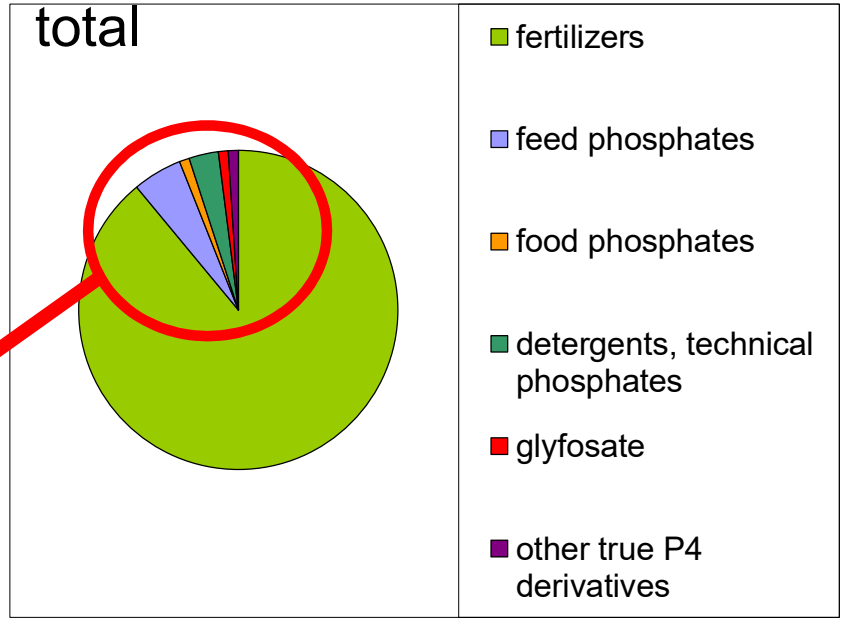
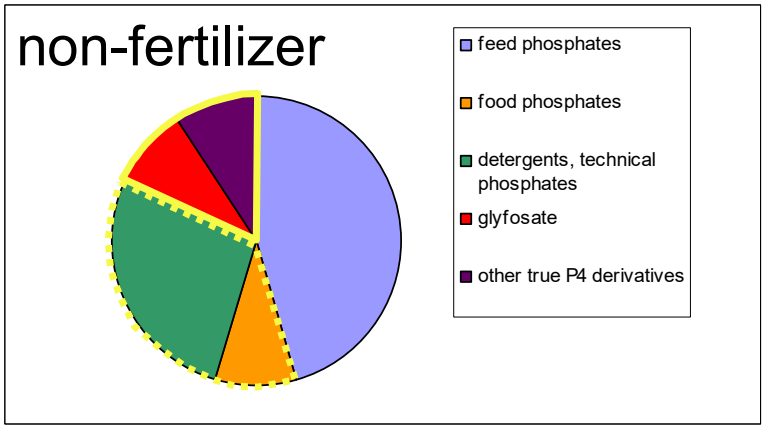
# Phosphorus in industry and society

Willem Schipper

Willem Schipper Consulting

# world usage of phosphorus



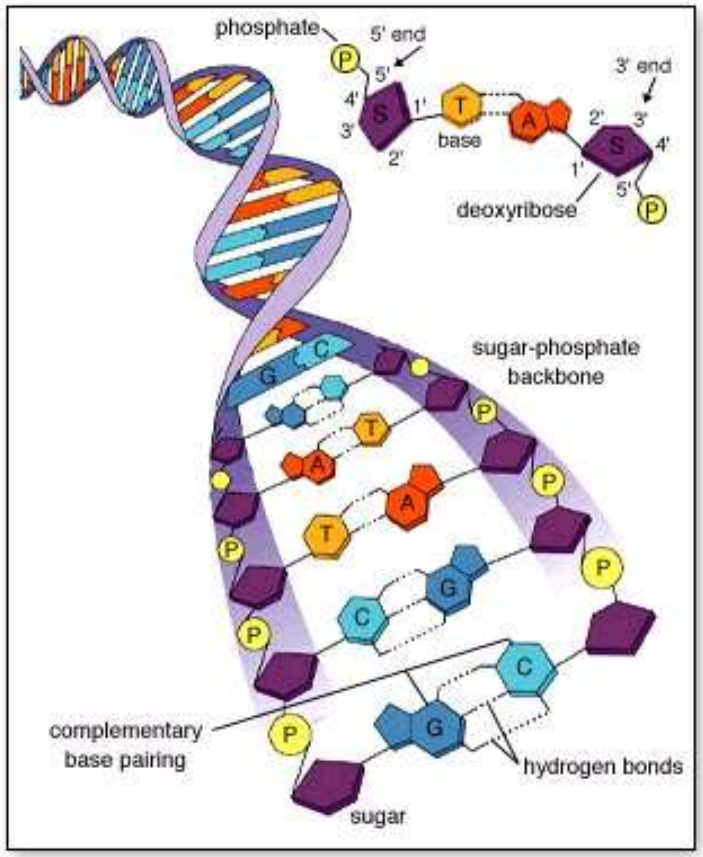

Worldwide 21 Mt/y P

# fertilizers

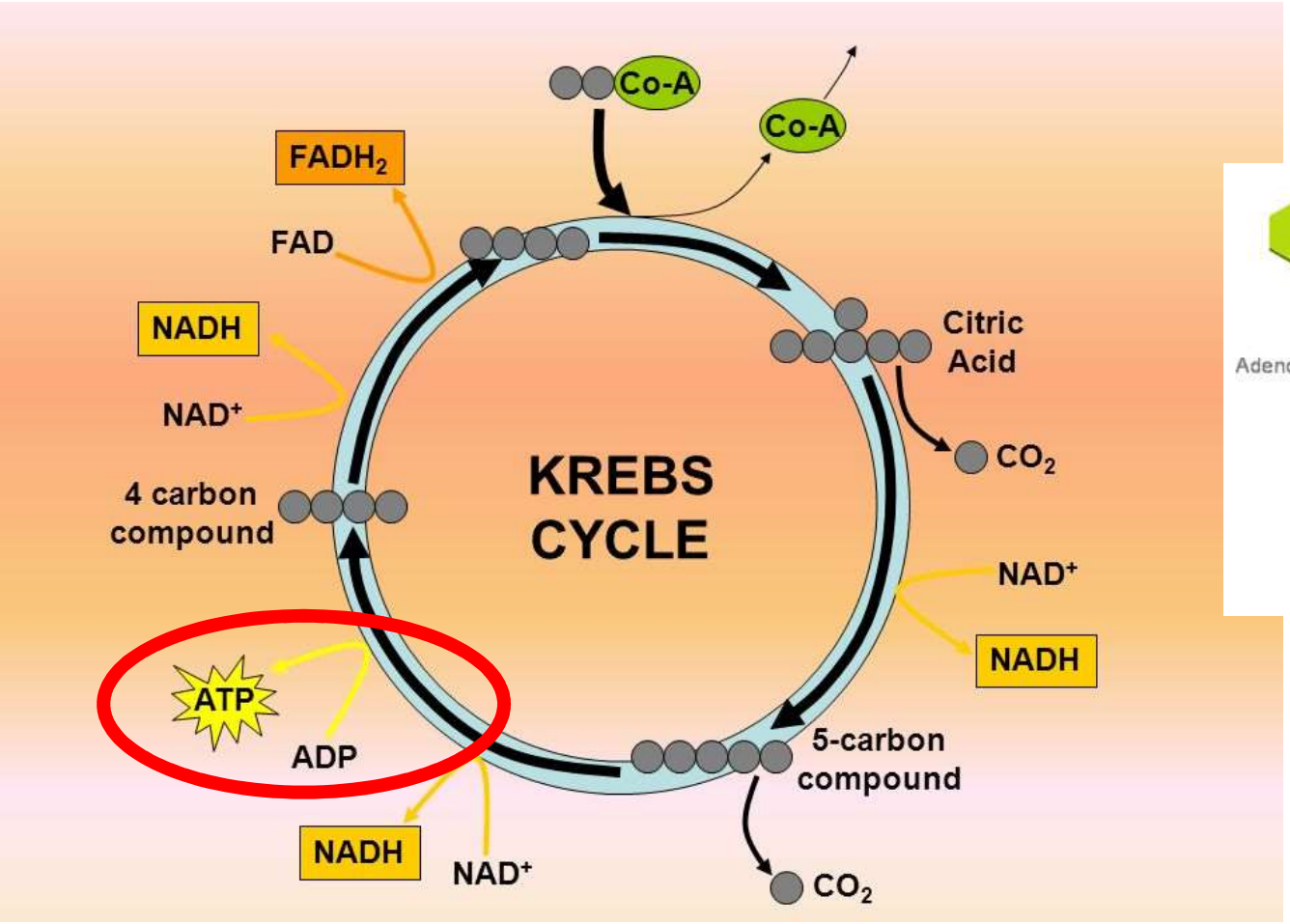
- main use of phosphorus worldwide
- P indispensible to life

