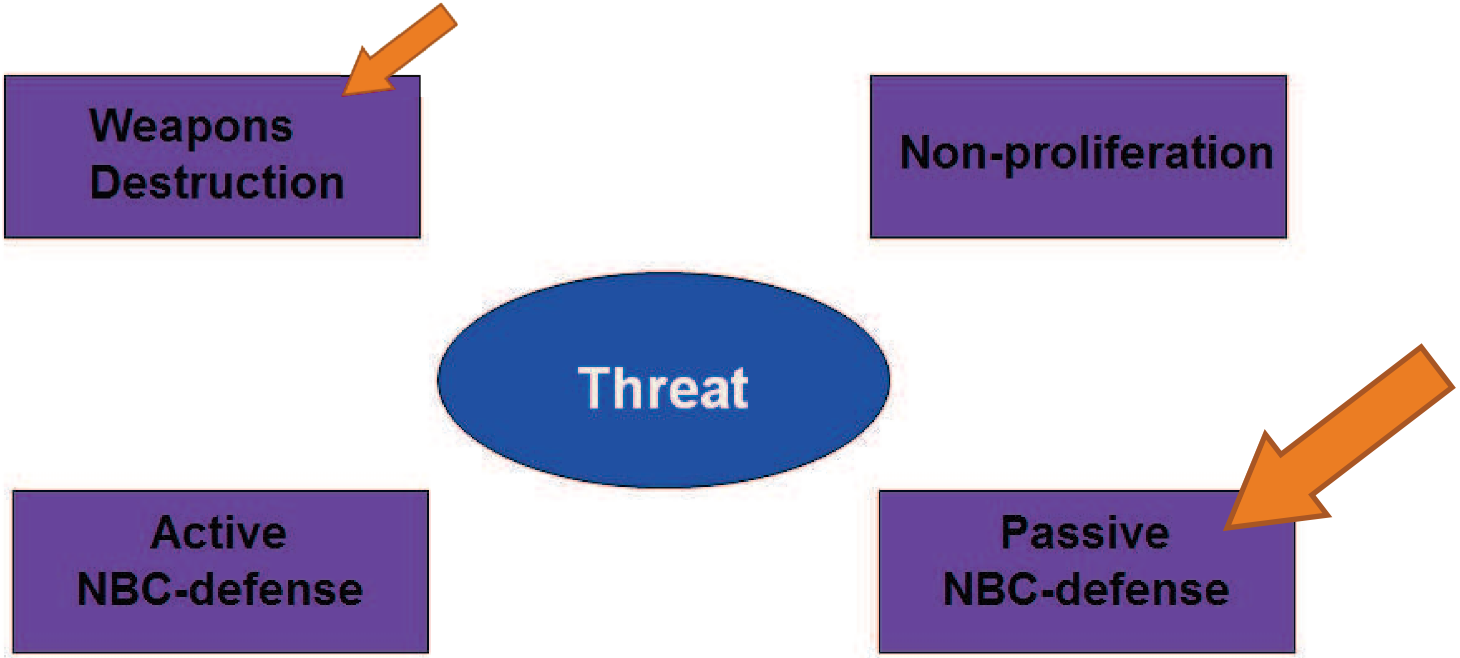
- Warfare
  - Reasonably **well defined threat**
  - Battlefield impact = casualties + contamination
  - Iraq, Syria, ……..

- Terrorism
  - Fuzzy, small amounts, **very broad threat spectrum**
  - Societal impact = casualties + psychosocial, economy, politics, …
    Tokyo, ……

