Environmental Applications of Particle Accelerators

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- Waste water and sewage sludge, including pharmaceuticals & microplastics
- Exhaust gases from marine diesel engines
- Ship ballast water
- Seeds and bulbs
- “Cleaner” sterilisation, avoiding the use of chemicals

- Work carried out in collaboration with Institute of Nuclear Chemistry and Technology in Warsaw, who lead the world in this area

Basic Process

- Use of accelerated electron beams
- In water:

$H_2O \rightarrow [2.7]\ OH\bullet + [2.6]\ e^-_{aq} + [0.6]\ H\bullet + [2.6]\ H_3O^+ + [0.45]\ H_2 + [0.7]\ H_2O_2$

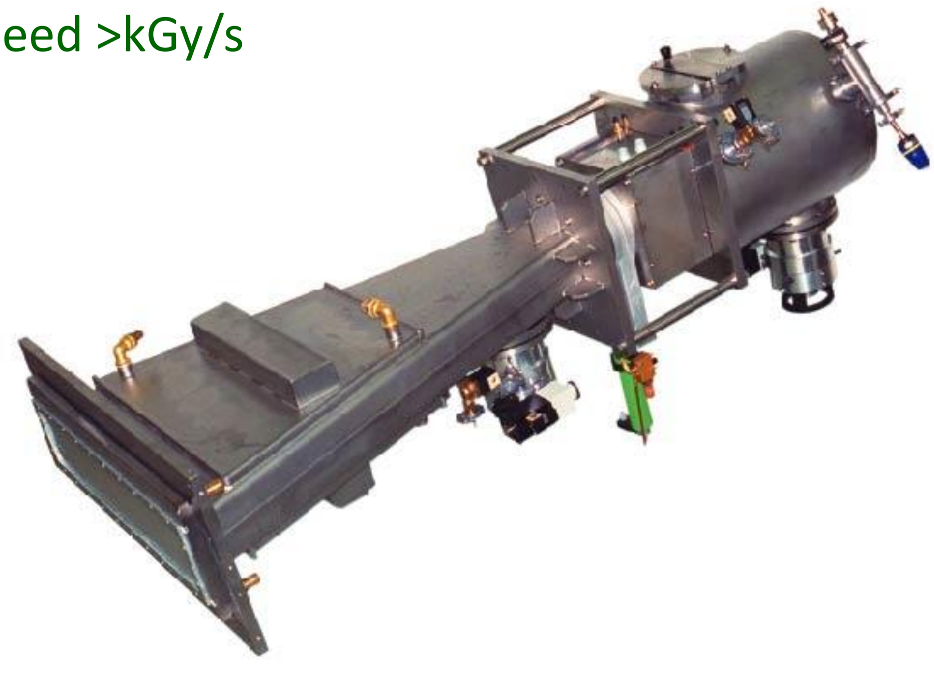
- G-value: molecules/100 eV

- In living organisms:
  - Radicals react with and damage cell DNA
  - Results in cell death
  - Same as cancer therapy with x-rays
- In everything else
  - Various reactions with organic and inorganic molecules
  - More complex
  - But usually results in the breakup of the molecules

Accelerators Used

- Beam energy:
  - ~300 keV to 10 MeV
  - Depends on penetration depth required
  - Lower is better
- Beam current:
  - As high as possible
  - Dose rate ~current
  - Cancer therapy: 2 Gy/min; we need >kGy/s

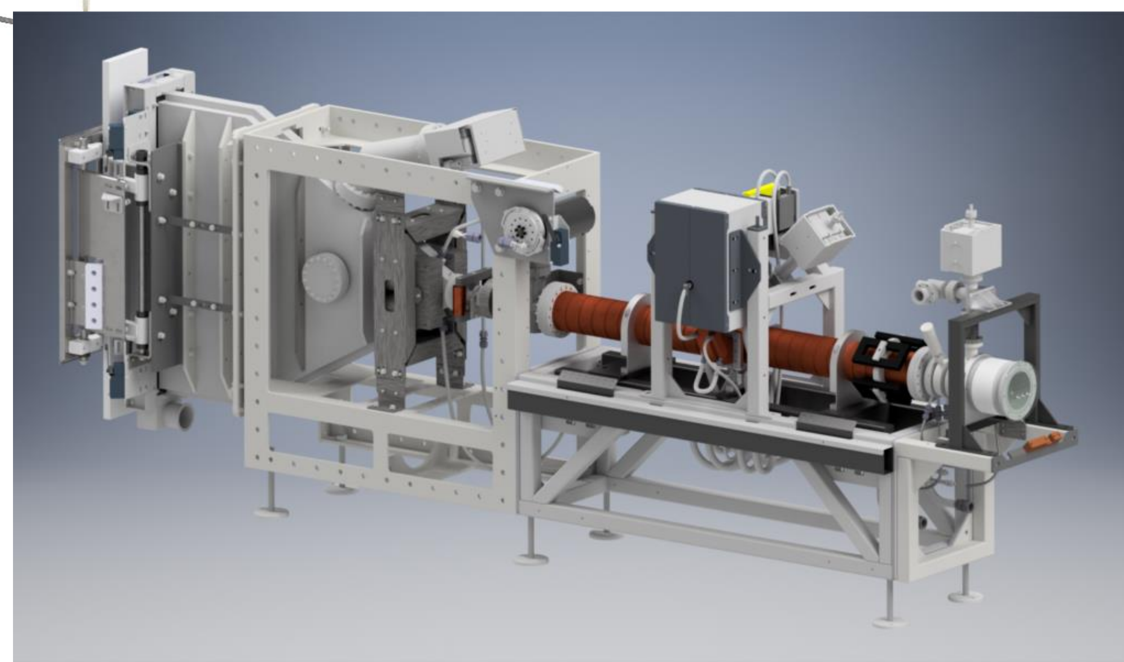
300 keV
Electron Cross-linking



Accelerators Used

5 MeV
IBA

10 MeV
Mevex

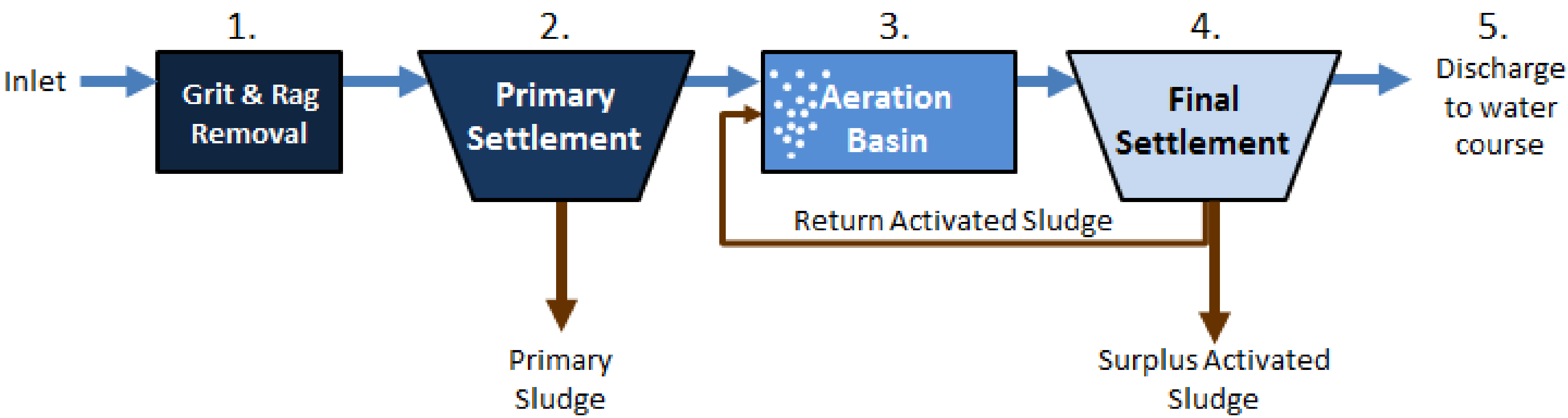


Microorganisms

- Include bacteria, viruses, archaea, fungi, algae, protozoa,etc
- Oldest evidence: presence in 3.45B year old Australian rocks
- Live in almost every habitat from poles to equator
  - 7km below Earth surface
  - Deep sea
  - High temperature: 130°C; low temperature: -17°C
  - Up to 1000 atmosphere
  - Can survive for extended periods in vacuum
  - Some are radiation resistant, up to 5 kGy
- Responsible for killing more humans than anything else by far
  - Influenza, malaria, plague, TB, cholera, polio, etc
- They can evolve very rapidly:
  - Influenza, malaria, etc
  - AMR
- They should not be under-estimated!

