Japan's experience and prospect on resource management of Phosphorus: policies, strategies, and technologies

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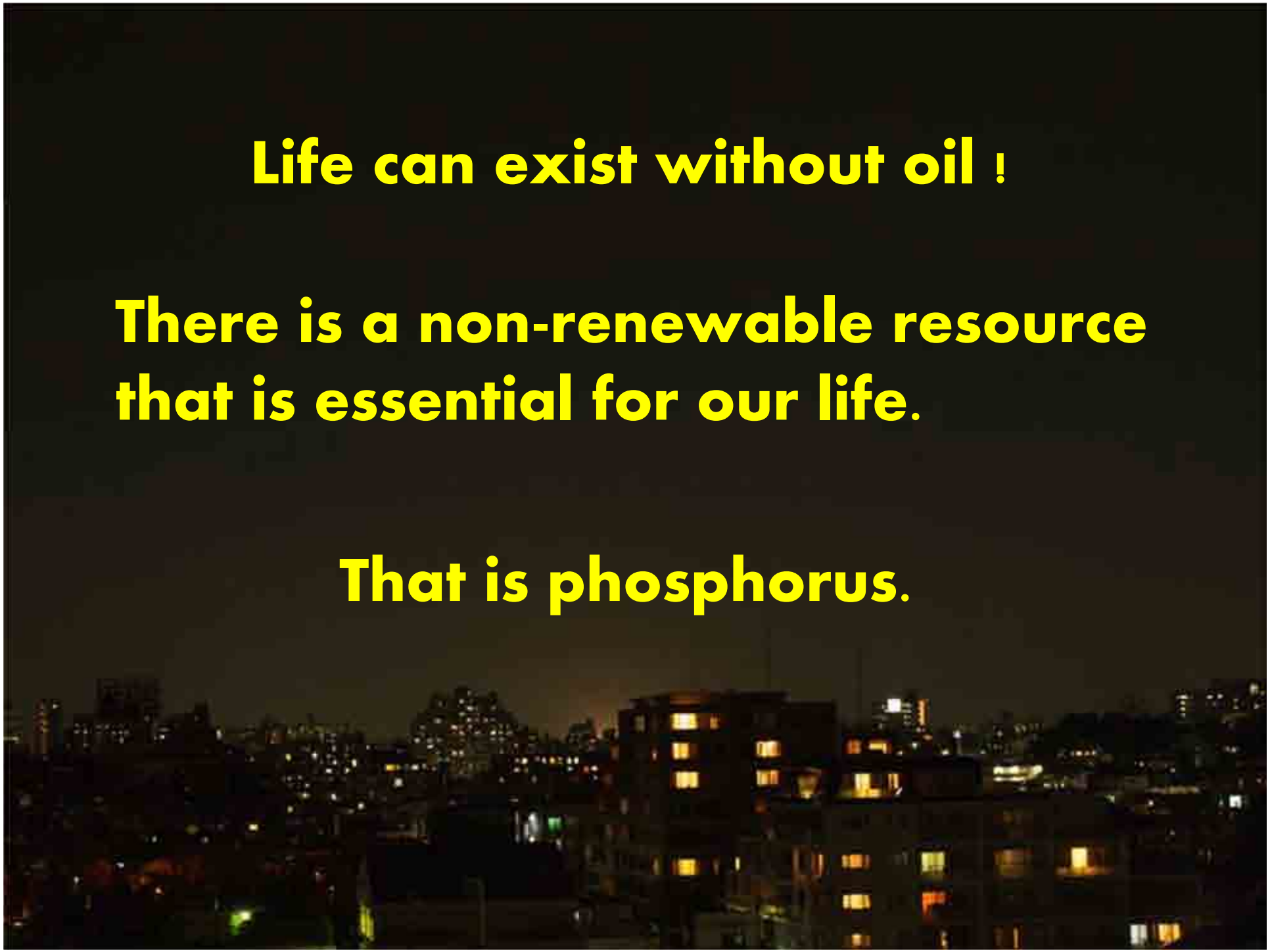