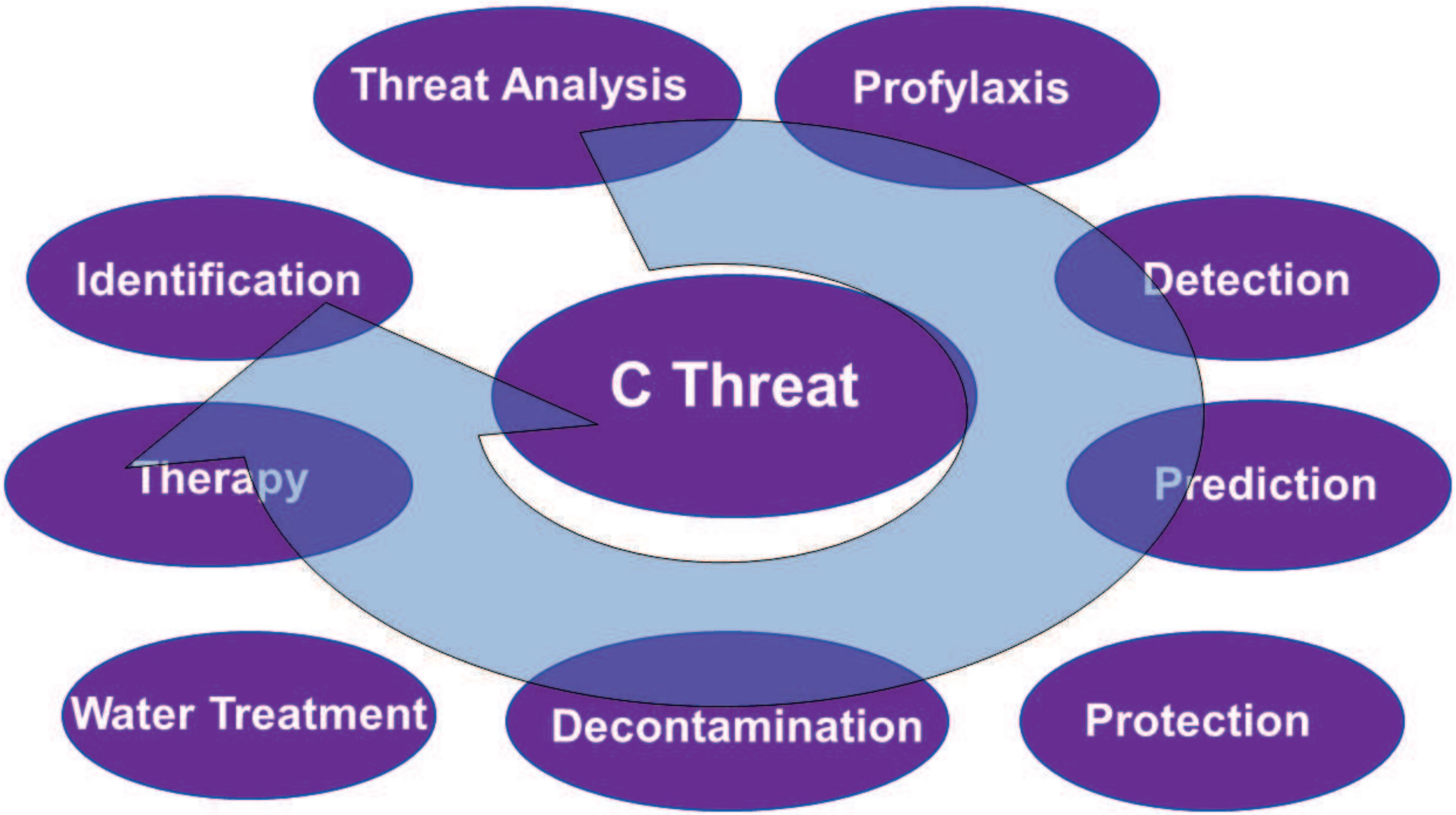
General characteristic of C warfare and terrorism