Sewage Sludge Treatment

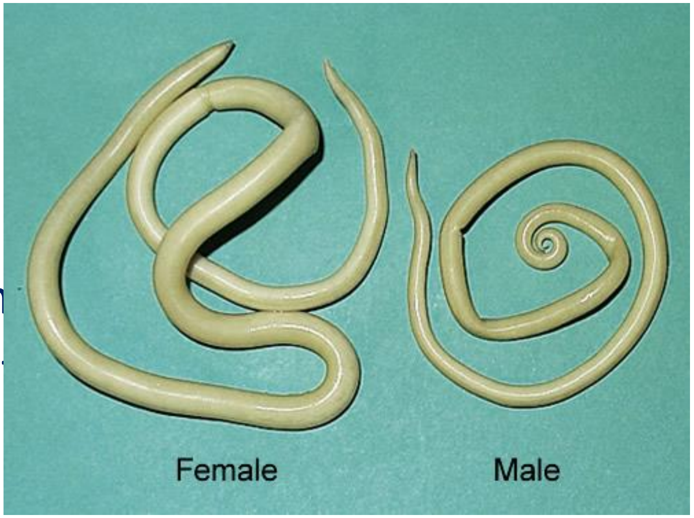
- Municipal waste water treatment plant

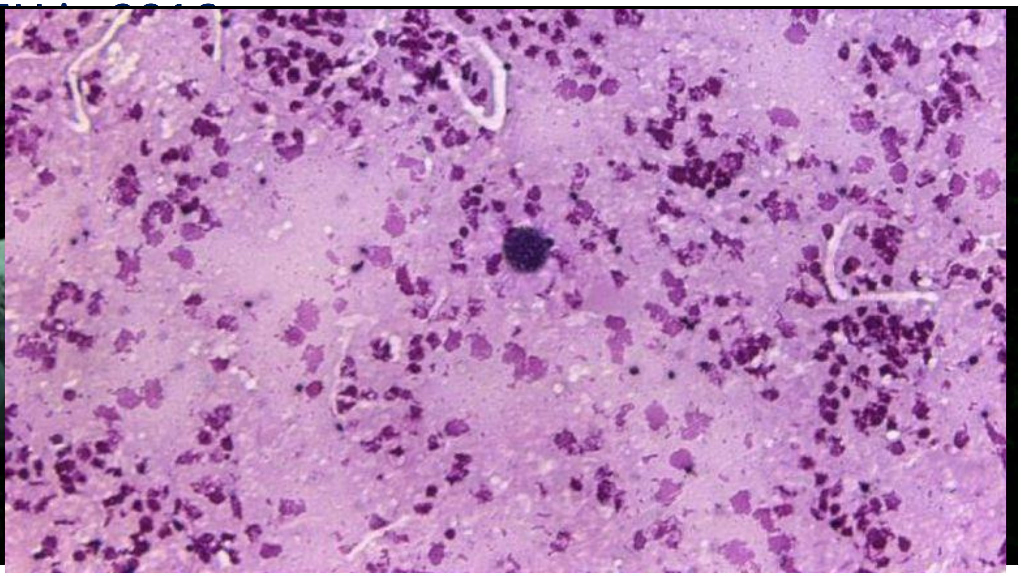


- Sludge: highly contaminated – bacteria, viruses, parasite eggs, micro-plastics, pharmaceuticals, PCP, etc
- Developed world: difficult to dispose of
- Developing world: major source of ill-health and death

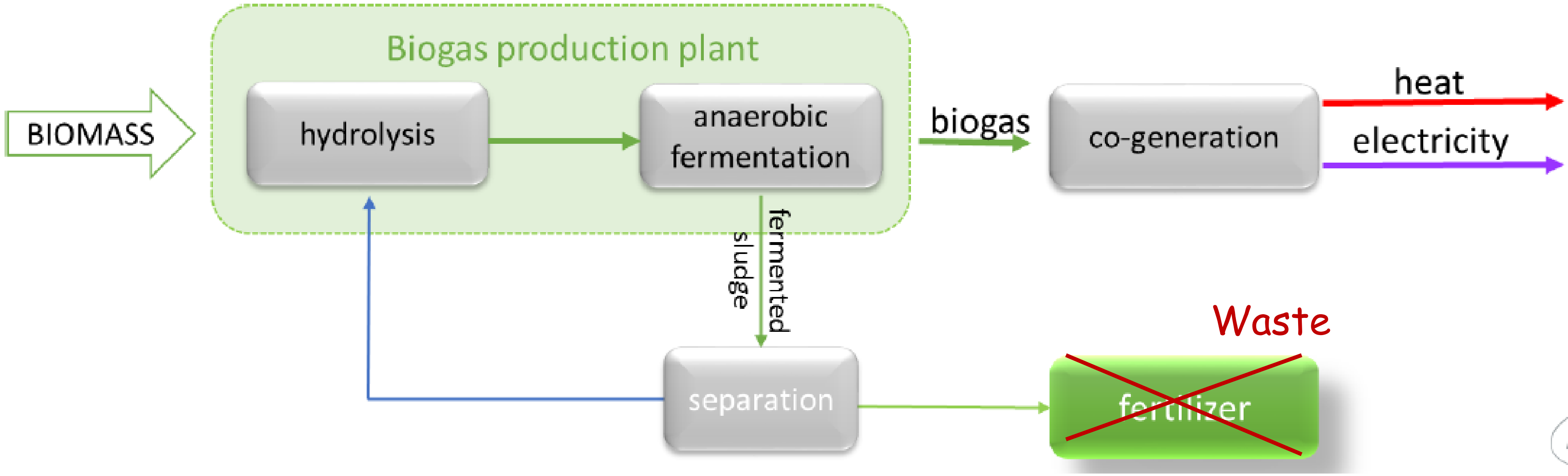
Diseases Related to Poor Sewage Sludge Treatment

- Ascaris parasites: 22% of world population have these -
  - African countries: 40-98%
  - Southeast Asia: 73%
  - Central and South America: 45%
  - United States: 2%
- Entamoeba histolytica: >500M people have th
- Giardia lamblia: most common parasite in US - Oregon
- Toxoplasma gondii: causes 3500/annum birth
- Salmonella spp: 94530
- Escherichia coli: 6378 (S
- Shigella: ~300000 cases





Anaerobic Digestion



- *Anaerobic digestion:* micro-organisms break down organic matter
- Typically runs at 35-39°C, takes around 20 days
- Outputs
  - biogas: only 10% efficient
  - digestate: poor quality "fertiliser"
  - 50% less organic material

Digestate use

- EU restrictions:

Table 7: Safe Sludge Matrix

Crop Group	Untreated Sludges	Conventionally Treated Sludges	Enhanced Treated sludges	
Fruit	X	X	✓	10 month harvest interval applies
Salads	X	X (30 month harvest interval)	✓	
Vegetables	X	X (12 month harvest interval)	✓	
Horticulture	X	X	✓	
Combinable and Animal Feed Crops	X	X	✓	

Digestate use

- Implemented by different countries in different ways
  - UK: 90% AD; SSM used directly
  - Germany: Much AD, but sludge can't be used at all, incineration required
  - Latvia

    Sewage sludge shall not be dispersed in the period from 15th of December until 1st of March.

    Sewage sludge and compost may not be dispersed and cultivated:

    - on slopes the sloping angle of which is more than 7°;
    - on frozen or snow-covered soil;
    - in flood and flood endangered territories;
    - closer than 100 m from individual water intakes;
    - closer than 100 m from residential houses, food processing facilities and food stocks; or
    - closer than 50 m from the shoreline of a waterbody or watercourse; and in locations where it is prohibited in accordance with the regulatory enactments regarding protective territories.

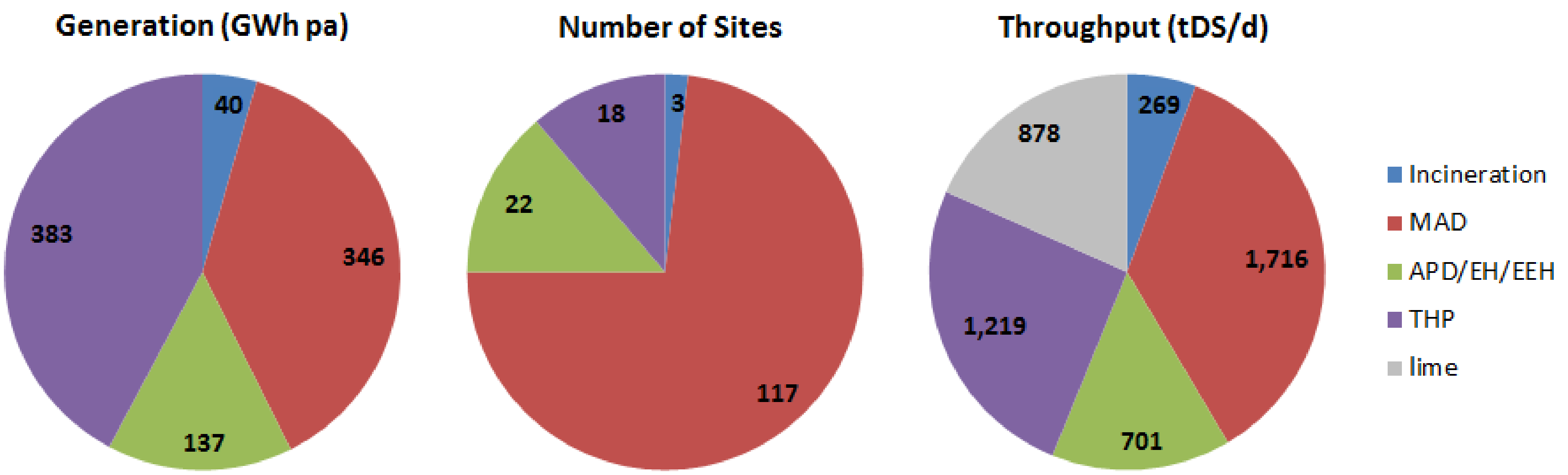
    Sewage sludge and compost may not be utilized:

    - for growing vegetables and berries in covered areas;
    - for growing potatoes, vegetables and berries in open field with area less than 0.10 ha;
    - as surface fertiliser and row fertiliser during the vegetation period of food and animal feed crops; and
    - as surface fertiliser in grazing in the year of use thereof, except for cases when the sward is renewed by the re-ploughing of soil and sewage sludge and the compost thereof are cultivated into the soil.