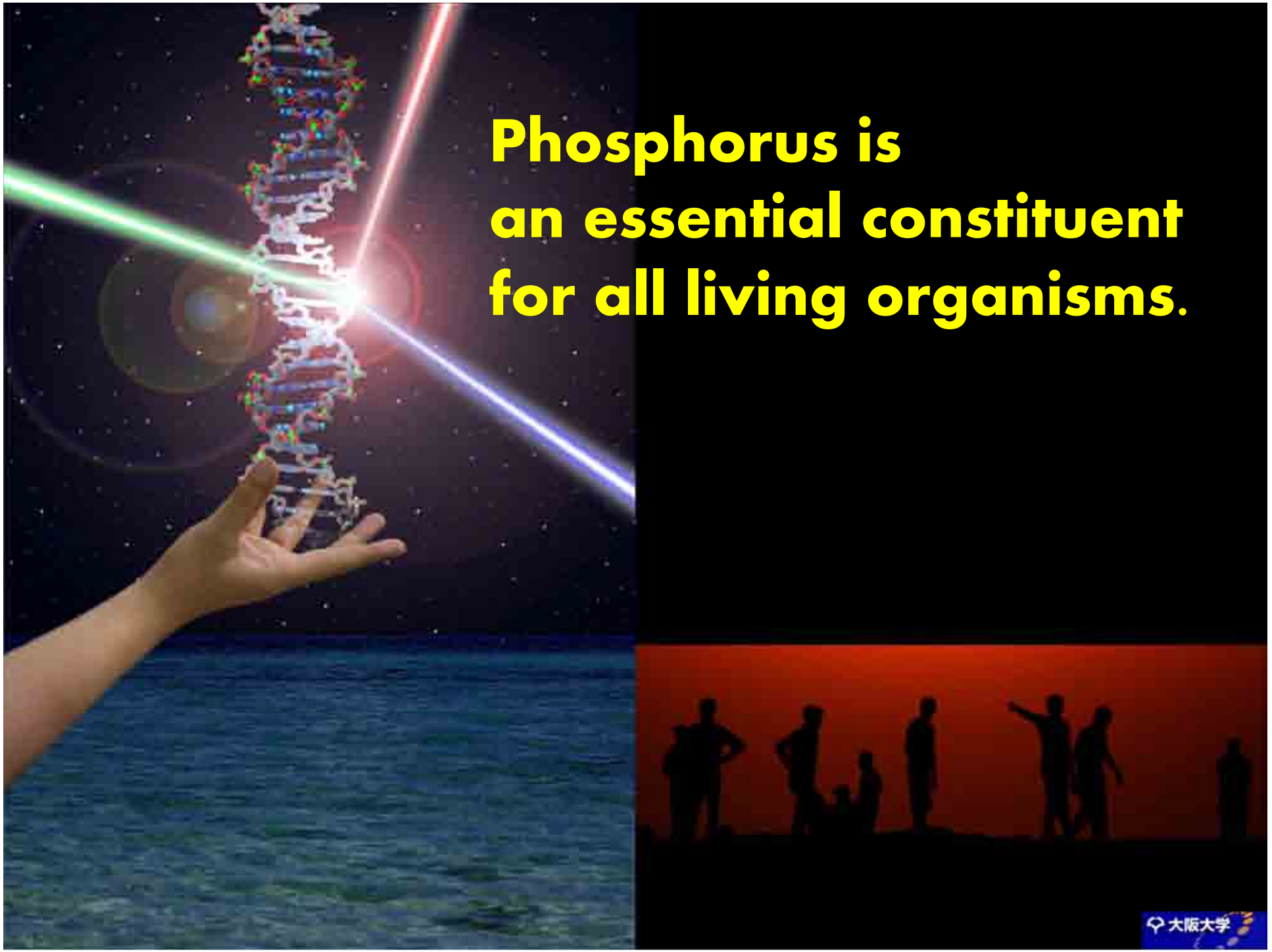

Life can exist without oil !
There is a non-renewable resource that is essential for our life.
That is phosphorus.