Low Probability x High Impact

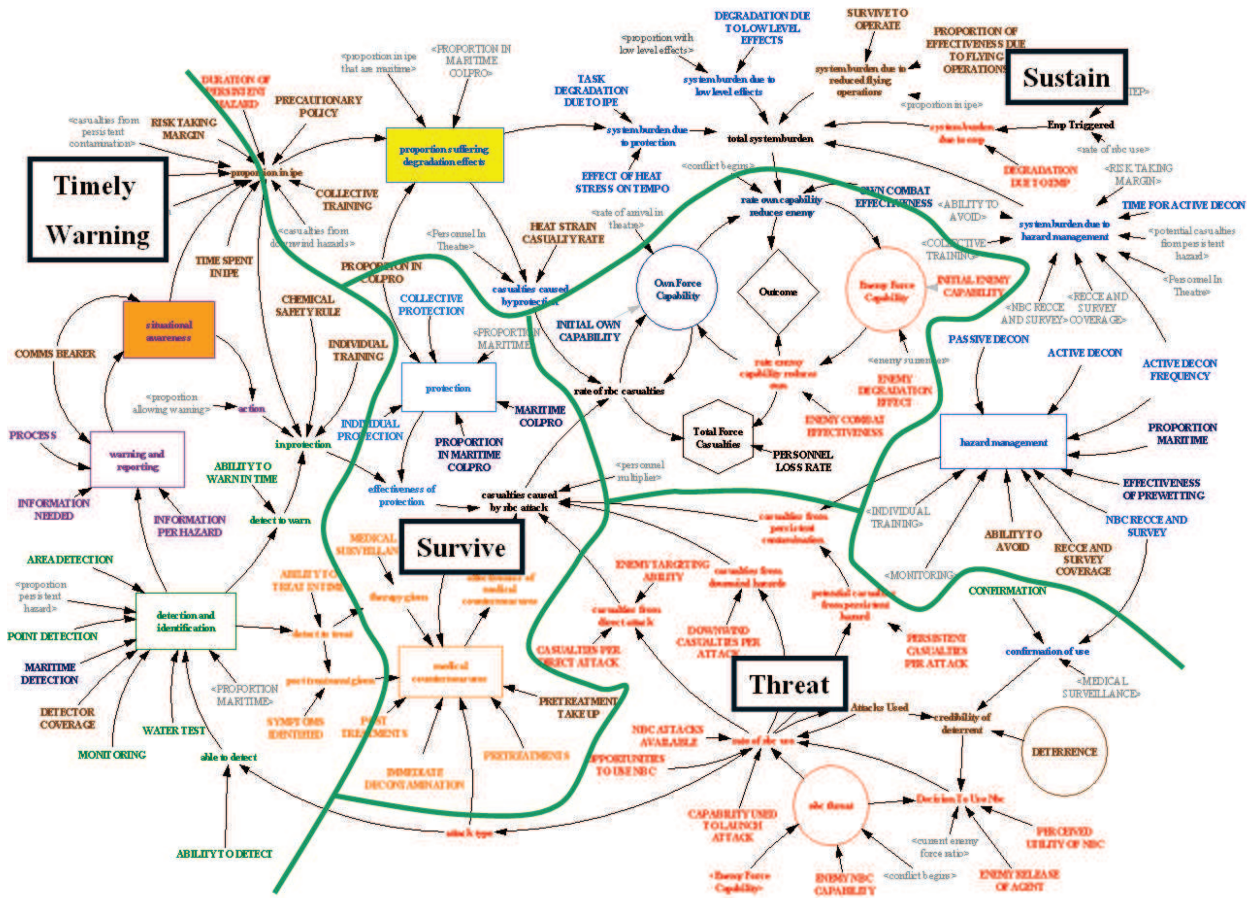
The 4 pillars




Passive Defence

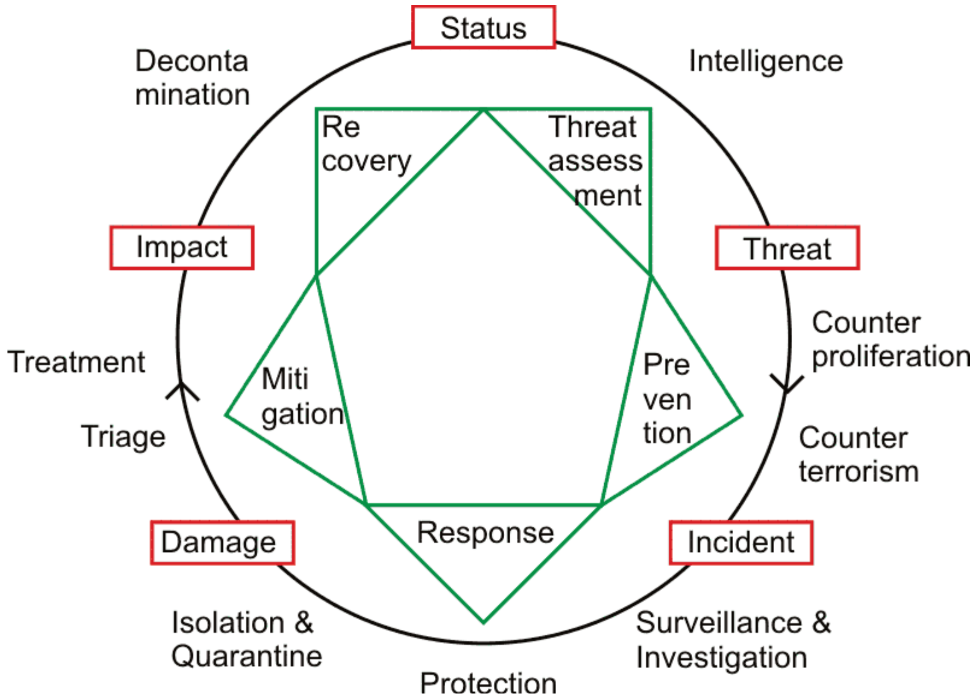


UK system description



The scary model

EU: Security Cycle

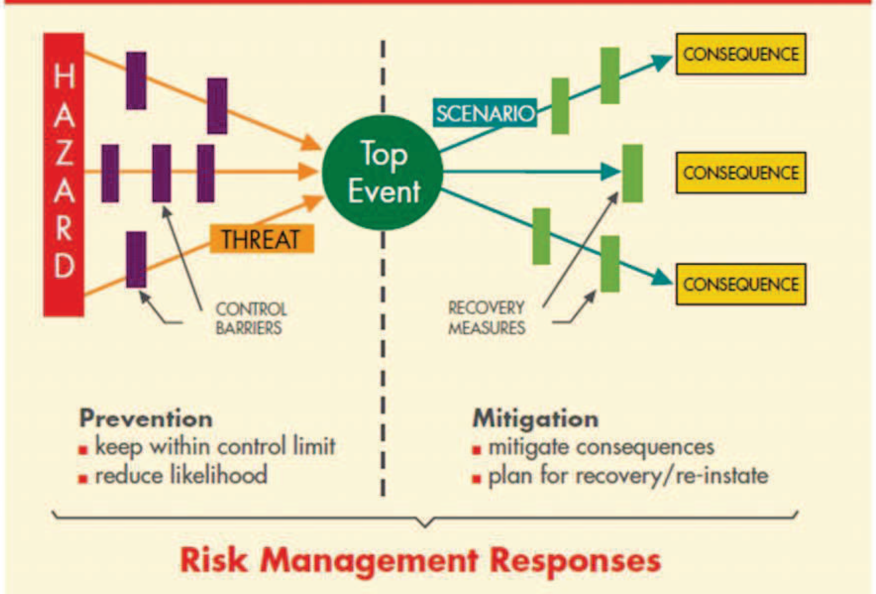


TNO innovation for life

Shell Oil: The Bow Tie concept

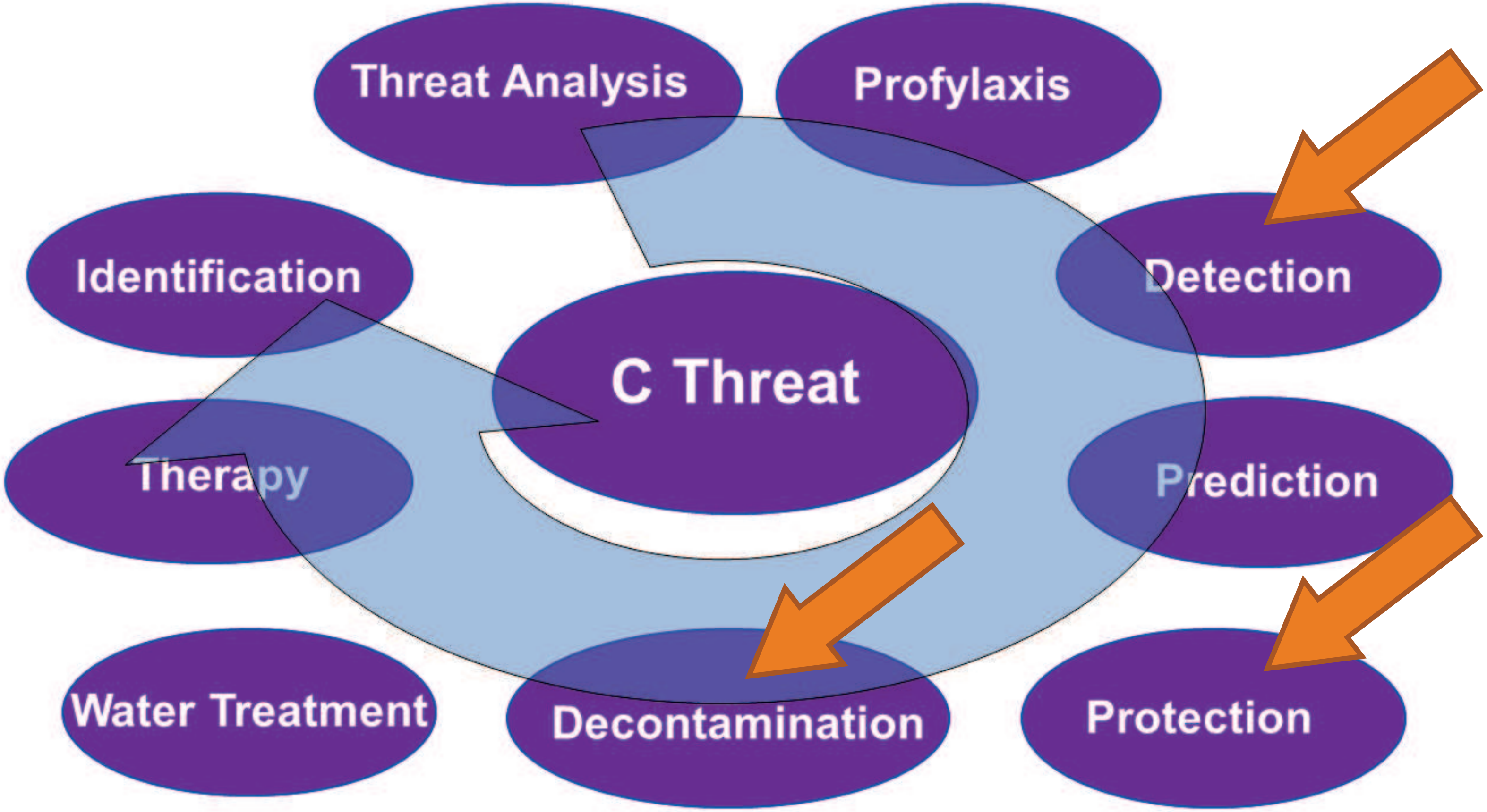
The 'Bow Tie' Model

The 'Bow Tie' Model illustrates the importance of both preventive and recovery measures in dealing with risk. Risk is defined as the likelihood that a Top Event (hazard release) will occur, combined with the severity of the consequences of the event:



Hazard:	Potential to cause harm.