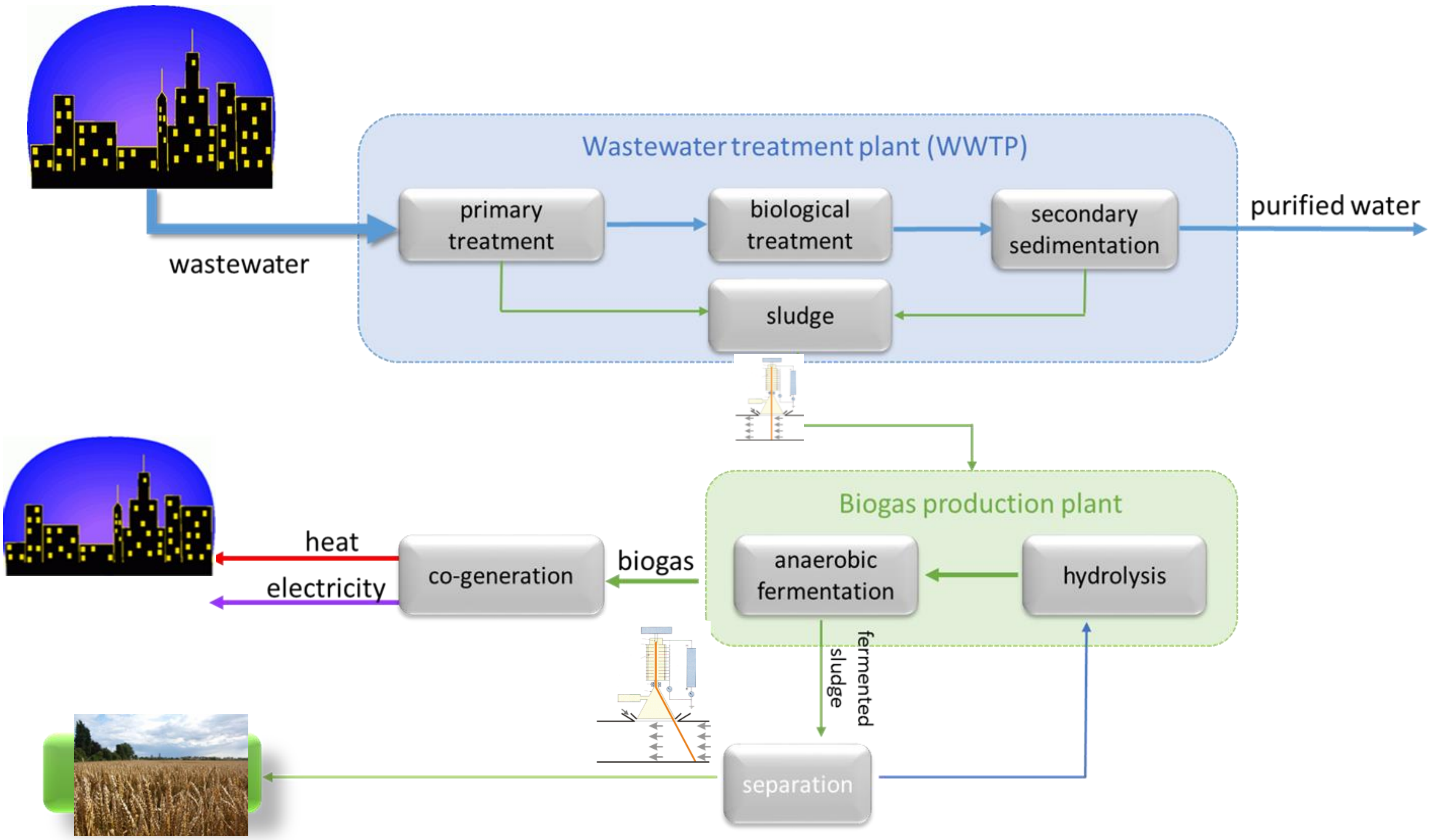
  - Poland: 50% AD, rest is stored at WWTF
  - Ukraine: No AD, 100% is stored at WWTF, ~1 billion tons already

Enhanced Treatments

- Thermal Hydrolysis Pre-treatment (THP): ~15% bio-gas efficiency
- Biological hydrolysis: Acid Phase Digestion (APD) & Enzymatic Hydrolysis (EH)
- UK 2015:



Electron Beams



Pre-AD

	Reactor A (unirradiated sludge)			Reactor B (1 kGy)			Reactor C (3 kGy)			Reactor D (6 kGy)		
Parameter	20 d	15 d	10 d	20 d	15 d	10 d	20 d	15 d	10 d	20 d	15 d	10 d
OLR (g VS/[L·d])	1.06	1.33	1.84	0.94	1.31	1.92	0.94	1.25	1.90	0.96	1.25	1.87
OLR (g COD_{sol}/[L·d])	50.3	62.0	87.0	87.9	110.9	143.6	102.5	149.8	198.5	114.5	163.7	224.1
Reactor pH	7.1	7.3	7.1	7.0	7.1	6.8	7.0	7.1	6.9	7.0	7.1	6.9
Reactor alkalinity (mg/L as $CaCO_3$)	2050	2410	1980	2220	2350	2100	2380	2500	2150	2300	2460	1940
Influent VS (%)	1.92	2.15	1.81	1.91	1.96	1.83	1.88	1.91	1.85	1.90	1.89	1.85
Influent COD_{sol} (mg/L)	890	910	870	1675	1690	1550	2040	2270	2105	2290	2480	2350
VS removal (%)	36.7	32.5	22.3	51.4	42.0	30.2	56.7	48.1	32.3	60.3	50.4	38.2
Biogas (L/[m^3·d])	82	95	65	155	180	175	230	260	235	236	290	231
Methane contents (%)	69	65	59	68	66	60	72	69	61	71	64	62
VFA (mg/L as C_2)	97	102	100	123	109	121	129	135	154	152	156	142
SRF ($\times 10^{12}$ m/kg)	32.0	39.7	70.1	28.7	34.4	72.1	26.8	36.2	80.4	29.5	44.4	94.5

[a]SDs were less than ±10% over average value.

K. Shin and H. Kang, Appl. Biochem. Biotechnol., vol. 109, pp. 227–239, 2003

Pre-AD

- Has been tested in laboratories and pilot plants
- Two full scale plants under construction in Poland

MWWTP Józefów

Pre-AD

Process	Cost per TDS (2005 US$)	Value (2005 US$)
Incineration/co-generation	600 to 1100	3 to 30 as ash reuse
THP	500 to 1500	30 to 150 as a fuel and fertiliser
Anaerobic digestion	350 to 650	30 to 200 as a fuel and soil amender
Aerobic digestion	350 to 700	30 to 70 as a soil amender
Advanced alkaline stabilisation	350 to 550	80 to 120 as a Ag lime agent
Acid stabilisation/disinfection	350 to 550	30 to 70 as a soil amender
E-beam treatment	100 to 250	30 to 70 as a soil amender

Post-AD

- Target pathogen reduction to meet "organic" requirements: 6 orders of magnitude
- AD:
  - Standard: ~2
  - THP, etc: ~4
- Electron beams

Microorganism	D_{10} Value (kGy)
Acinetobacter radioresistens	1.3-2.2
Ascaris ova	1.6-7.9
Aspergillus fumigatus	0.6
Aspergillus niger	0.5
Bacillus pumilus	1.4 to 1.8
Bacillus subtilis	0.6
Brucella abortus	0.15
Campylobacter sp.	< 0.2
Candida albicans	0.9
Clostridium botulinum	1.4 to 4.2
Clostridium difficile	0.9
Clostridium sporogenes	1.6 to 2.2
Clostridium tetani	2.4
Cryptococcus albidus	2.7
Cryptococcus laurentiii	3.1
Cryptococcus uniguttilans	1.4
Escherichia coli	0.3-0.4
Klebsiella pneumonia	0.12-0.28
Lactobacillus brevis	1.2
Listeria monocytogenes	0.62
Micrococcus radiodurans	2.2
Mycobacterium fortuitum	0.6
Mycobacterium tuberculosis	0.3
Pseudomonas spp.	0.06
Poliovirus	1.85
Saccharomyces cerevisiae	0.5
Salmonella muenster	0.6
Salmonella sp.	0.6
Salmonella typhimurium	0.2 to 1.3
Shigell dysenteriae	0.6
Staphylococcus aureus	0.2-0.5
Streptococcus faecalis	1.56
Yersinia enterocolitica	0.2
Vibrio cholerae	0.48