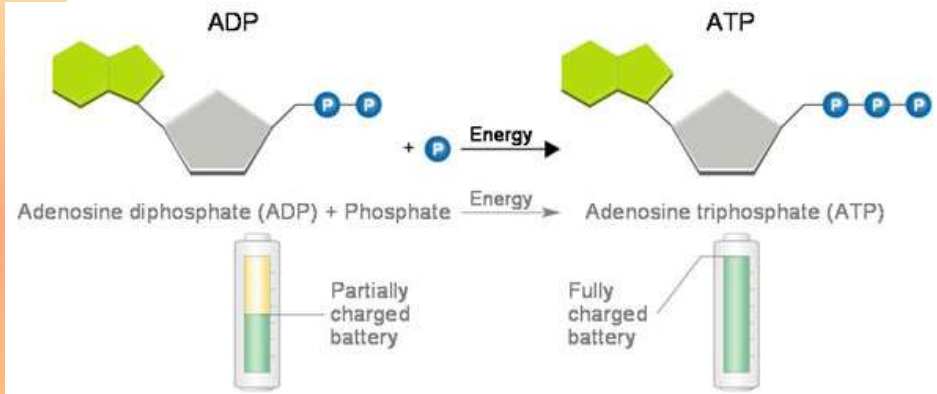
- energy
- DNA
- bones

# DNA


phosphate
5' end
3' end
base
deoxyribose
sugar-phosphate
backbone
complementary
base pairing
hydrogen bonds
sugar

# your body gets its energy here



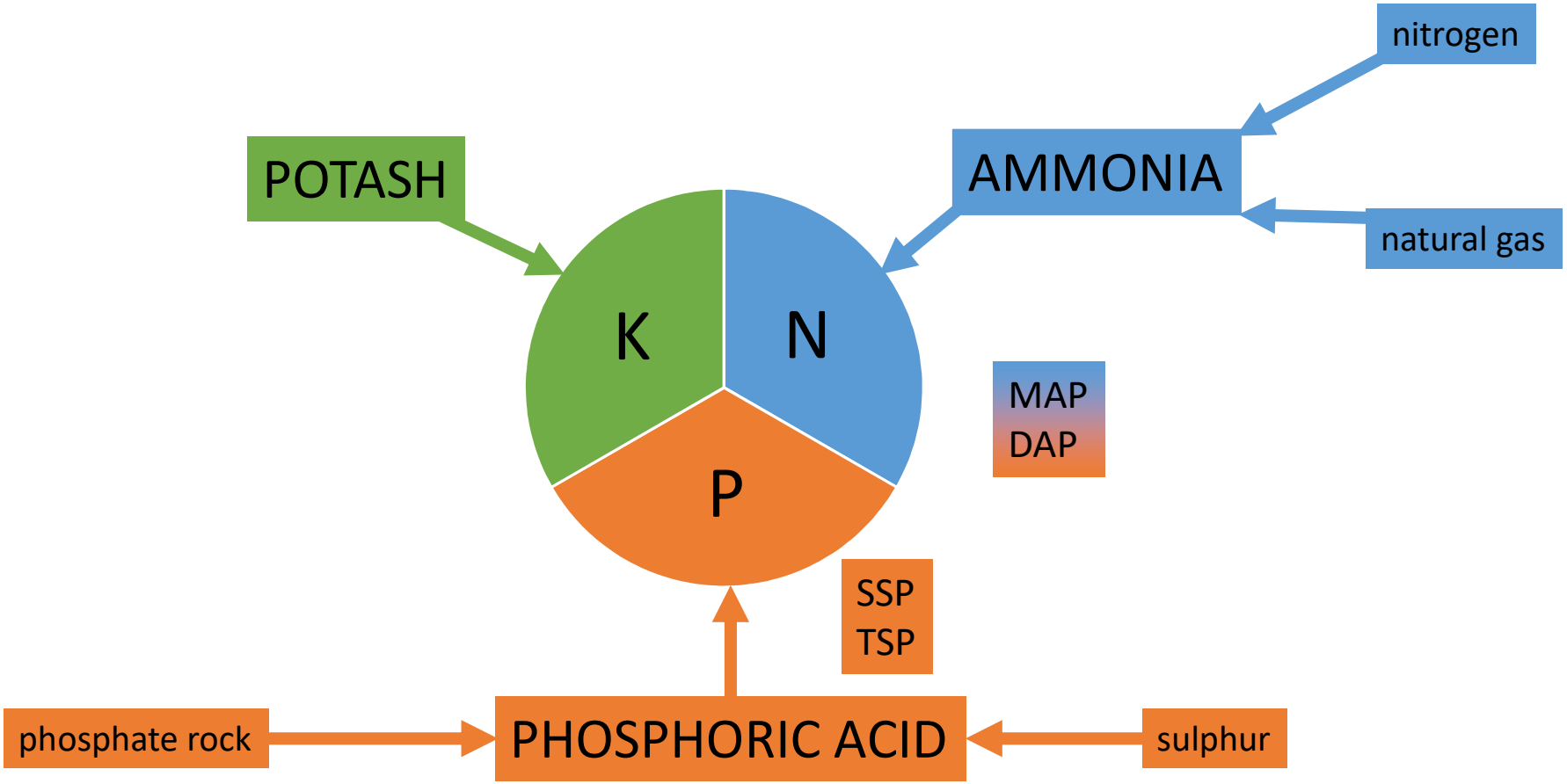



with
phosphate

without
phosphate

# Fertilizers

Sulfur, boron, zinc, magnesium...