Threat:	A possible cause that will potentially release a hazard and produce a 'Top Event'.
Control Barriers:	Measure to prevent threats from releasing a hazard.
Top Event:	The 'release' of the hazard, i.e. the first consequence.
Recovery Measures:	Limit the consequences arising from Top Event.
Consequence:	Event(s) that result from the release of a hazard.

Passive Defence



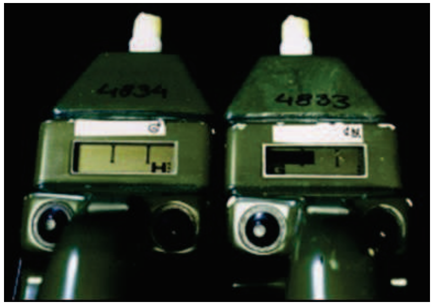
Detection

Detection, identification, diagnosis

- Smelling is not enough
- Therefore analytical technology to detect it:
  - Detection → In the field: fast, low-false alarm rate
  - Identification → In the lab: sensitive, unambiguous
  - Diagnosis → From the body to the lab, triggers therapy


Detection (1)

- Now → A myriad of technologies and products
  Military or adapted military products
  Focused on dedicated threat

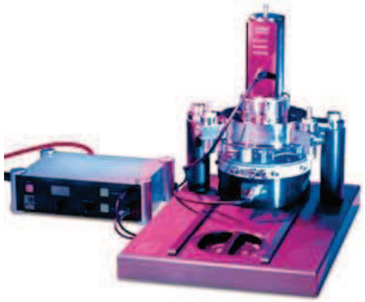




Detection (2)

- Future → Host-based paradigm (bird in the cage revisited)
  Focused on threat/hazard as-a-whole
  - living cells
  - artificial organs (stem cells, 3D printing)

→



Cultex

→

Organ printing: computer-aided jet-based 3D tissue engineering

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[3]Department of Physics and Astronomy, University of Missouri, Columbia, MO, USA
Corresponding author: Vladimir Mironov (mironovv@musc.edu).

