# The Story of Phosphorus



### why we care about P

- essential to life
- important industrial uses
- limited access for EU
- finite resources
- largely wasted in society
- element = suitable for recycling

# world usage of phosphorus



# fertilizers

- via H<sub>3</sub>PO<sub>4</sub> (phosphoric acid, MGA)
- with other crucial elements: NPK
- many varieties
- irreplaceable

DNA skeleton ATP: energy



### other uses of P





Lithium ion batteries



herbicides

#### flame retardants



### food uses of P



# solid acid for baking powder







emulsifying agent

moisture retention in cooking





Na, K, Horthophosphates pyrophosphates tripolyphosphates *blends* 

chelation

acidulation

### Phosphorus family tree

+31 113 68950 phosphate animal coke, gravel, electrical energy www.thermpho rock bones or recycled phosphates -sodium hydroxide, calcium hydroxide -water (phosphoric acid), partial conversion to P-redwhite phosphorus P, air, water sulphuric acid ree gelatin wet phosphoric product ferrothermal phosphoric acid H,PO, phosphorus pentoxide P.O. sodium hypophosphite NaH production or acid H, PO, incineration phosphorus strong acid or . cressurizing for special waste ion exchange steel calcium phosphorus phosphite low quality oxychloride -evaporationpurified hypophosphor dicalcium POCI, (phosphinic) acid (extraction) phosphate o phosphoric curification. bone meal calcium purification unsaturated acid linear 1-olefins, hydroxide/ (ash) hydrocarbons sodium axide aromatics specially hydroxide. chemicals ammonia potassium formaldehyde formaldehyde potassium hydroxide ethers hydrochloric acid sulphuric acid phosphate unea (urea) rock alcohols phenols. polyols. metal ethoxyalcohols. axides αxida -tion akoxydes orthophosphate melamine Ca phos-(ethylene coide etc) (thio-) polysolution phate mono, di, tri- alkyl ite phosphoric phos slurry or phosphines, mixed phialcohols, acid aryl/ alkyl phosphines nates solution wet çure phenols, alkoxydes urea / ammonia (ethylene dammonium zinc oxide olefins DL-homoalanine. alkyl groups oxygen chlorine oxide etc) phosphate (harium ovide) elic water, ammoria acid or sulfur food grade STPP. NH,/ phosphine Zn tetrakis tetrakis SAPP.TSPP. metal oxides, aminomethyl (or Ba) superphosphine special (hydroxy-(hydroxy-MSP. DSP. TSP. phos-0.0-dialkvi lithium sulfides APP. phosphate phosphonates 0,0-dialkyl liquid methyl) methyl) sodium under very pure specialty SHMP, SALP, phites; hexaphosphophosphoroother metal mixed O/S STPP phosphate (glyphosate dithiodialkyl dithiophosphine phospho phosphines phosphonium NH, phosphates MCP. ammonium phosphate pressure l phosphoniun fluorolead lenes. thionohypocompounds NPK technical esters diaryl dithio phosphate under nium (BINAP. chloride : urea melamine DCP, polyesters phospha 5 triphenyl phosphate metal (optional: sulphate; phosphites K phos. SHIPHNER phosphate phosphosphoglufochloridates and (thio-TCP Na<sub>3</sub>PS<sub>2</sub>O SMFP AMPs) ZDDP fertilizers phosphate grade phosphate (mono, di) (tri) zenes LiPF, phite phosphonates phosphine lanes sinate (RO), PSCI phosphates phosphides in CO<sub>2</sub>) pressure salts phosphinates phobane etc) condensate condensate (Mn, Zn etc) flame retardants (esp. tri), processed meat, drying; antioxidants, flame retardant extraction reducing food additive. emulsifiers, surfactants (mono, di), dehydration UV stabilizers fish and seafood; dehydration lubricant matchboxes, agents; agents, scale and corrosion inhibitors. etching chlorichlorination agent in (RM for) and pyrotechnics, catalysts, RM potato processing agent in herbicides, flame phase agent, fibre industrial cleaners, wetting and agent for specialnation fertiolefin hydraulic water treatment. organic organic retardants. pesticides. flotation molybdite pigment, doping transfer for synthesis. plastics/nylon spinning intistatic agents, curing, defoamers, ties: pharmaceuagent addition; fluid additives, lizers builder in bakery, anticaking, chemistry: chemistry chlori chelating agents/ flame catalysts and minina P bronze, for semicatalysts animal feed flame flame flame fumigation mining and electroless solvent, RM solvents, flotation agents, ticals batterv plastics (carboxylic supplement; for agri- retarasphalt asphalt nation vitamin A additive conducnickel plating pharma, in catalyst detergents; dairy, toothpaste retarinsecticides, hydraulic oil additives, retarproduction electrostabiwater treatment. retardants flame extraction agent organic (phosphine ionic extraction catalyst flame ífatty bone china culture dant svnthesis bleaching production cement tablets additive dant additive antiwear for metal working fluids agent dant (7-ACA etc) surfactants plasticizers retardants herbicide pesticides (antiwear) agents (Nokes) matches synthesis generation) fumigation tors liquids agents ligands retardant biocide acids) lyte izer