# most commonly used fertlizer ingredients (P)

- phosphoric acid (MGA)

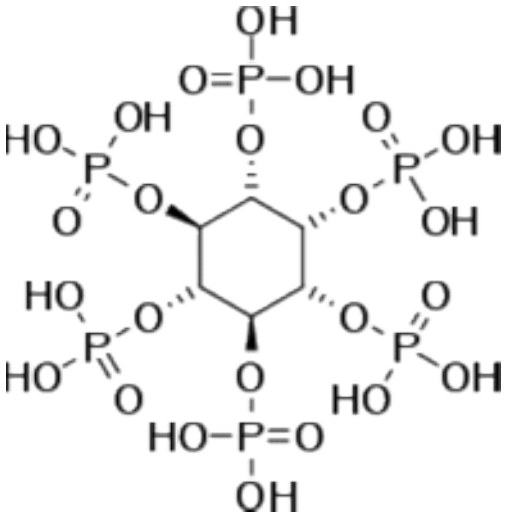
- MAP
- DAP
- TSP
- (SSP)

# feed phosphates

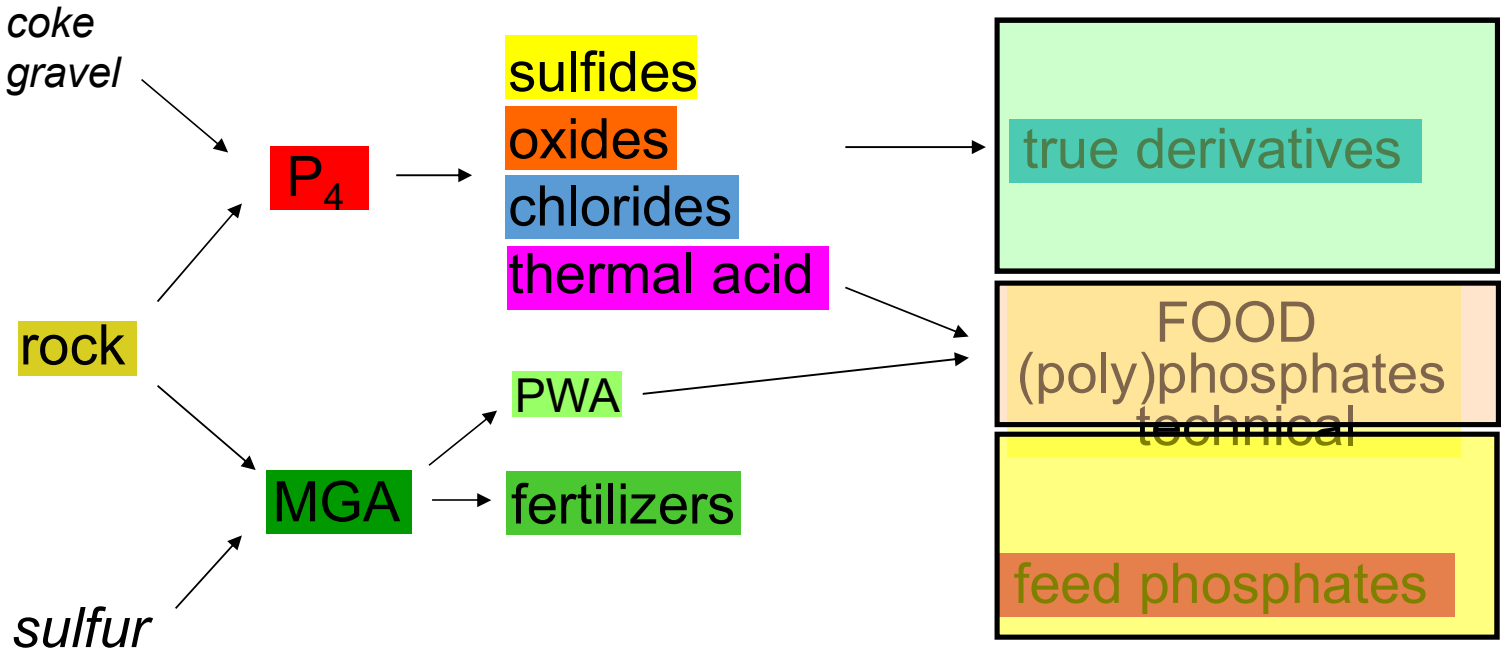
- animal husbandry
- animals need P to exist AND grow
- P in fodder not sufficient and not all digestible
- feed additives needed
- MCP, DCP, mixtures
- about 5% of P use

linked to manure issue

phytic acid
(largely non-digestible but rich in P)