Tissue engineering technology promises to solve the organ transplantation crisis. However, assembly of vascularized 3D soft organs remains a big challenge. Organ printing, which we define as computer-aided, jet-based 3D tissue-engineering of living human organs, offers a possible solution. Organ printing involves three sequential steps: pre-processing or development of 'blueprints' for organs; processing or actual organ printing; and postprocessing or organ conditioning and accelerated organ maturation. A cell printer that can print gels, single cells and cell aggregates has been developed. Layer-by-layer sequentially placed and solidified thin layers of a thermo-reversible gel could serve as 'printing paper'. Combination of an engineering approach with the developmental biology concept of embryonic tissue fluidity enables the creation of a new rapid prototyping 3D organ printing technology, which will dramatically accelerate and optimize tissue and organ assembly.

'Give us the tools and we will finish the job'
-Winston Churchill

Although the terms 'tissue engineering' and 'organ printing' were introduced only recently (1987 and 1999 respectively), the study of cell coalescence and tissue assembly has a much longer history and is deeply rooted in developmental biology [1]. The classic work of several generations of outstanding marine and developmental biologists studying cell and tissue coalescence phenomena [2,3], tissue affinity [4], cell adhesion [5] and especially the fluidity of embryonic tissues [6,7] built the biological foundation for modern tissue engineering. In recognition of this, special chapters on developmental biology are included in modern tissue-engineering textbooks [8]. Tissue engineering itself is now often considered to represent a type of applied developmental biology [9]. Organ printing – the application of the principles of rapid prototyping technology (i.e. layer by layer deposition of cells or matrix) – is evolving into a promising approach for engineering new tissues or organs. Here, we show how developmental biology can be applied to organ printing and describe the essential steps and elements of this novel technology. We discuss the challenging technological barriers, the possible strategies to overcome them and estimate the overall feasibility of printing 3D human tissues and organs.

'Secundum Naturam or Contra Naturam?'

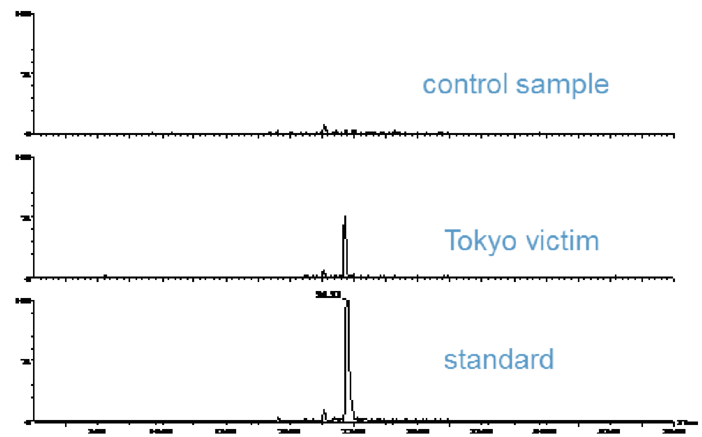
The fact that tissues, such as a blood vessel, can be successfully assembled without any synthetic polymer [10] supports our strong opinion that future progress in the field of tissue engineering will be increasingly based and dependent on the effective application of principles of developmental biology. It is safe to predict that the credo of the next generation of tissue engineers will be '*secundum naturam*' (according to nature) not '*contra natura*' (against nature). Both tissue engineering and developmental biology currently deal with the processes of tissue self-assembly, extracellular matrix deposition and accumulation, and stem cells. We believe that the fusion of these fields could, and will, lead to unprecedented achievements.

Another factor that we believe will accelerate the development of organ printing is time. Tissue engineers, as well as doctors and their patients, do not have the luxury to wait years until engineered tissues and organs become morphologically, biochemically, mechanically and functionally differentiated. Existing tissue technologies do not enable rapid assembling of tissues and organs. The timing issue can be addressed by developmental biology, in which we have learned that embryonic tissues are qualitatively and quantitatively viscoelastic fluids [6,7] with well described flow and fusion behavior. As the work by Thompson *et al.* [8] demonstrates, when embryonic avian heart tubes are initially cut into isolated myocardial 'rings' and placed on a supporting tubular framework in close apposition, they fuse and morph overnight into a single, synchronized, beating heart tube (Fig. 1a,b). The processes involved in this fusion process are still not completely understood, but the nature and time-scale of this phenomenon is inspiring for tissue engineers. Probable candidates for tissue fusion processes include remodeling of the extracellular matrix, cell migration, re-establishment of cell-to-cell contacts or combinations of all these. However, the above simple developmental biological experiment provided us with a powerful insight, which represents a starting point to the proposed concept of organ printing as laid down in present work.