Phosphorus is
an essential constituent
for all living organisms.
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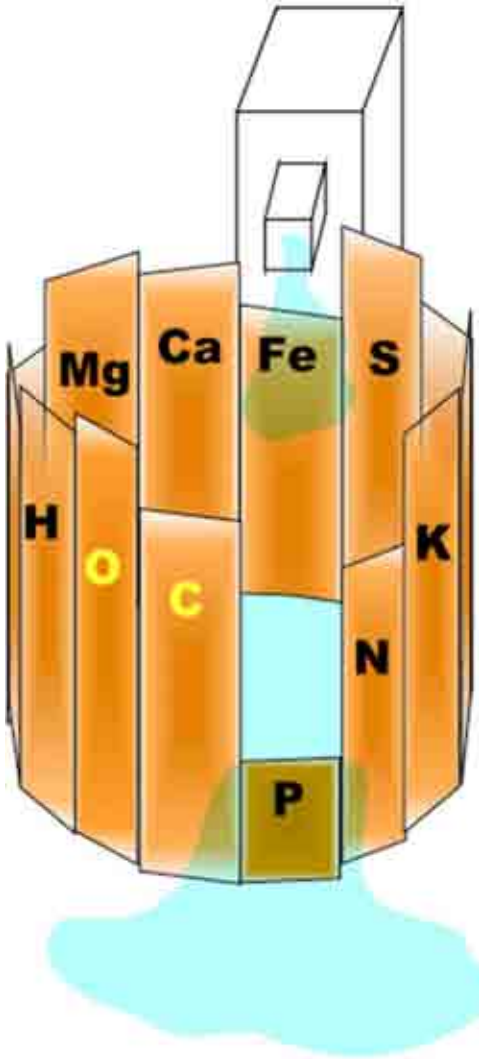
Why Phosphorus • • • ?

An essential element for animals and plants nutrition.

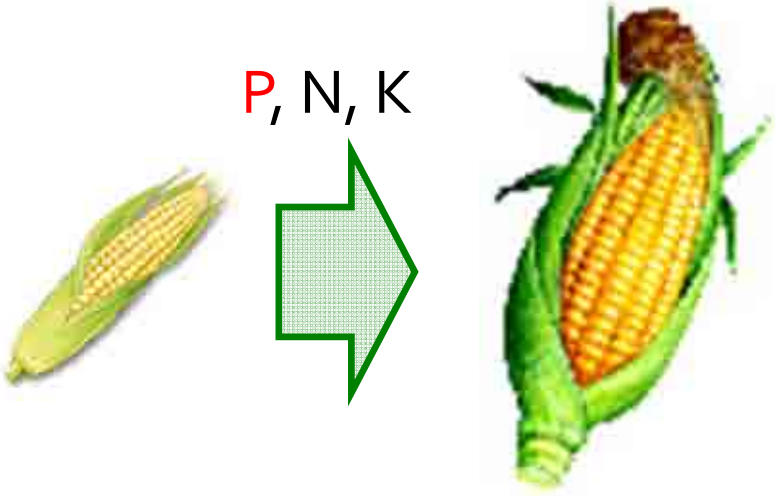


Supply of P often becomes critical for growth of plants

Nutrition barrel

Water level in the barrel, which is determined by the shortest plate, means growth degree of plant.

P, N, K



Without phosphorus, there will be no biomass, no biofuel, no agriculture, nor life.