Thermphos Inte PO Box 406 4380 AK Vilissin The Netherland +31 113 689501



# keeping P in cycles



### **Traditional phosphorus cycle**



# Modern phosphorus use



### things should not work this way

### we need to get P back in cycles

- Being an element, P is perfectly suited for this
- dilution and availability
- use wisely
- get it back
- start where P is found in **concentrated form**
- necessity for everybody (and industry...)
- advantages: Cd, U -> Zn, Cu



Vaccari D.A; Scientific American 300, 54 - 59 (2009)





### your dream beach?

- P often limiting for life / growth
- P input to environment = algal bloom
- we need sewage treatment, manure limits



### too much or too little?

- mineable resources are finite
- diluted phosporus is lost to reuse

### The P issue – beyond scarcity

- Strategic / geopolitics; supply security
- Sensible waste management cost avoidance, environmental issues, preventing landfill
- Societal: circular economy, urban mining, Cradle-to-Cradle...
- rock prices
- EU critical materials list-P rock added 2014



# agriculture, an important contribution to preserving P (50%)

- P washed out or bound to soil in some form - prevent runoff
- soil often saturated (NL)
- optimize agricultural practices
- soil management
- precision fertilizers, hydroponics etc



# industry contribution: recycling

- about 50% of total solution to issue
- urbanisation breaks the P cycle
- more complicated / technological / centralized
- from waste

### drivers

- recycling makes sense regardless of scarcity issue
- political measures expected or implemented (Switzerland, Germany) to prevent dilution and loss of accessability [EU: ??]
- rock price and quality decrease are incentives

### where do we access P?

wherever it presents itself in *concentrated form*:

- sewage
- meat industry (meat and bone meal)
- manure
- chemical / metallurgical industry

#### NATIONAL PHOSPHORUS METABOLISM IN JAPAN



courtesy H. Ohtake

Yokoyama, et al., ISIJ International, 47: 1541-1548 (2007)

### EU P recycling potential

[kton P/year]	Total	Recycled	
Sewage sludge (human P)	300	40%	
Biodegradable solid waste	130	30%	
Meat & bone meal	130	5%	
Total	560 (+)	160	400
Manure		2000	
Mineral fertiliser use		1500	

Van Dijk & Oenema "Overview of phosphorus flows in wastes in Europe", 2013, Fertilisers Europe seminar, 6 Feb. 2013.

very significant amounts

### sewage

- human excretion: 1-2 g pppd
- minor contribution: (dishwashing) detergents (0.1-0.2)
- P needs to be taken out

### not a new idea



Joseph Wright, The Alchemist in Search of the Philosopher's Stone

stumbling onto phosphorus

...by boiling his own urine with charcoal!





### P recovery routes from sewage



0% recovery efficiency (% of total in sewage) 100%

# sewage sludge in agriculture

- some love sewage sludge ("biosolids") in agriculture, some hate it
- F: +, DE/NL: -; USA:+
- pathogens, drug residues, heavy metals (Zn, Cu) less in rural areas
- plant availability of P = ??? Fe phosphate



# sludge on fields

"Die Ausbringung von Klärschlamm ist jedem Bauern strengstens untersagt" "Spreading of sewage sludge is strictly forbidden for all farmers"



### Die Kartoffel Kontrollierte Qualität

geprüft. Die Anbauflächen wei den bei gleichzeitiger Verpflichtung zur Einhaltung einer dreijährigen Fruchtfolge genau festgelegt. So konnen Monokulturen und Fruchtfolgek inkheiten vermieden werden.

#### Rezepte

Produkte

#### Kartoffel Daten & Fakten Geschichte Sorten Kontrollierte Quali

Kontrollierte Qualität Das ist drin AMA-Gütesiegel

Historie

Fun & Gewinne

Kinder Ecke

Kontakt



Gede Kartoffel hat andere Ansprüche. Also wird nach dem spezifische. Bedarf der jeweiligen Sorte auf Basis von Bodenanalysen gedüngt. Die Ausbringung von Klärschlamm ist jedem Bauern strengstens untersagt!

#### Datenerfassung

Daten & Fakten

Hier ist alles gespeichert: Die Daten jedes einzelnen Kartoffelfeldes werden in Schlagkarteien gesammelt und liefern somit Informationen

Sorten

Geschichte



http://www.pfanni.at/at/kontrolliertequalitaet.asp

"Sewage sludge must not be spread on fields that are used in farm production activities" (Industry requirement, Arla Foods requirement)



### Arlagården<sup>®</sup> Quality Assurance Programme



It is not permitted to fertilize fields with sewage sludge from municipal sewage treatment plants or private domestic sewage treatment plants, as this may pose a risk of introduction of unwanted substancesinto the farm production cycle. [...] If sewage sludge has been spread on fields, no coarse fodder may be grown in these for at least three years from the time of spreading.