Post-AD

- Pharmaceuticals and personal care products

Compounds	Subgroup/Class	Conc. (mM)	Radioactive source	Removal efficiency (absorbed dose)	Mineralisation (absorbed dose0
Metronidazole	Antibiotics/Nitroimidazoles	0.14	^{60}Co	50% (0.4kGy) 90% (1.4kGy)	5% (0.7kGy)
Chloramphenicol	Antibiotics	0.1	^{60}Co	100% (1.5kGy)	60% (7-10kGy)
Sulfadiazine	Antibiotics/Sulfonamide	0.04	^{60}Co	95% (1.1kGy)	Not given
Sulfamethazine	Antibiotics/Sulfonamide	0.07	^{60}Co	95% (1.0kGy)	9% (1.0kGy)
Sulfamethoxazole	Antibiotics/Sulfonamide	0.1	^{60}Co	100% (5.0kGy)	58% (10kGy)
Tetracyclines	Antibiotics/Tetracycline	0.05	^{137}Co	100% (0.6kGy)	27% (2.0kGy) 51% (4.0kGy)
Penicillin V penicillin G amoxicillin with	Antibiotics/β-Lactam	1.0	^{137}Co	81% (~12kGy) 92% (~12kGy) 95% (~12kGy)	Not given
Cefaclor	Antibiotics/β-Lactam	0.08	^{60}Co	100% (1.0kGy)	20% (60-1000kGy)
Cytarabine	Antineoplastic drug	0.04	^{60}Co	100% (0.6kGy)	40% (1.0kGy)
Ibuprofen	Anti-Inflammatory drug	0.14	^{60}Co	100% (1.1kGy)	70% (1.1kGy)
Ketoprofen	Anti-Inflammatory drug	0.4	^{60}Co	100% (2.0kGy)	~70% (5kGy)
Diclofenac	Anti-Inflammatory drug	0.5 0.14	^{60}Co EB	100% (2.0kGy) 100% (0.5kGy)	80% (20kGy) 6.5% (2.0kGy)
Acetovanillone	Anti-Inflammatory drug	0.5	^{60}Co	100% (15kGy)	50% (40kGy) 100% (80kGy)
Acetylsalicylic acid	Anti-Inflammatory drug	0.5	^{60}Co	70% (6.0kGy)	50% (30kGy, 1.0mM)
Paracetamol	Antipyretic drug	0.066	^{60}Co	100% (8.0kGy)	50% (40kGy)
Diphenolic acid	EDC	0.35	^{137}Co	90% (0.6kGy)	73% (1.0kGy)
p-nonylphenols	EDC	0.01	^{60}Co	100% (20Gy)	20% (37.5Gy)
17 β-estradiol	EDC	$1.8x10^{-6}$	^{60}Co	98% (10Gy)	Not given
Iopromide	X-Ray contrast agent	0.1	EB	90% (20kGy)	40% (150kGy)
Metropolol	B-blocker	3.75	EB ^{60}Co	97% (28kGy) 89% (25kGy)	94% (28kGy) 74% (25kGy)
Clofibric acid	Lipid regulator	0.5	^{60}Co	100% (5.0kGy)	80% (40kGy)

Emerging Problems

- And those which look closest to resulting in new legislation
- Anti-microbial resistance:
  - Sludge plants are an important source of growth
  - No clear method for dealing with this
  - Except electron beams
  - Measurements to demonstrate part done
  - E-beam facility being added to largest pharma plant in China
- Microplastics

Microplastics

- <5mm in size (<1µm: nanoplastic – very hard to measure)
- Really interesting topic!
- Main source: break up of macroplastics
- Not yet clear if they are dangerous to consume
- Also not clear how to remove them from sludge or anywhere else

Microplastics

- Studying removal from sludge
- Tested 6 types of microplastics in various forms
- Doses: 2, 5, 10, 56, 100, 200 kGy
- Irradiation at INCT
- Measurements at UoH
- All but PP changed in some way:
    - Physical structure
    - Chemical bonds
- Still very early days
- Much further work needed and planned
- Example….

Microplastics

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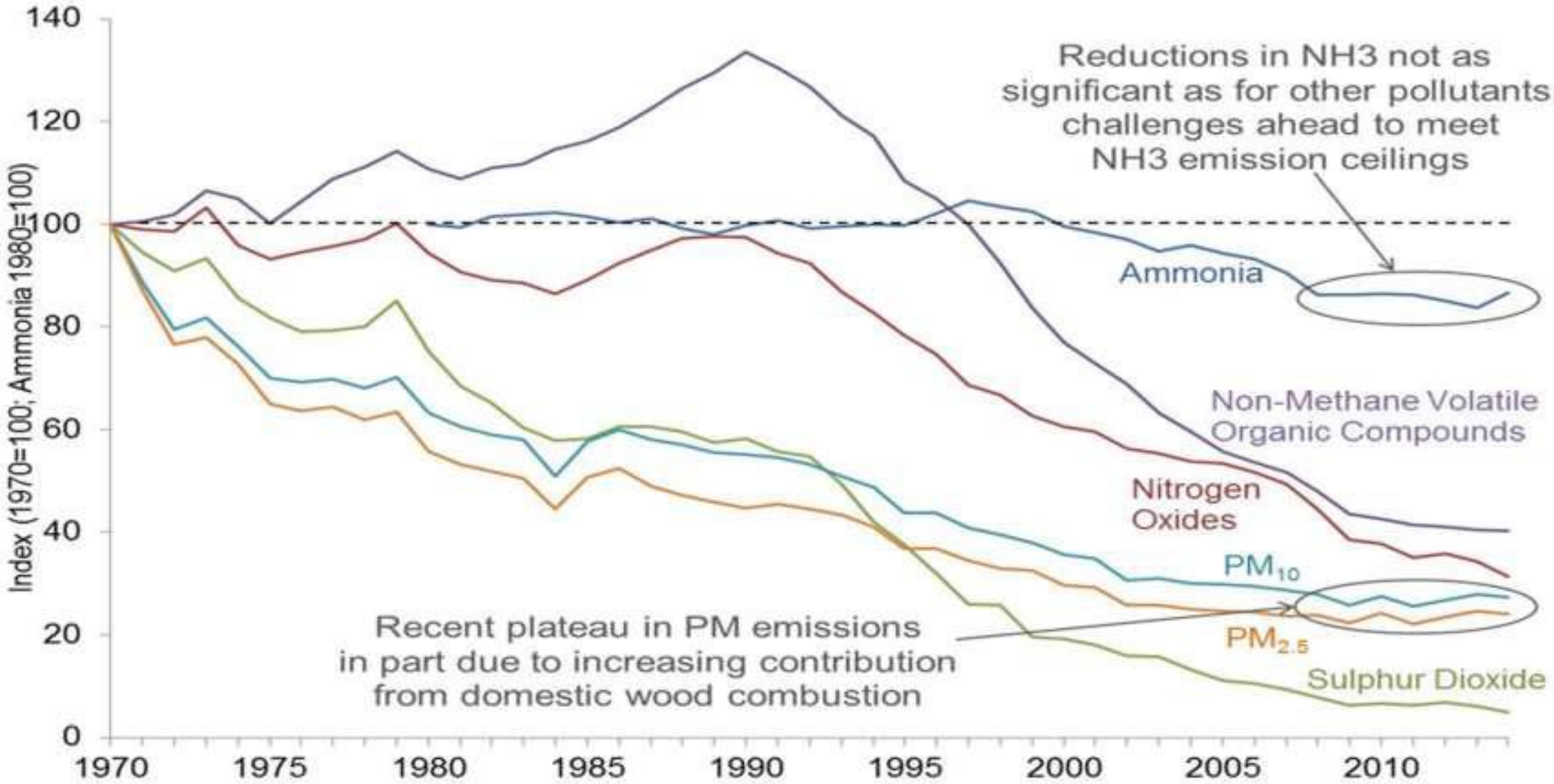
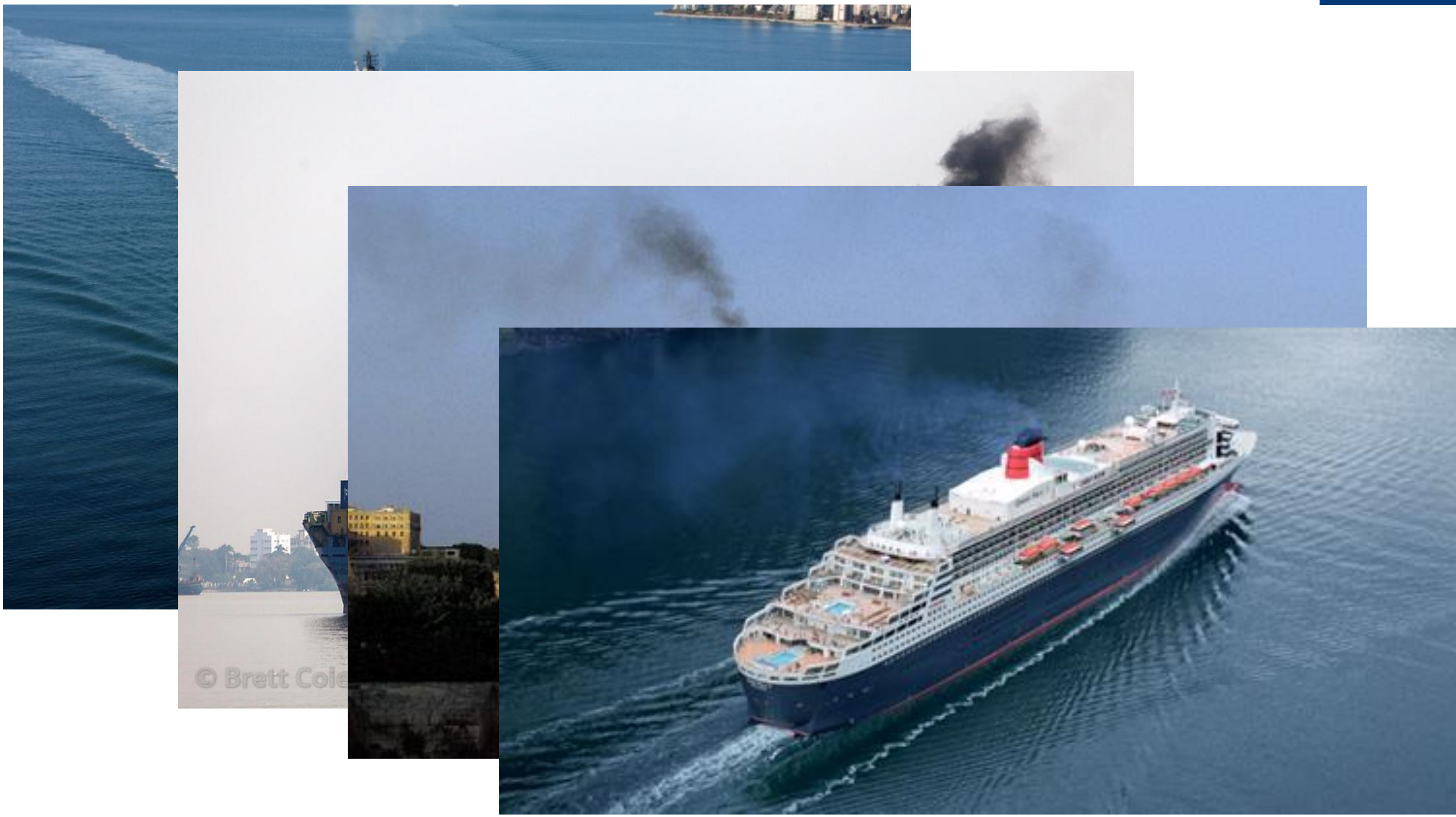
Air Pollution