Surface treatment chemicals


Etching agent

Flame-retardants

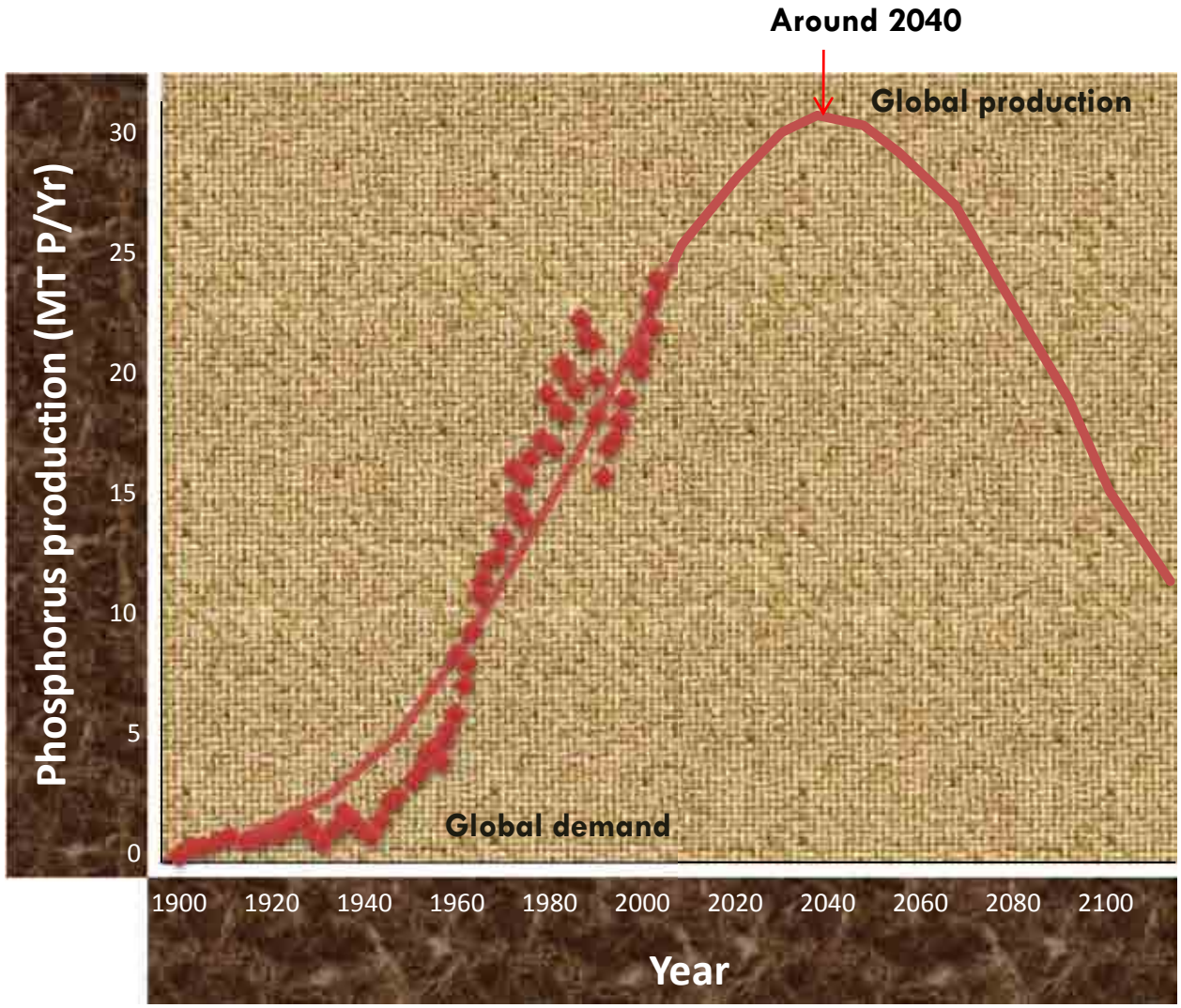
Phosphorus is used in a wide variety of manufacturing industries.


Food additives

Today, phosphorus is mostly obtained from mined rock phosphate which is a non-renewable resource.