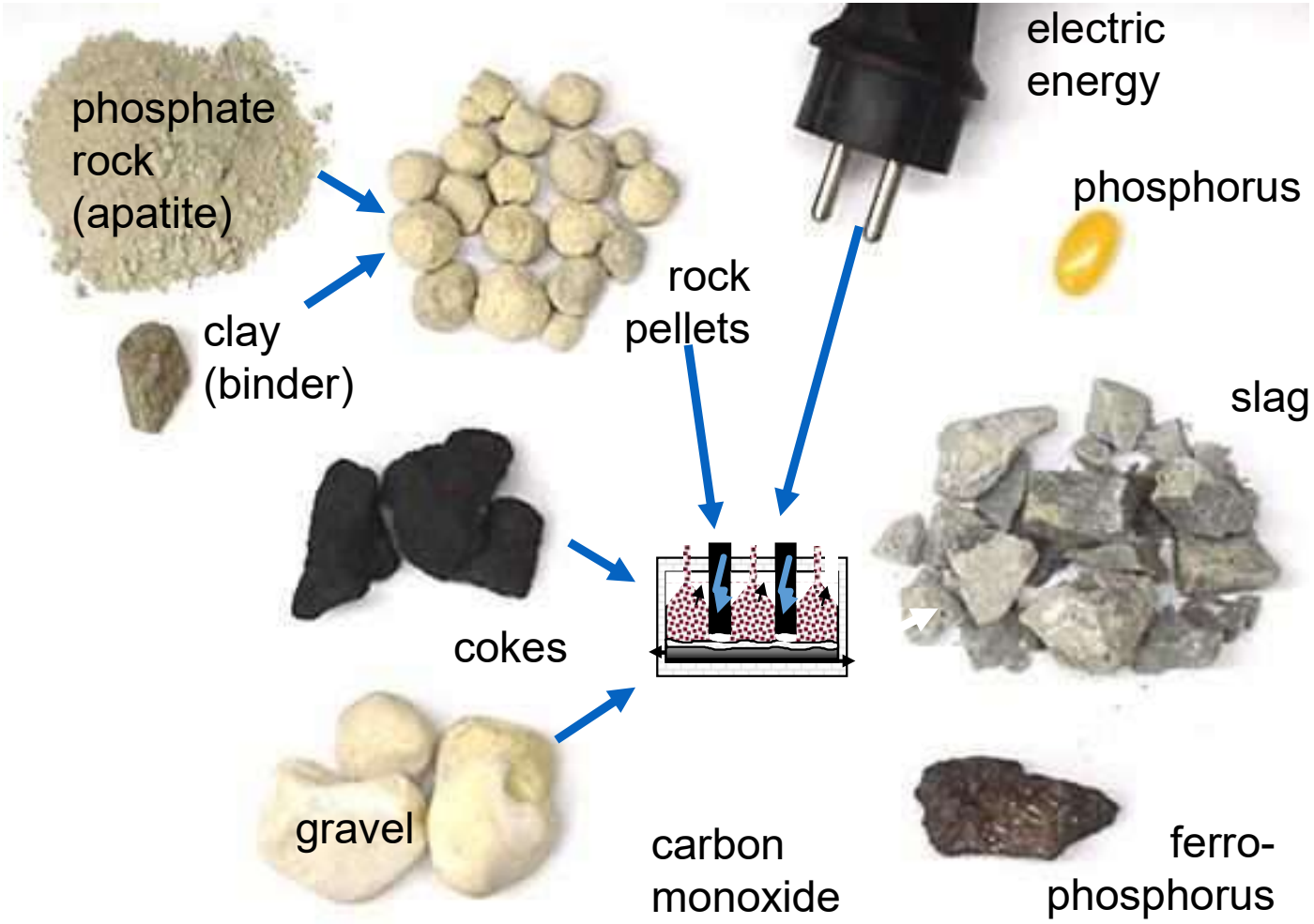
# value chain for phosphorus



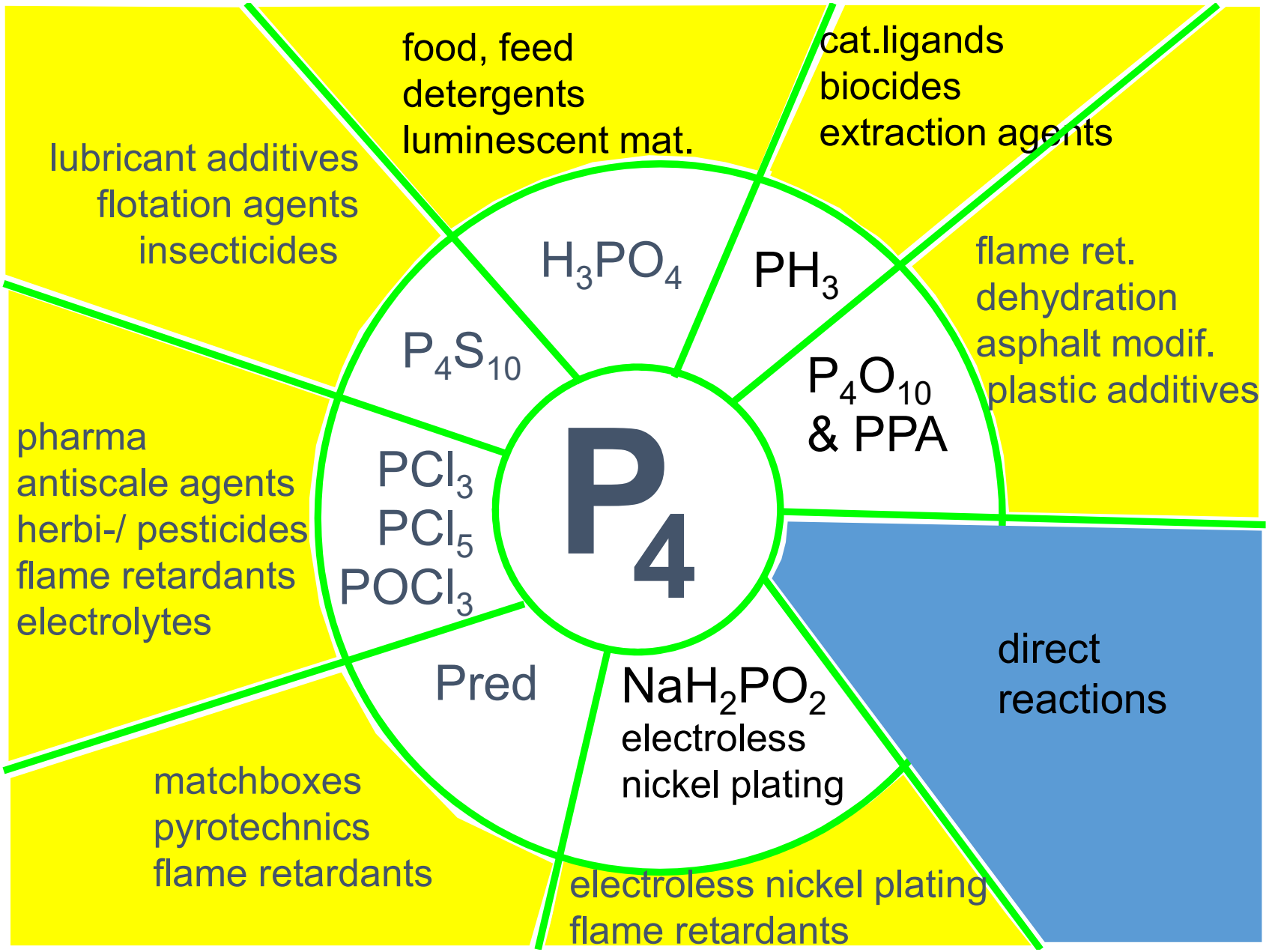
# $P_4$ - the key to P chemistry

- made in submerged arc furnace process
- not unlike a blast furnace
  - submerged arc furnace