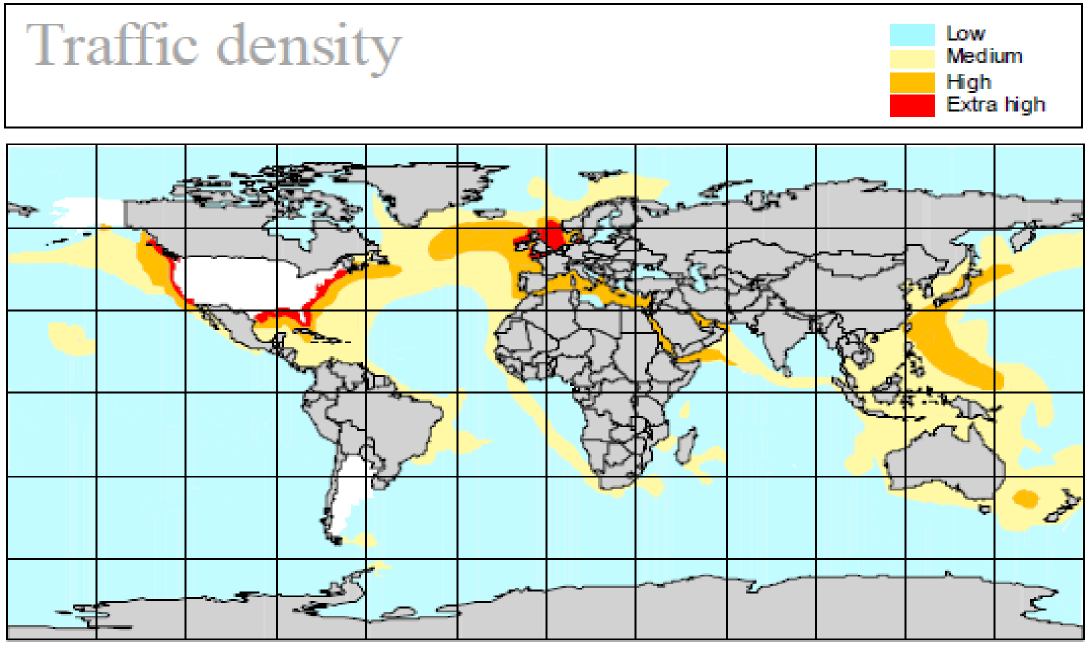


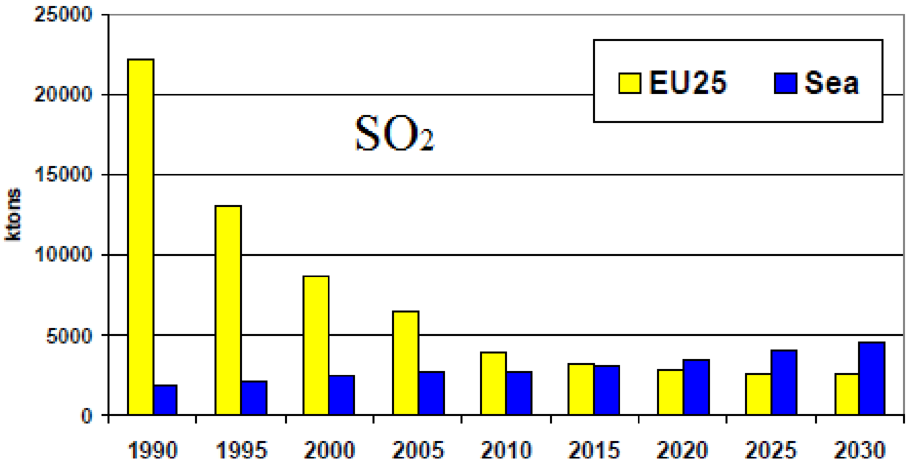
Air Pollution

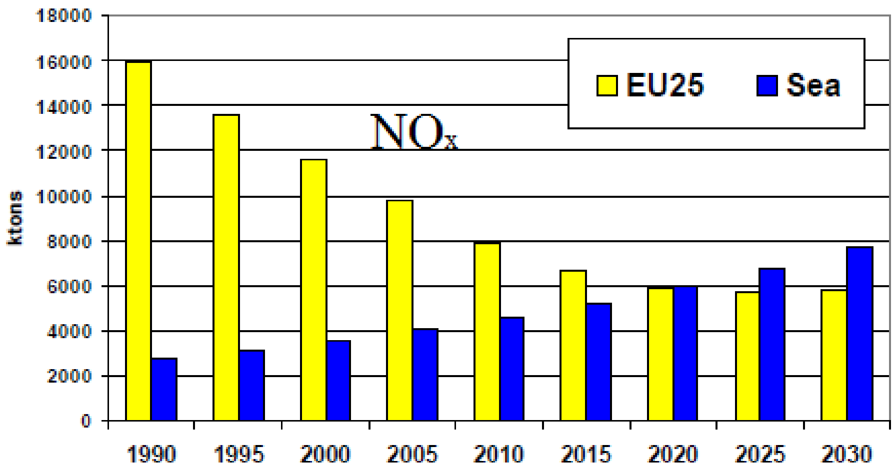


Larger ships: 80-100 MW diesel engines
134 kHP

Air Pollution from Shipping







IMO Control Areas and Limits

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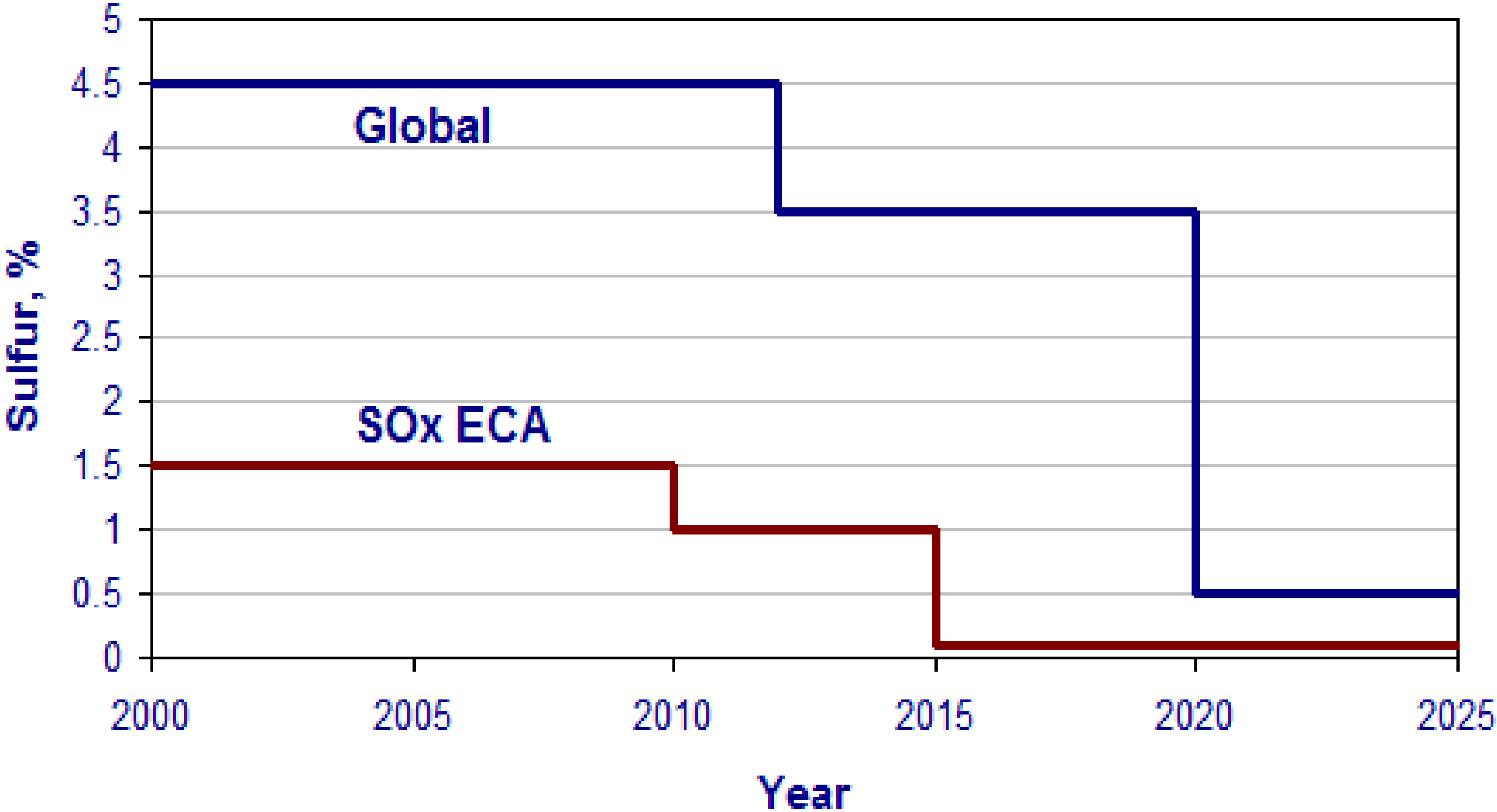