Version 4.4 / January 2015

http://www.arla.com/Global/responsibility/pdf/arlagarden/Quality-assurance-programme-Arlagaarden\_UK.pdf

# P wastage: sewage sludge

- P misplaced as fertilizer ("diffuse landfill")
- or used for its fuel value in cement works
- phosphorus end up diluted in cement
- same for other P rich biomass with heating value
- cement works like the ash, but not the P
- separate onsite incineration possible

### P recovery from sludge

- possible e.g. struvite
- economic? application?
- or incinerate

# STRUVITE

- is formed in WWTPs anyway
- antiscale technology > P recovery
- rollout NA, EU
- 10% of total, maximum
- uses limited
- incompatible with industry





 $\rm NH_4MgPO_4\cdot 6~H_2O$ 

# sludge incineration (mono)

- energy recovery (but moisture)
- works for all sludges
- ash currently landfilled etc
- ash needs to go to re-use
- increasing trend EU, NA, Japan

PROS / CONS + health/safety

- +/0 energy recovery
- + > 90% P yield
- + centralized
- C, N lost to reuse

### example



Bundesweites Phosphor-Rückgewinnungskonzept für Klärschlamm und Klärschlammaschen aus der Monoverbrennung. Everding W.; Pinnekamp J. *Gewässerschutz – Wasser – Abwasser* **2012** 228 Ch. 13

### sewage sludge ash

- centrally collected, dry powder
- contains almost all P from sewage
- industry compatible as raw material?

## like rock, but not quite the same

- this is what we get
- not necessarily what we want

# a challenge for technology

- basic transformations
- bulk, cheap
- low energy and water

# sewage ash to P<sub>4</sub>: **Rec Phos**

- EU FP7 funded project
- from sewage ash
- new furnace concept inductive heating

www.recophos.org

ICL: ash to fertilizer



### manure

- "wrong" nutrient balance in manure
- P often limiting
- treatment needed
- separation of liquid (N, K) and solid (C, P)
- ash from solids?

# manure (pig/cattle)

- NL: more pigs than people
- P management issue: production vs spreading
- oversupply: value -> cost
- transport cost



### slaughter waste

- protein/bone mixture MBM
- BSE driven (MBM cat I) no cannibalism for ruminants
- currently chiefly to cement industry = CO<sub>2</sub> credits
- P is lost
- monoincineration needed

This and similar "sustainable" practices are BAT in Europe

politics

## policies

- prevent wastage
- stimulate implementation
- research: largely covered, careful approach
- first movers risks, etc
- see DE, CH

### **P** recycling research

GEWÄSSERSCHUTZ · WASSER · ABWASSER

International conference on Nutrient Recovery from Wastewater Streams

May 10-13, 2009

MAR

**IFTENREIHE** 

the westin Barytone Hotel and Reson nestin construct notes and nestin ower, British Columbia, Canada

IMA

**38. ESSENER TAGUNG** FÜR WASSER- UND ABFALLWIRTSCHAFT VOM 9.3. - 11.3.2005 IN AACHEN

AACHEN 200

'ears

300 studies 100+ repeats 10-20 different main routes 1-2 large scale introduction

BERLIN

2003

### **Nutrient Platforms**

- collaborative approach
- variety of stakeholders
- industry, technology providers, agriculture, NGOs, wastewater operators / service providers, governments, etc......
- NL / BE /DE/ NO/ UK/ FR
- EU

#### http://phosphorusplatform.eu/

### ESPP

- European platform
- involves all stakeholders
- meeting place for politics and stakeholders
- information exchange and sharing



### ZÜRICH REFERENDUM

Tages-Anzeiger - Montag, 4. März 2013

#### Bau zentrale Klärschlammverwertungsanlage

Stadtkreise	Ja	Nein	% Ja	
Kreis 1+2	9161	543	94,4	
Kreis 3	10449	571	94,8	
Kreis 4+5	7 601	404	95,0	
Kreis 6	8553	412	95,4	
Kreis 7+8	14828	791	94,9	
Kreis 9	10252	919	91,8	
Kreis 10	10'621	702	93,8	1
Kreis 11 🕔	12209	969	92,6	1
Kreis 12	3935	405	90,7	1
Total	87609	5716	93,9	and a
	Stimmbe	teiligung:	43,8%	N

### 93,9 % pro new mono sewage sludge incinerator!

### Klärschlamm begeistert

Eine Überraschung ergab die Abstimmung zum 68 Millionen Franken teuren Bau einer Klärschlamm-Verwertungsanlage in der Abwasserreinigung Werdhölzli. Dagegen war keine Partei, doch 93,9 Prozent Ja gibt es nie in Zürich. Neue Altersheime kommen auf 90 oder 92 Prozent, Spitäler auf 89, Krankenheime auf 85, Schulhäuser auf über 70 Prozent, aber 94 Prozent Ja ist Rekord. Auch die dritte Vorlage hatte keine Gegner und kam auf fast 90 Prozent: die Anpassung der Vormundschaftsbehörde ans übergeordnete Recht.

### Thank you!



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