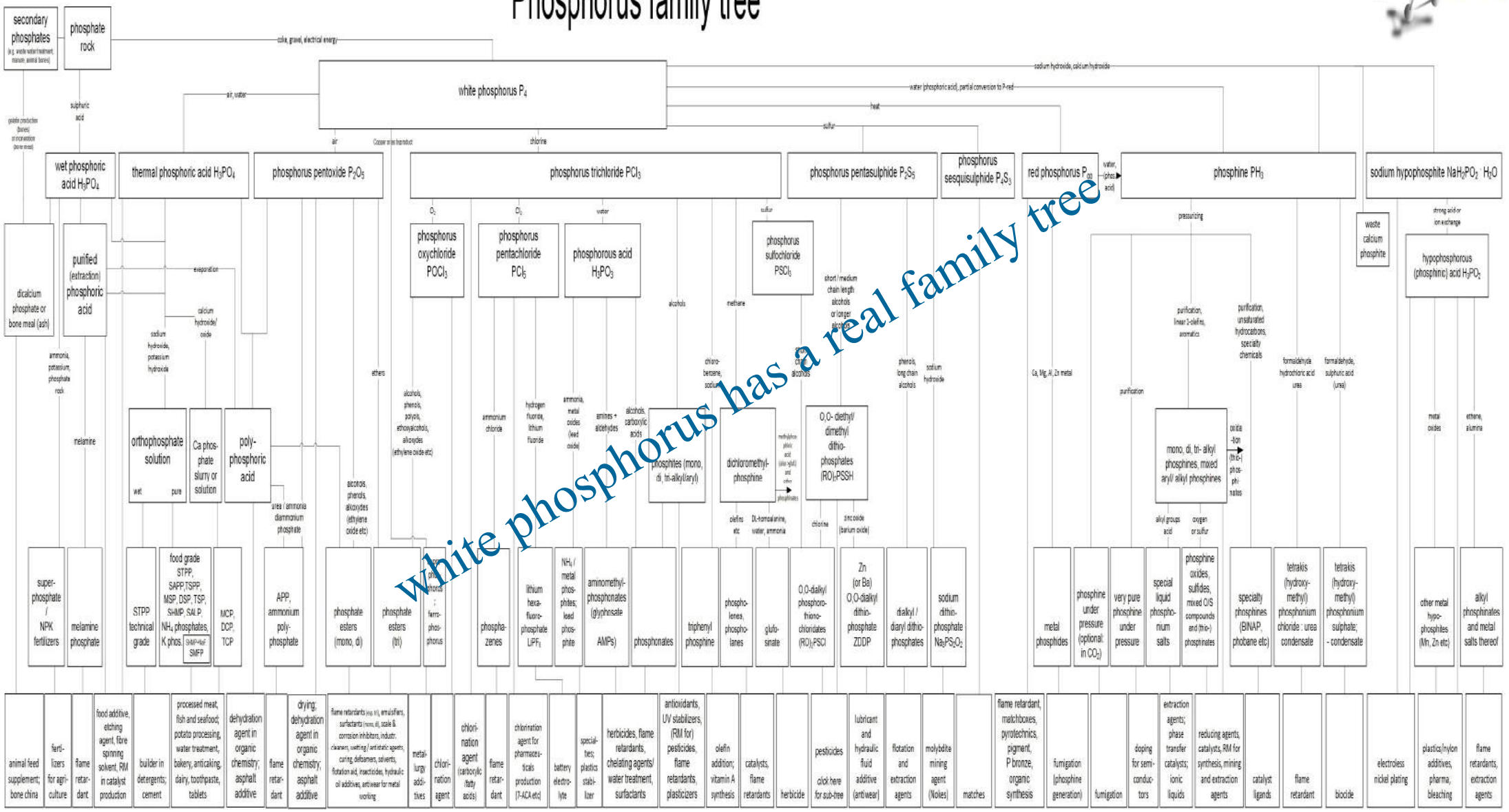
# the phosphorus production process



Tennessee Valley Authority P furnace, 1942


food, feed
detergents
luminescent mat.
cat.ligands
biocides
extraction agents
lubricant additives
flotation agents
insecticides
$H_3PO_4$
$PH_3$
flame ret.
dehydration
asphalt modif.
plastic additives
$P_4S_{10}$
$P_4O_{10}$
& PPA
pharma
antiscale agents
herbi-/ pesticides
flame retardants
electrolytes
$PCl_3$
$PCl_5$
$POCl_3$
P4
direct
reactions
Pred
$NaH_2PO_2$
electroless
nickel plating
matchboxes
pyrotechnics
flame retardants
electroless nickel plating
flame retardants

# Phosphorus family tree



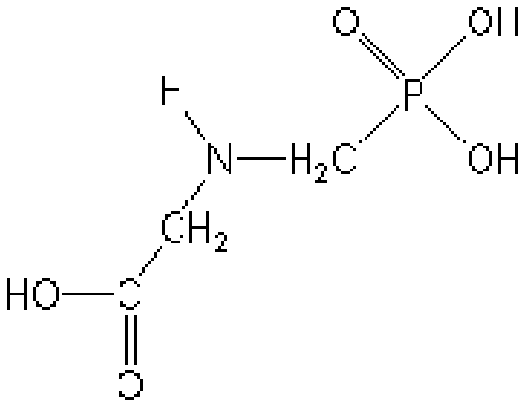
# uses of $P_4$ as such

limited:

- military (incendiaries, e.g Hamburg 1943)
- smokescreens
- rat poison (obsolete)
- homeopathy

Emsley J; The 13th Element: The Sordid Tale of Murder, Fire and Phosphorus; Wiley and Sons: New York, **2000**

# glyphosate



$P_4$ -> $PCl_3$

$PCl_3$ + IDA + $CH_2O$

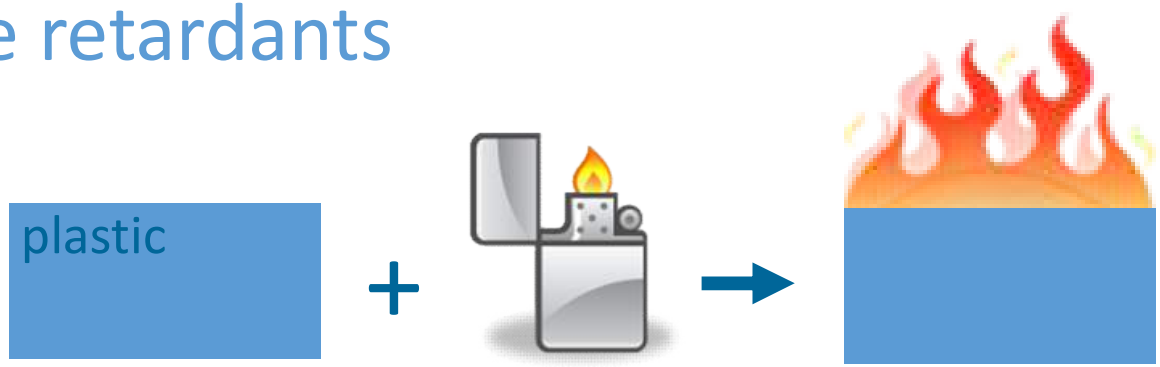
-> glyphosate

blocks 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase (shikimate pathway to amino acids)

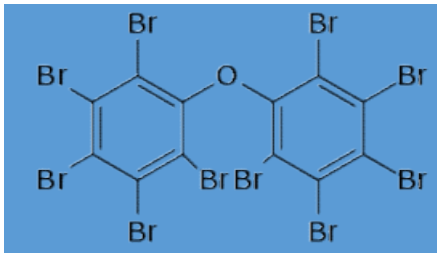
most sold herbicide worldwide


*US EPA 2000–2001 Pesticide Market Estimates*

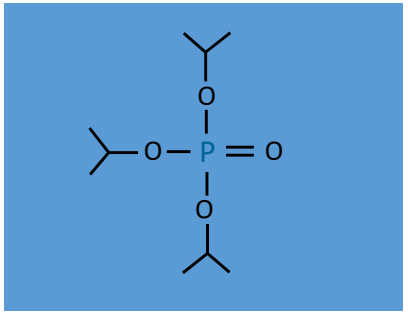
# flame retardants

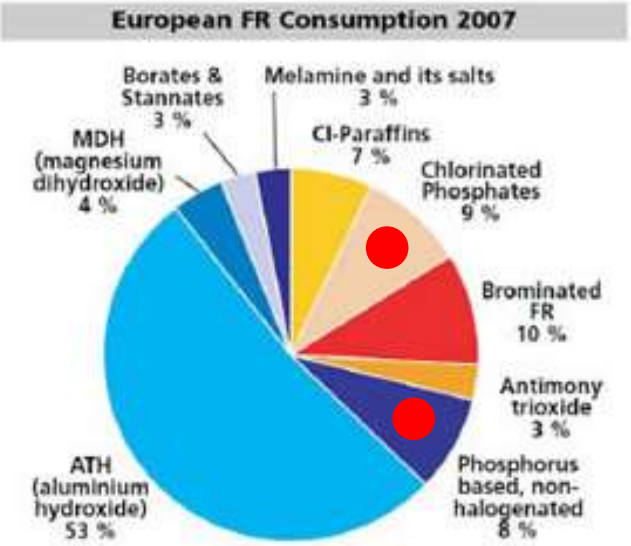



concerns about brominated flame retardants




phosphate based alternatives

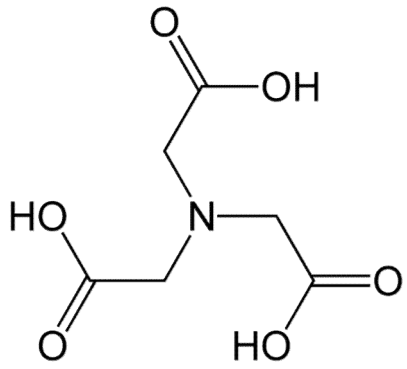


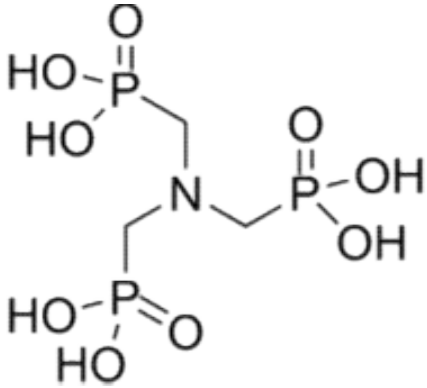

Weil, E.D.; Levchik, S.V.; *Flame Retardants for Plastics and Textiles;* Hanser, München 2009