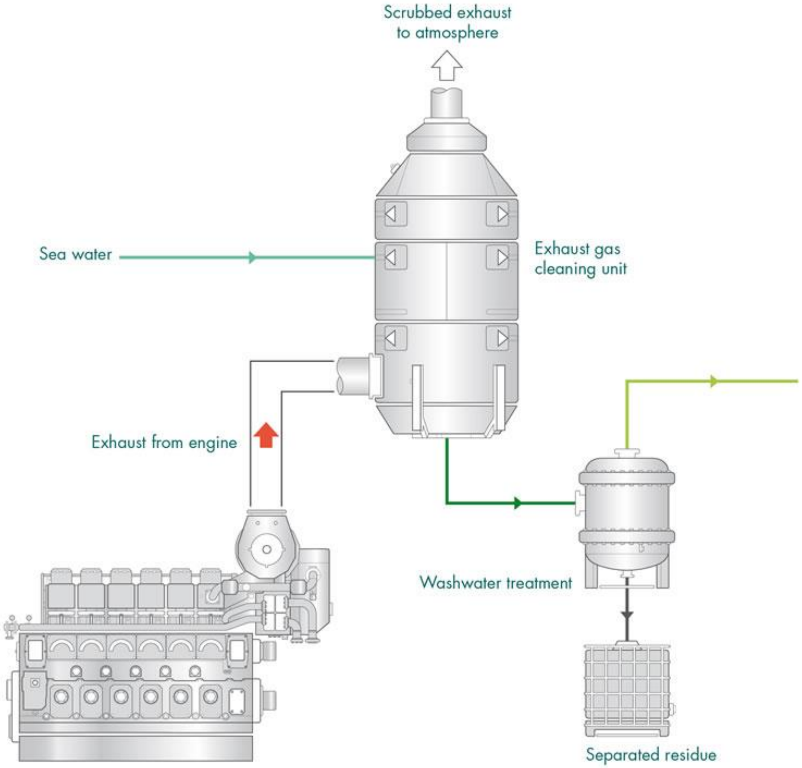
1.5% = 6g SO_2/kWh

Limit is only on SO_2, but it is well-known that NO_x,VOC and PM limits are coming

Existing Solutions

1) Low sulphur fuel:
   - works
   - but only for SO_2
   - costs >2 x current fuel

2) SO_2 scrubbing:



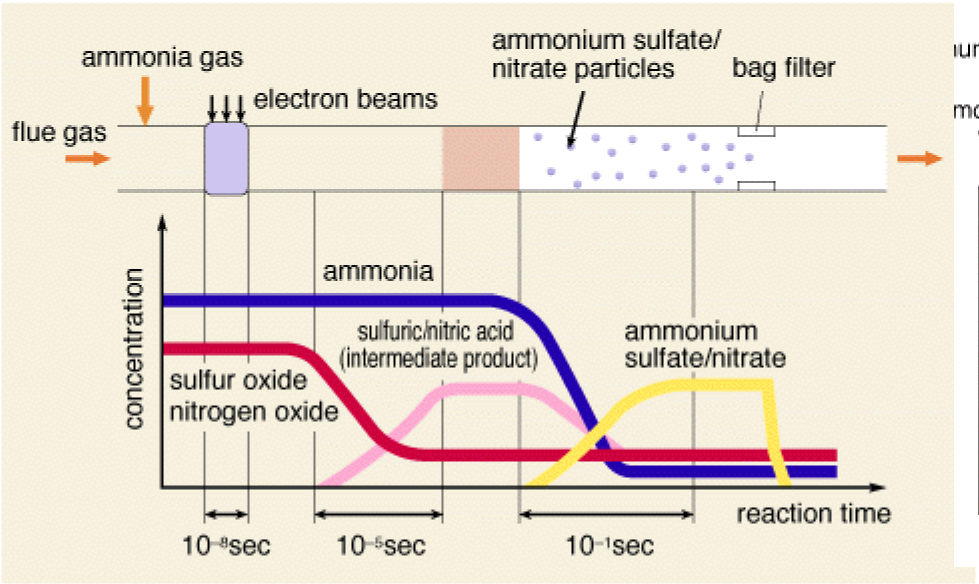
Existing Solutions

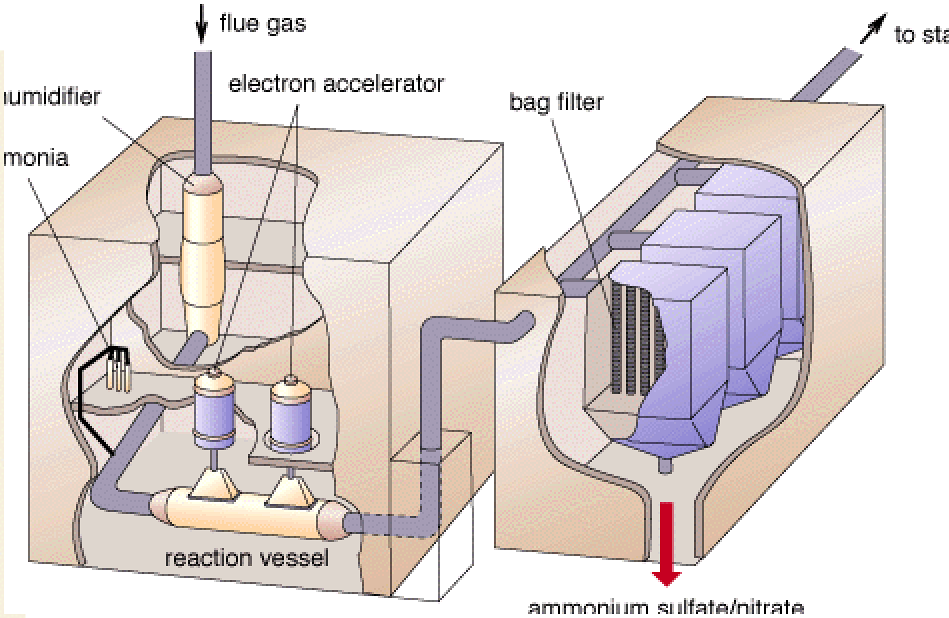
1) Low sulphur fuel:
   - works
   - but only for SO_2
   - costs >2 x current fuel

2) SO_2 scrubbing:
   - works
   - costs about 1 MEUR to install
   - requires about 1 month in dry dock
   - >50% bigger than standard exhaust systems
   - does not work for NO_x or VOC
   - separate NO_x system would be required and is incompatible

Electron Beams

- Have been used for removal of NOx, SOx and VOC from power stations
- Current technique:
  - chemical
  - bi-product is gypsum
- Electron beam technique:





Electron Beams

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~4 pilot plants
Not used in production yet