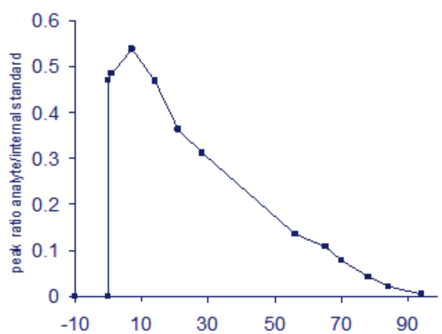
In analogy with the embryonic heart ring fusion experiment, we hypothesize that if cell aggregates are placed in close apposition within a 3D matrix, they

Diagnosis

- Persistent biomarkers in blood/urine/saliva
  - Intact agent: disappears fast
  - Metabolites: disappear fast
  - Adducts with DNA
  - Adducts with proteins (Syria case)



LC-MS analysis of blood sample of Japanese victim of Tokyo subway incident
(Fidder et al. Chem. Res. Toxicol., 2002)



Protection (1)

- Now → Dedicated products




  - Protective clothing
    - Military: Mostly permeable
    - First responders: Impermeable
  - Gas masks
    - A myriad of different products




  - The problem: Balance between protection and physiological burden

Protection (2)

- Future → Modular approach
  Reactive surfaces vs. Absorption only
  Nanotechnology for protection

Protective underwear

CBRN Uniform

Combination

Decontamination (1)

- Now
  - Basic detergent based decon solutions

Decontamination (2)

- Future
  - Self-decontaminating materials
  - Advanced powders (nanotechnology)

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Research Article

Functionalized, carbon nanotube material for the catalytic degradation of organophosphate nerve agents

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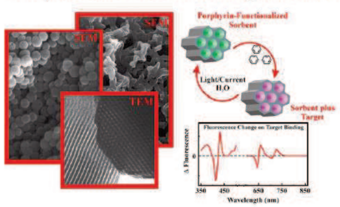
KEYWORDS
single-wall carbon

ABSTRACT
Recent world events have emphasized the need to develop innovative, functional materials that will safely neutralize chemical warfare (CW) agents *in situ* to protect military personnel and civilians from dermal exposure. Here, we demonstrate the efficacy of a novel, proof-of-concept design for a Cu-containing catalyst, chemically bonded to a single-wall carbon nanotube (SWCNT) structural support, to effectively degrade an organophosphate simulant. SWCNTs have high tensile strength and are flexible and light-weight, which make them a desirable structural component for unique, fabric-like materials. This study aims ... nanotube-derived material that can ... bric or protective material to minimize ... ve agents and to prevent accidental ... lures. Carboxylated SWCNTs were ... ined Cu-chelating bipyridine groups, ... nophosphate simulant was measured ... lized nanomaterial was characterized ... scopy. Assuming zeroth-order reaction ... ophosphate simulant, as monitored

NAVAL RESEARCH LABORATORY
TECHNOLOGY TRANSFER OFFICE

Catalytic Self-Decontaminating Materials



Advantages/Features

- Rapid target sequestration
- Stimulation of catalysis by electric current or illumination
- Tunable selectivity
- Multiple possible material formats
- Resistance to temperatures of up to 150°C
- Excellent chemical stability
- Reusable / Regenerable

Applications

- Catalytic surface coatings and fabrics
- Chemical protective clothing
- Self-decontaminating hardware
- Catalytic membranes

For more information contact:

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(202) 767-3083
rita.manak@nrl.navy.mil

Identification Number:
BIO07

The Naval Research Laboratory (NRL) has developed self-decontaminating structures based on porphyrin-embedded, target imprinted, porous, organosilicate sorbents. The materials rapidly sequester targets as a result of the affinity of the sorbent structures. Catalysis proceeds upon stimulation of the porphyrin moieties through illumination or by an applied current. This potential for dual stimulation provides the opportunity for utilization of the materials in sunlit or low light environments. Catalysis in aqueous solution and under ambient conditions in the absence of liquid water has been demonstrated. Target selectivity can be controlled through selection of porphyrin and sorbent characteristics. The spectro-photometric characteristics of the porphyrin catalytic component also offer the potential for self-reporting materials. Attachment of the materials to fabrics and surfaces has been demonstrated using standard techniques. Materials with activity against organophosphate pesticides, aromatic solvents, and nitroenergetics have been described.