# phosphonates

- P analogs of EDTA etc
- chelating agents
- **industrial water treatment, RO, detergents**




NTA




ATMP

# Li ion batteries

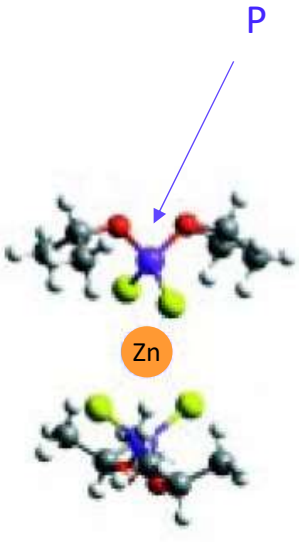
P compounds in battery

- conductivity
- Li storage

$LiPF_6$ and $LiFePO_4$

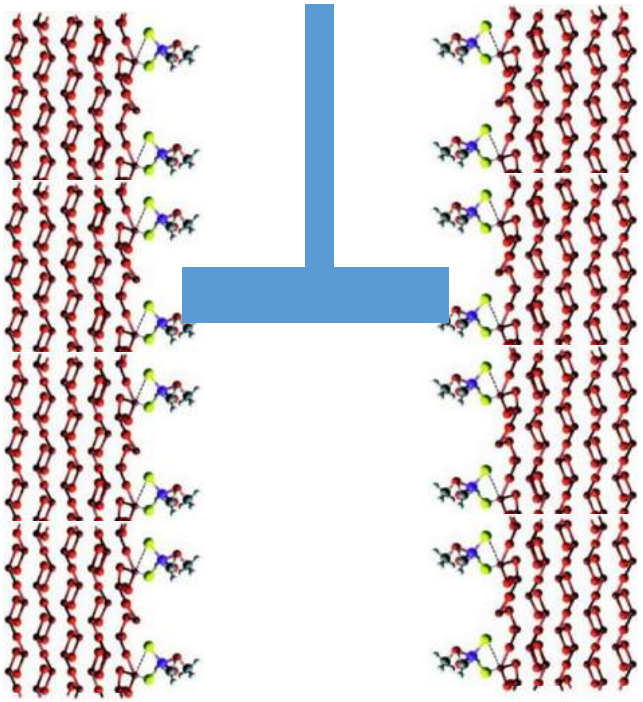

# engine oil additive

## ZDDP




increases wear resistivity; antioxidant

$P_2S_5$ + iPr-OH + ZnO -> Zinc O,O'-diisopropyl dithiophosphate



# electroless nickel plating

$P_4$ + NaOH -> $NaH_2PO_2$

$NaH_2PO_2$ + Ni salt
-> Ni layer

Actually Ni / $Ni_3P$

A. Wurtz; *Compt. Rendus Acad. Sc*. **1844,** 18, 702

# FOOD

solid acid for
baking powder

emulsifying
agent

moisture retention
in cooking


chelation
(detergents)

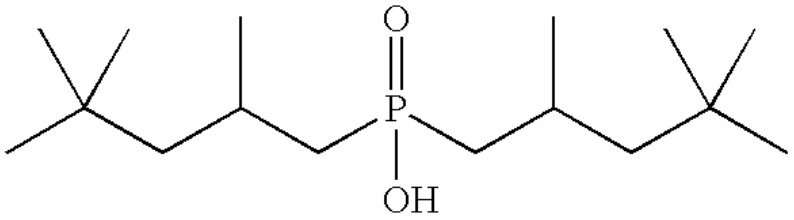

acidulation

Na, K, H-
orthophosphates
pyrophosphates
tripolyphosphates
*blends*
…

# metal extraction

separation of cobalt from nickel

most of the world's cobalt is produced by using this chemical

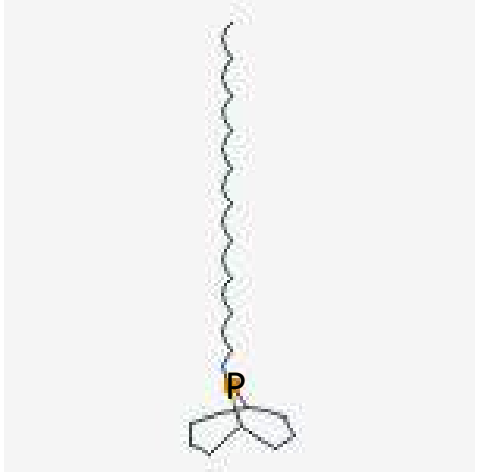


# catalysis

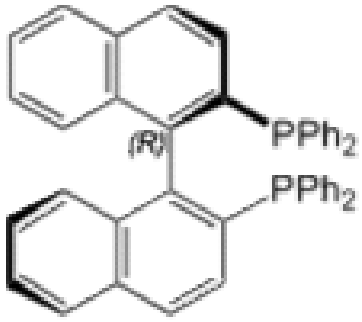
phosphine chemicals are essential parts of catalysts