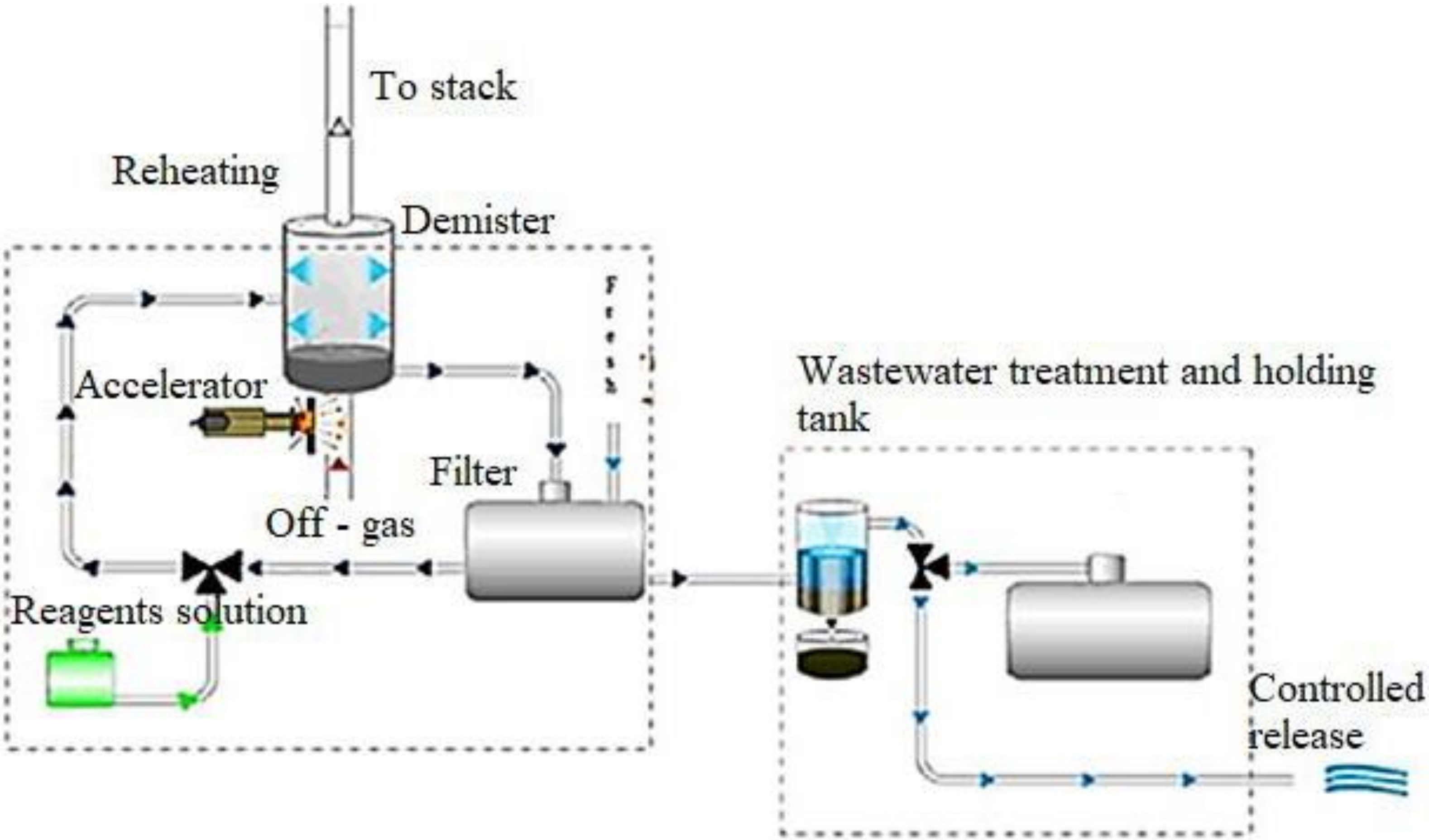
Electron Beam Treatment of Diesel Engines

Inlet of the installation
Exhaust gases with high concentration of NO_X and SO_X and VOC (PAH)

Electron Beam
Oxidation of the NO to NO_2, NO_2 to higher oxides and HNO_3, and SO_2 to higher oxides and H_2SO_4

Wet scrubbing
Absorbtion of NO_2 and higher ntrogen oxides, SO_3 and higher sulphur oxides, HNO_3 and H_2SO_4

Outlet of the installation
Clean exhaust gases matching the imposed regulations



Electron Beam Treatment of Diesel Engines

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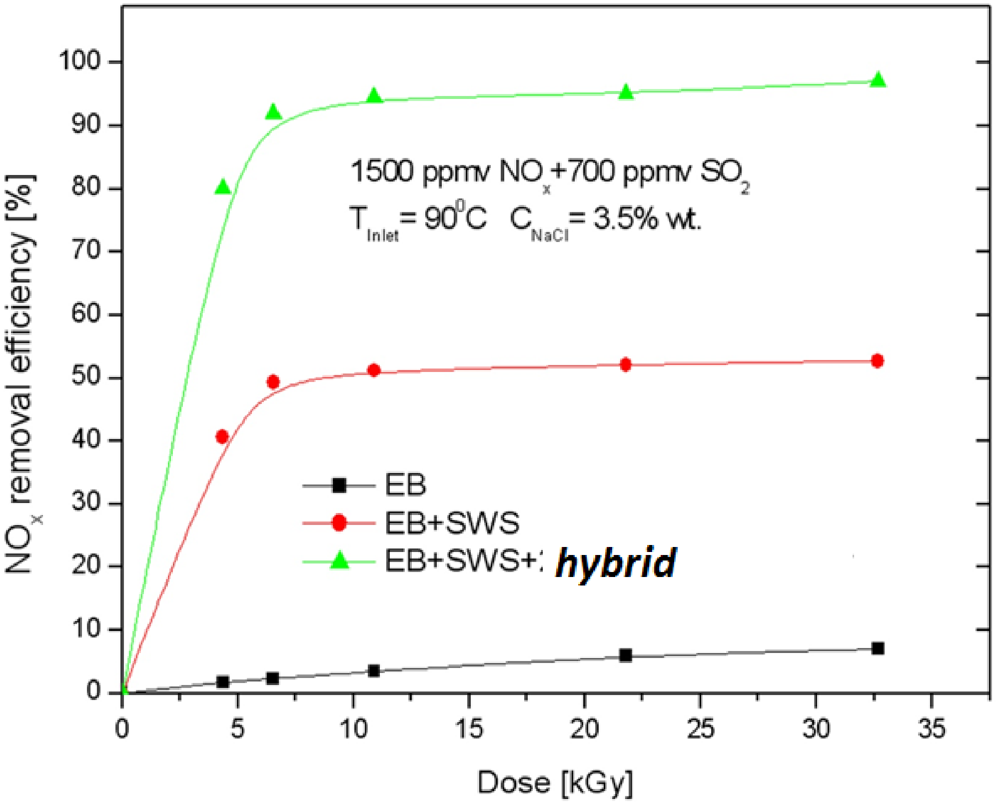
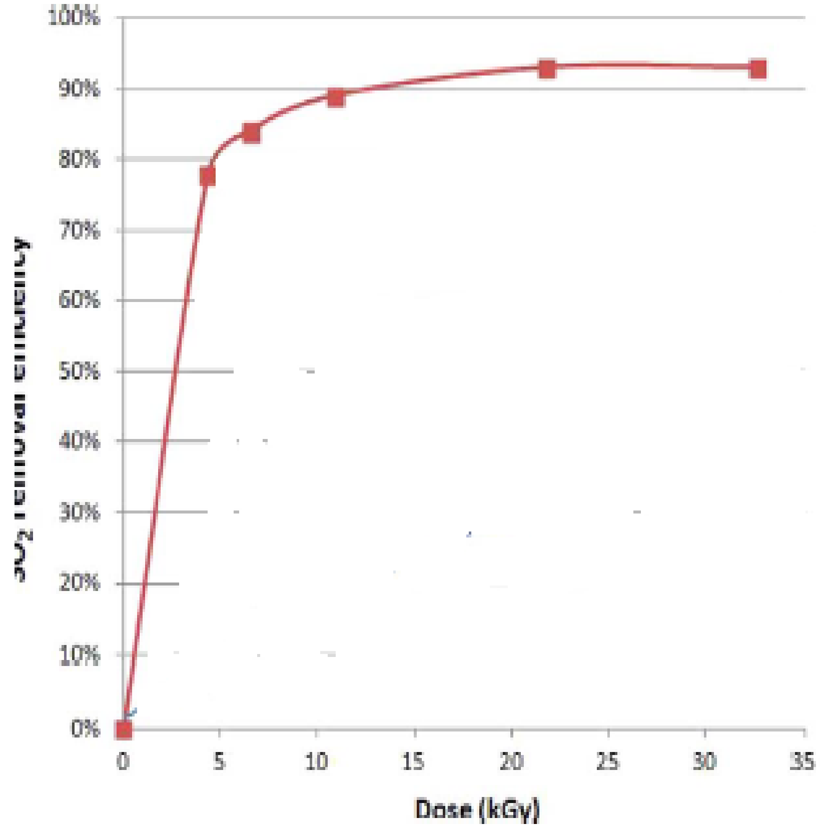
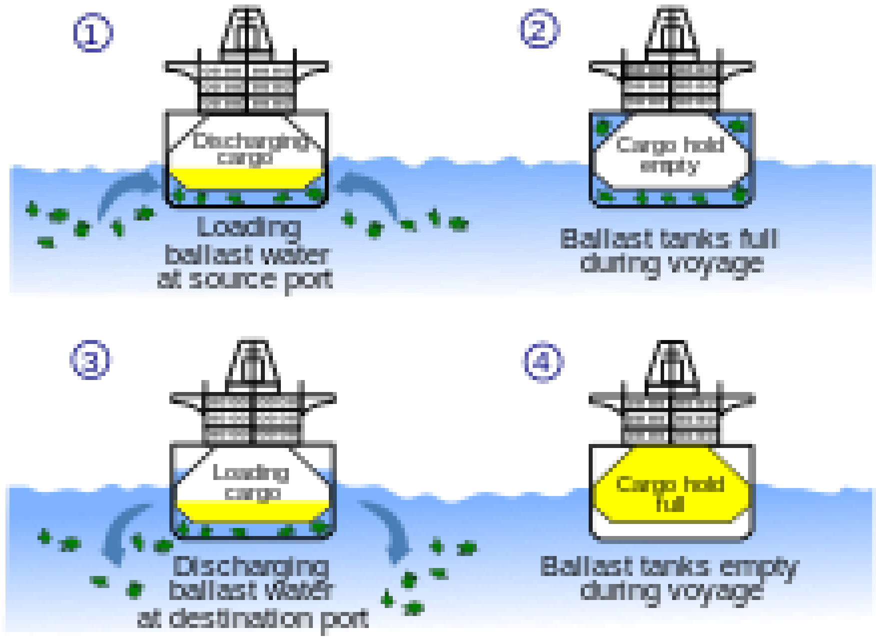