References

Related U.S. patent number 7,749,438 entitled "Fluorophore embedded/incorporating/bridged molecularly imprinted periodic mesoporous organosilicas (PMOs) as recognition elements for optical sensors"

Related U.S. patent number 7,754,145 entitled "Fluorophore embedded/incorporating/bridged molecularly imprinted periodic mesoporous organosilicas (PMOs) as photo-decontamination catalysts"

"Sunlight Catalyzed Conversion of Cyclic Organics with Novel Mesoporous Organosilicas" B. Johnson-White, M. Zeinali, A. P. Malanoski, M. Dinderman. *Catalysis Communications*, 8, 1052-6 (2007).

"Porphyrin-embedded organosilicas for detection and decontamination," B.J. Johnson, B.J. Melde, P.T. Charles, A.P. Malanoski. *Proceedings SPIE Defense, Security, and Sensing: Optics and Photonics in Global Homeland Security V* (April 2009) v.7306, 73060E-1 to -11.

Licenses are available to companies with commercial interest.

technology

NEW ULTRA-STRENGTH NON-TOXIC CLEANERS FOR AFTERMATH OF TERRORIST ATTACK REVEALED BY MILITARY

5:09 PM ALTON PARRISH NO COMMENTS

Chemists with the United States military have developed a set of ultra-s
cleaners that could be used in the aftermath of a terrorist attack. The ne
are tough enough to get rid of nerve gas, mustard gas, radioactive isoto
anthrax. But they are also non-toxic, based on ingredients found in food
cosmetics, and other consumer products. A detailed evaluation of the c
appears in ACS' *Industrial* *Engineering and* *Chemistry* *Research*, a bi-r
journal: "All-Weather Hydrogen Peroxide-Based Decontamination of CE
Contaminants."

Military scientists have developed a suite of eco-friendly cleaners for ge
nerve gas, anthrax, and other toxic substances that might be used in a
attack.

Credit: iStock

George Wagner and colleagues explained that chlorine- and lye-based
decontamination agents have serious drawbacks. In addition to being p
hazardous, they can react with chemical weapons and materials in the
to form new toxic substances. If the military needed to decontaminate a
the runoff could harm people and the environment. To solve that problem, military
scientists developed the Decon Green suite of decontamination agents.

Chapter 8
Nano-Structured Solids and Heterogeneous Catalysts: Powerful Tools for the Reduction of CBRN Threats

Heterogeneous Catalysts Against CBRN Threats

M. Guidotti, A. Rossodivita, and M.C. Ranghieri

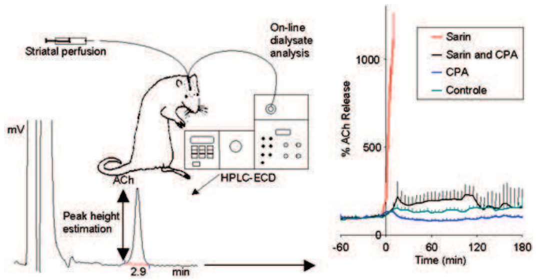
Abstract In the field of non-conventional CBRN weapons, the recent rapid development of nanotechnology and catalysis over nanosized solids provides innovative tools for the detection, protection and decontamination against these threats. By improving the efficiency of the countermeasures and by minimizing the negative effects of a deliberate use of CBRN agents, the practical application of the new technologies will readily represent a step forward in lowering the vulnerability of the civilian populations and in preventing the use of mass destruction weapons by terrorist groups or by 'rogue states' supporting terrorists' activity. In such scenario, some relevant examples of nanosystems applied to the defense from non-conventional warfare agents will be here presented and commented. The key role of nanotechnology and heterogeneous catalysis for a multidisciplinary approach in counteracting CBRN threats will be highlighted too.

Keywords Nanotechnology • Heterogeneous catalysis • Mesoporous materials • Non-conventional warfare agents • Decontamination • CBRN agent abatement


Therapy

- Very difficult subject due to the versatility of the threat
- Driven by chemical and medical diagnosis
- No dedicated solutions for all toxic agents
  - Costs of development vs. probability of events

- At TNO: focus on nerve agent therapy
  - Development of new reactivators
  - Improvement of seizure management
  - Efficacy testing of new auto injectors




Destruction

- Many activities in possessor states
- The Netherlands / TNO was involved in:
  - Destruction of former NL stockpile
    - Obong, Indonesia
  - Assistance Russian demil programme
  - Participation in UNSCOM