e.g. phobane in hydroformylation

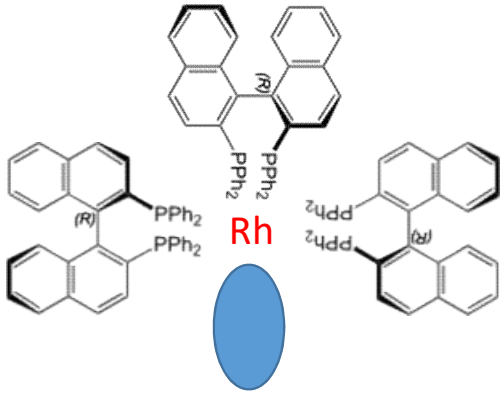
major pathways in petrochemistry



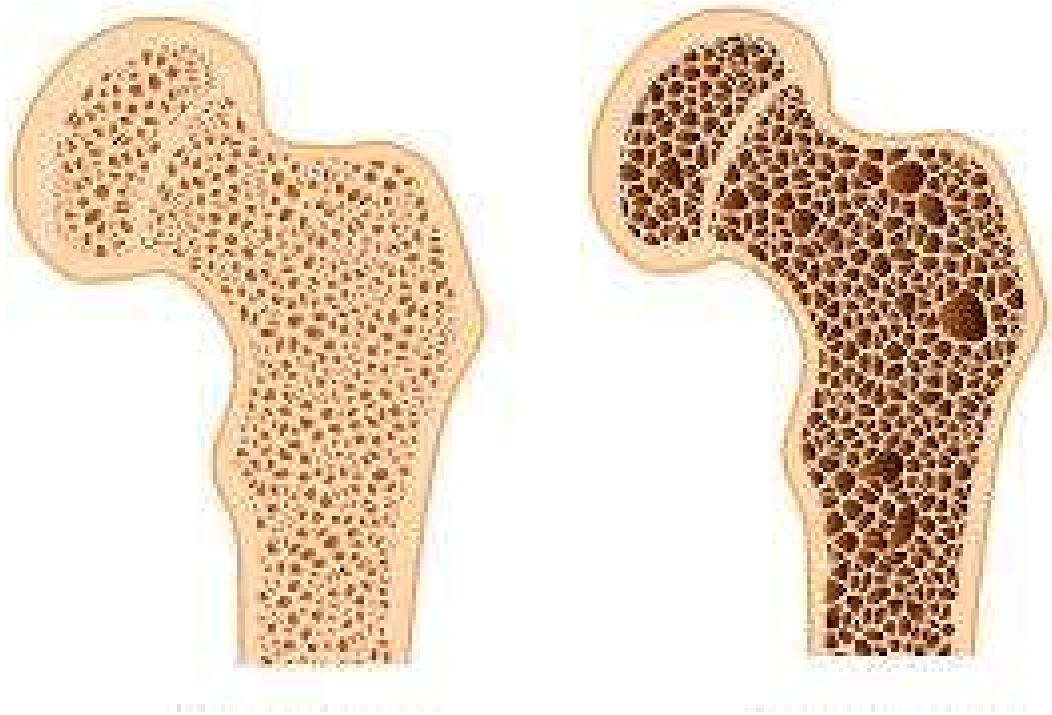

phobane

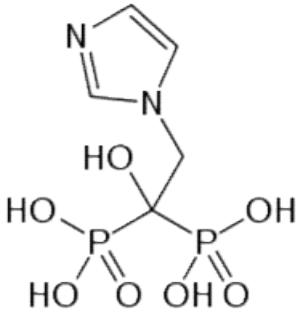



BINAP



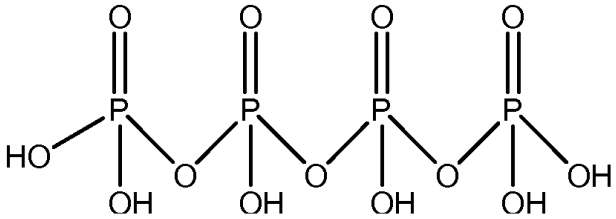

# osteoporosis drugs



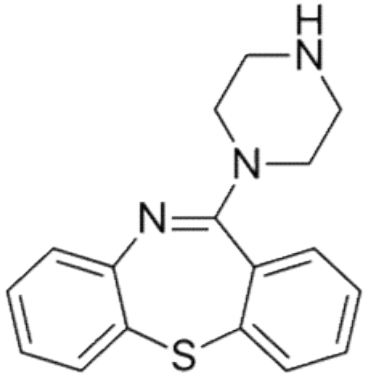



# drug synthesis

polyphosphoric acid



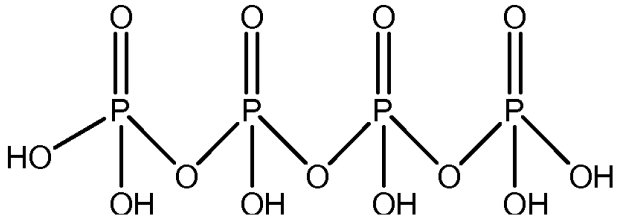

ring closure
for the production
of APIs




Quetiapine

treatment for
schizophrenia and depression

# asphalt additive




polyphosphoric acid

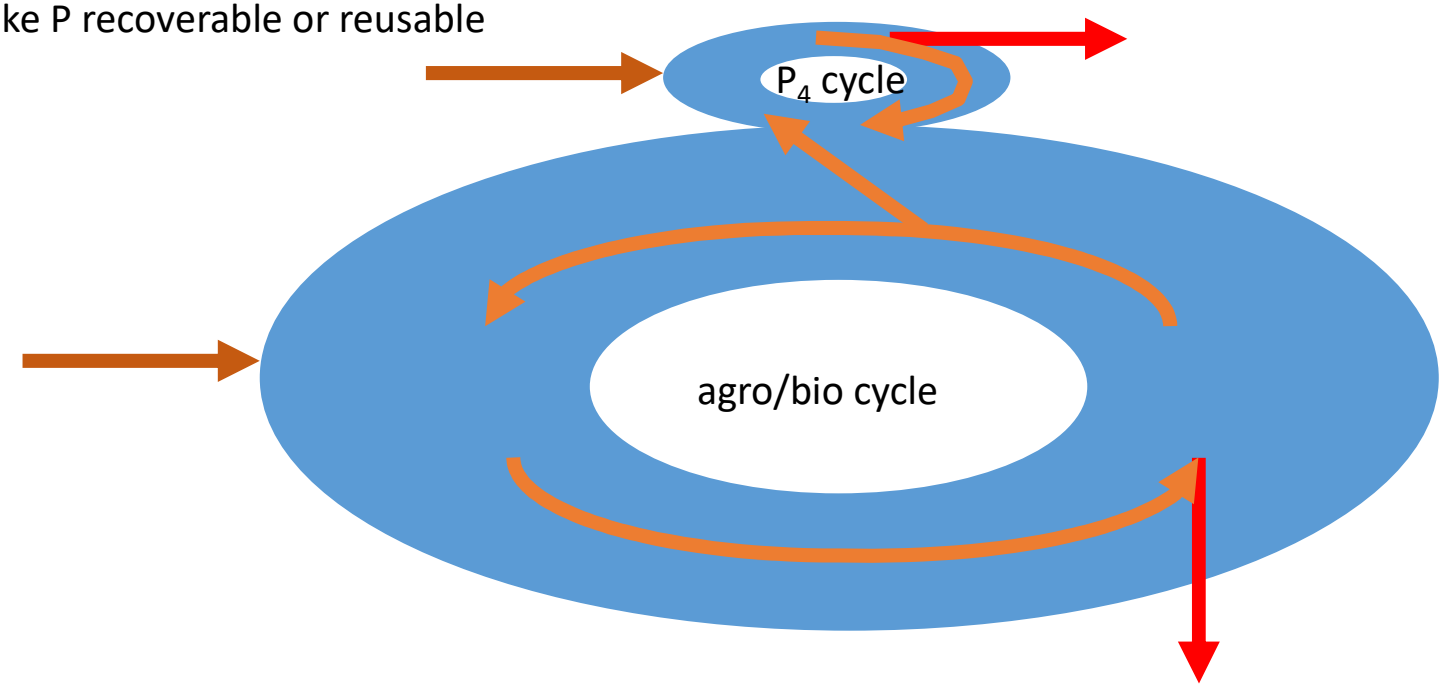
to improve asphalt characteristics
under extreme circumstances