Electron Beam Treatment of Diesel Engines

Ship Ballast Water



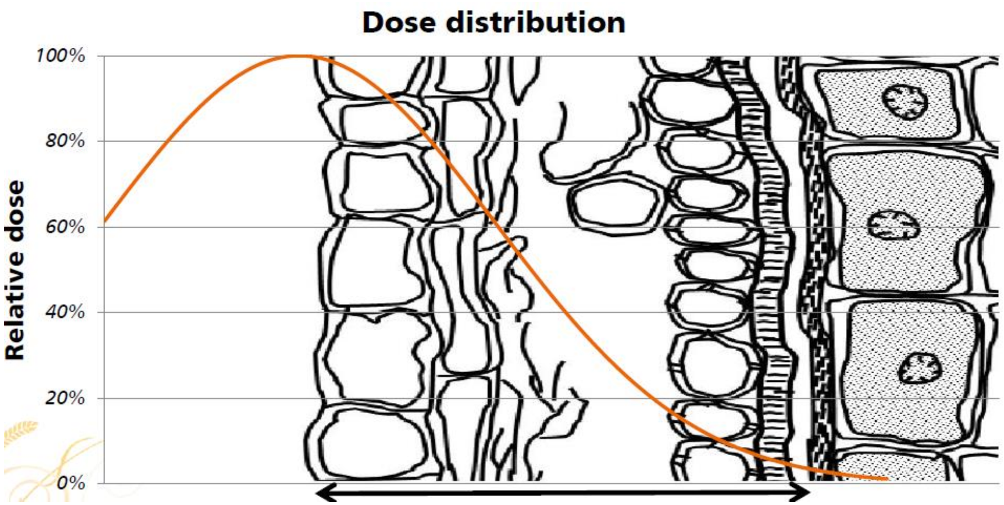
- Ballast water discharge typically contains a variety of biological materials, including plants, animals, viruses, and bacteria. These materials often include non-native, nuisance, exotic species that can cause extensive ecological and economic damage to aquatic ecosystems, along with serious human health issues including death.
- Controlled by IMO
- Usual method: chemical
- Oil tanker: typically 30000 m^3

Electron Beam Treatment

- Impossible to compete….unless there are regulations against dumping the chemicals
- But ballast tanks must be cleaned periodically
- Water is then much more contaminated
- Concept is a “green” dock developed in Poland
- Treat with e-beam
- Better contaminate removal
- Greater possibility of recycling
- First tests at Remontowa shipyard

Seed Treatment

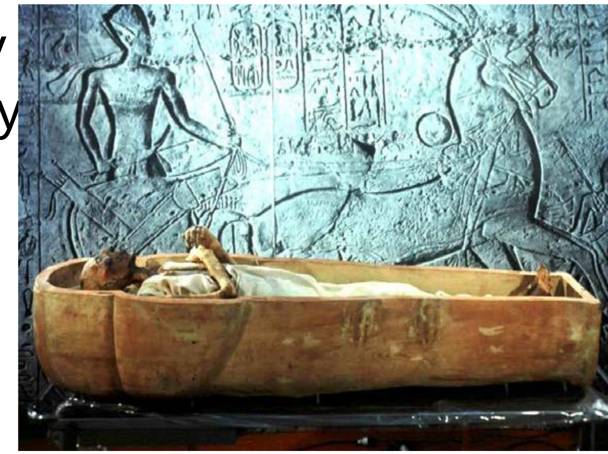
- Developed by Fraunhofer FEP in Germany
- Due to E-coli outbreak



Preservation of Cultural Artifacts

<u>HISTORY</u>

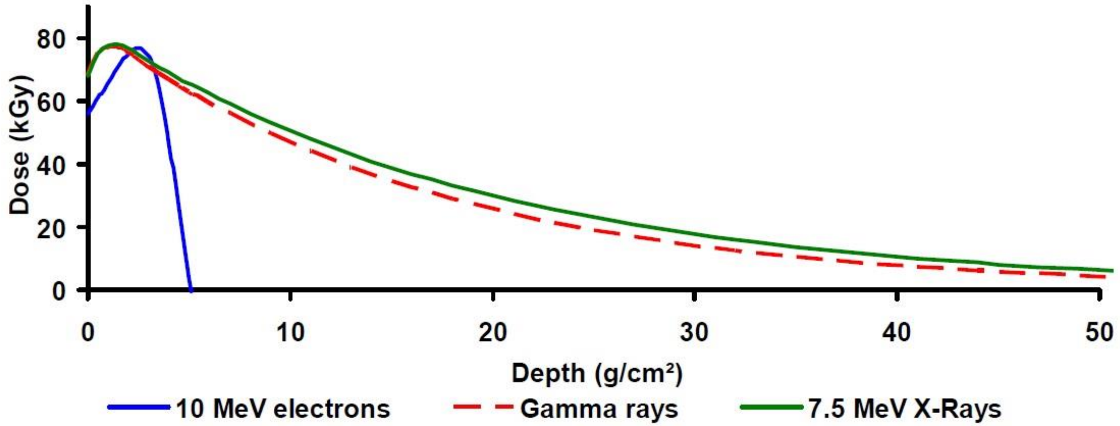
- 1977 the mummy of Ramses II, Nucléar laboratory CEA’s Grenoble Research Centre, dose 18 kGy
- 1980 The Gantt papers (U.S.A.), dose 4.5 kGy
- 1992 book collection, Leipzig University Library dose 12 kGy



- 1997 500 000 books, wet, library of the Colorado University, dose 15 kGy
- the end of 1990,National Film Archive of Romania, photographic films, dose 25-50 kGy

Preservation of Cultural Artifacts

- **Gamma rays**
- Neutral conditions
- No harmful residues
- Gamma allows treating dense and thick products
- Exposition time depends on the dose rate of the gamma cell (minutes-days)
- Oxidative degradation
- Safety precautions



EB, Gamma Ray and X-ray Penetration

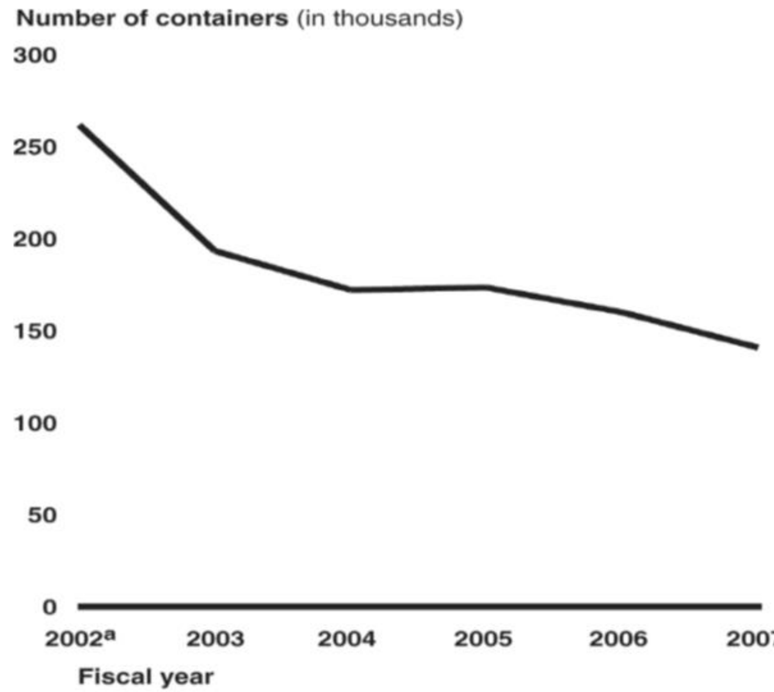
- **Electron beam**
- Fast process
- Neutral conditions
- Exposition time: short
- Much lower probability of oxidative degradation
- No harmful residues
- Limited depth of penetration

Preservation of Cultural Artifacts

Source: United States Postal Service.

A facility in Bridgeport, New Jersey, operated by Sterigenics International, uses a Rhodotron continuous wave electron beam accelerator built by IBA Industrial,

About 1.2 million containers of D.C. federal mail were irradiated from November 2001 through April 30, 2008.



Source: GAO analysis of United States Postal Service contractor data.

Conclusions

- Electron beams are already widely used
  - Polymer cross-linking (wires & cables, car tyres, hydrogels, etc)
  - Surface curing and preparation
  - Sterilisation: medical and food (including COVID-19)
  - Composite preparation
  - Thermal applications
- They have much further potential
- Environmental area is of particular interest
- They can do things which are otherwise very difficult
- Penetration into this area is a challenge
- As is getting funding, as usual