# Closing the loop

P stewardship in technosphere ($P_4$) and biosphere not independent

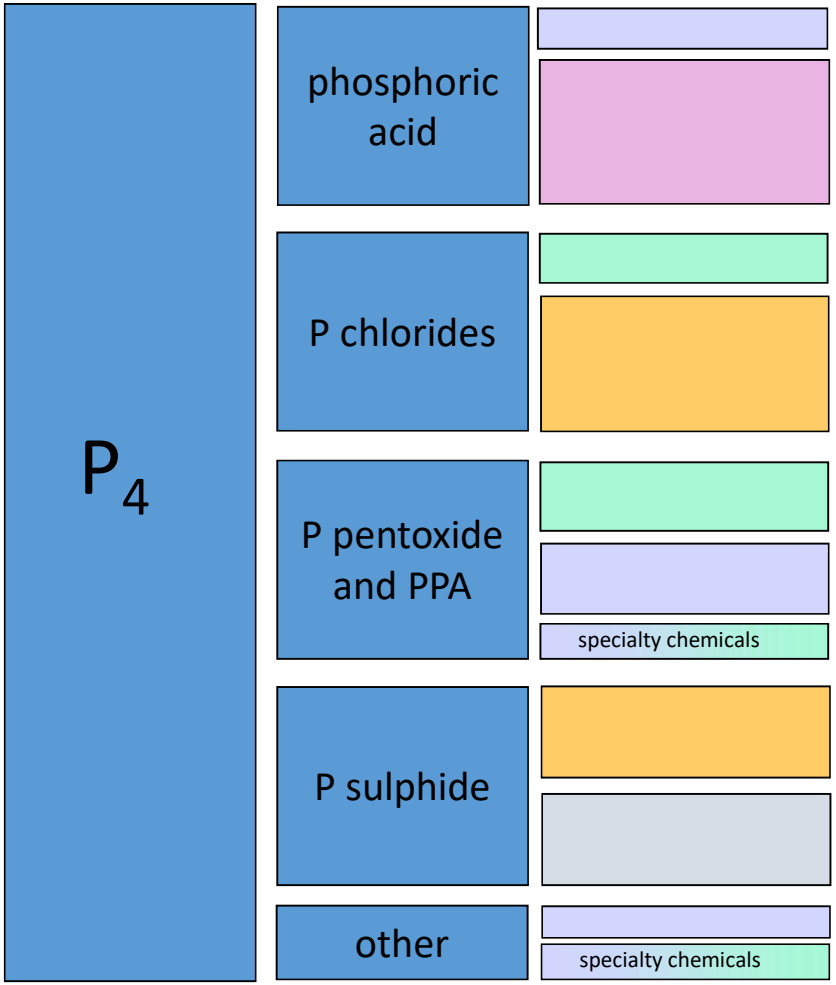
Recycle streams into technosphere P (white phosphorus ----- P rock replacement)

Design uses of P in technosphere to make P recoverable or reusable



# Phosphorus product routes

surprisingly, $P_4$ derivatives P ends up in five broad categories only




food and detergents
*P to wastewater*

plastic additives (FR/antiox.)
-> pl.recycling, waste, landfill
*P follows plastics routes*

surface treatment,
chemical water extraction
*P to side stream / waste*

pesticides for agriculture
*P follows fertilizer P*

lubricant additives
*P follows lubricant waste treatment routes*

# white phosphorus – sustainable?

- P essential use = agriculture, it should perhaps be “reserved” for that?
- however only 2% of P is used in true $P_4$ chemistry
- 2% more P use efficiency can probably be achieved more easily in agricultural applciation improvements and reducing meat consumption (feed phosphate – 5 to 10% of total)
- consider cradle-to-cradle design for P chemicals (e.g. recycle flame retarded plastics as such) – leading C2C principle: use freely and reuse, instead of abandon uses and forbid applications, therefore a limit on non-agricultural uses of P does not seem needed at this point

# Thank you
# for your attention!


Willem Schipper

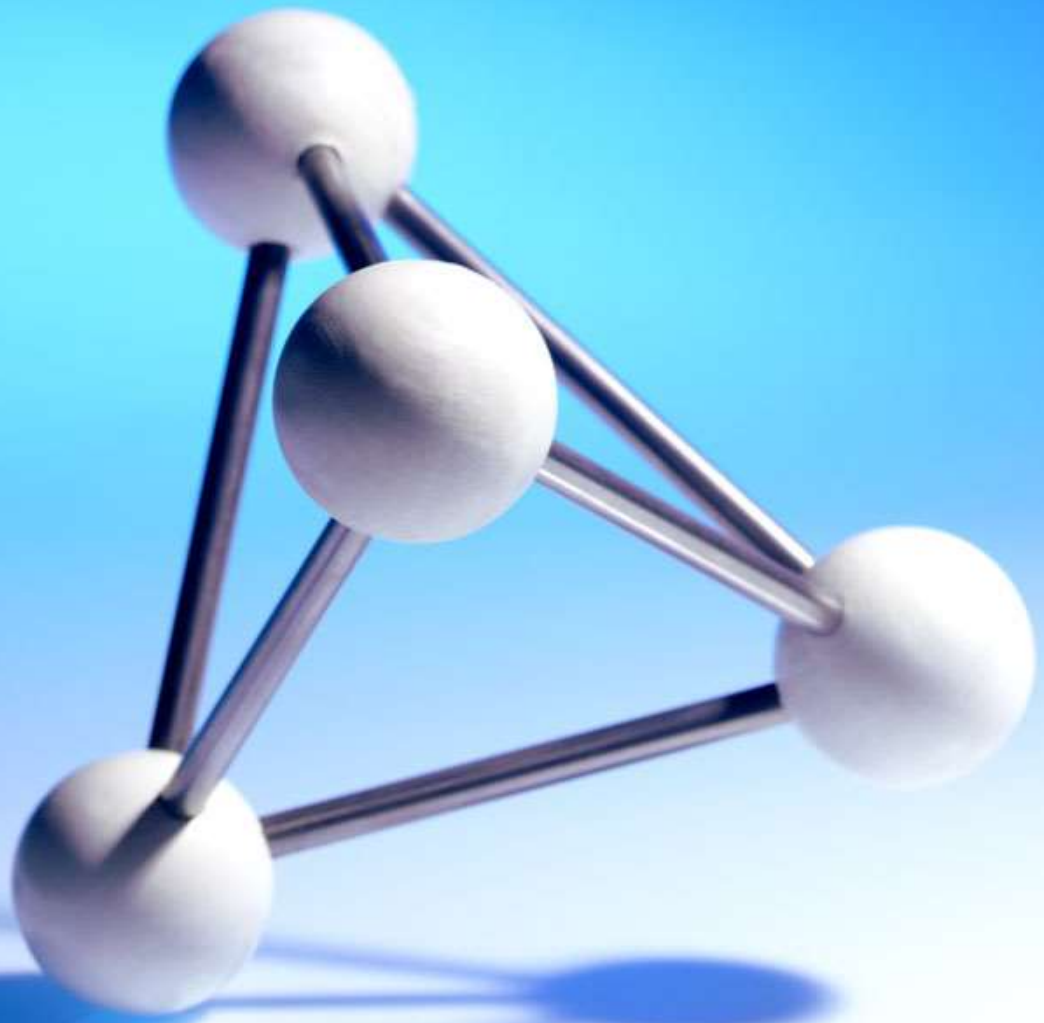
Consulting for phosphorus, P derivatives,
phosphoric acid and phosphates

Technology development, market studies

General ryclinging and sustainability

Innovation mamagement

www.linkedin.com/in/willemschipper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