From Prof. D. A. Vaccari

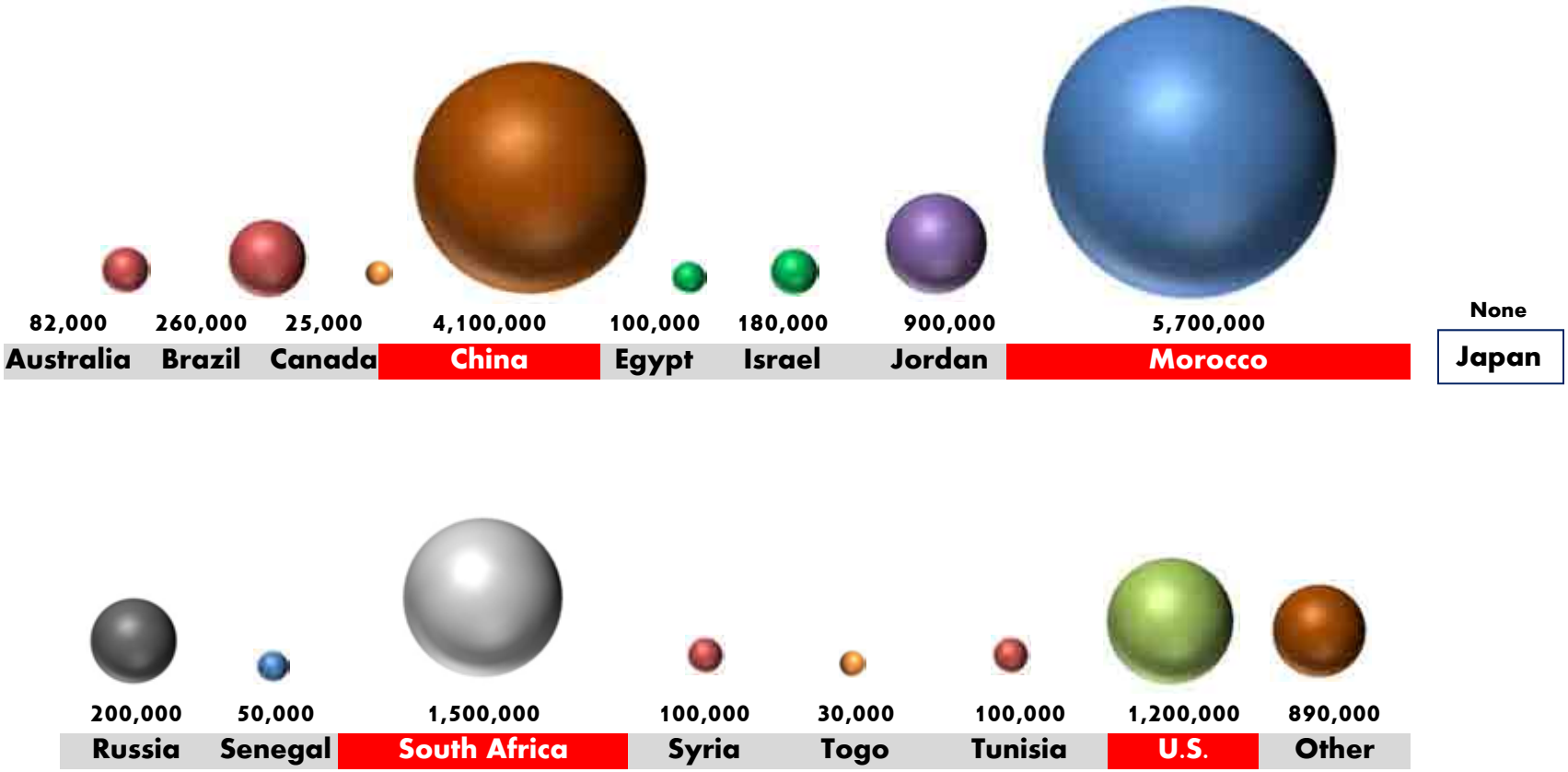
Peak phosphorus



Although the demand of phosphorus fertilizer is predicted to increase more than 50% by 2050, the global peak in phosphorus production is expected around 2040 .

D. Cordell et al., Global Environ. Change, 19：292-305

CONCENTRATED PHOSPHORUS RESOURCES

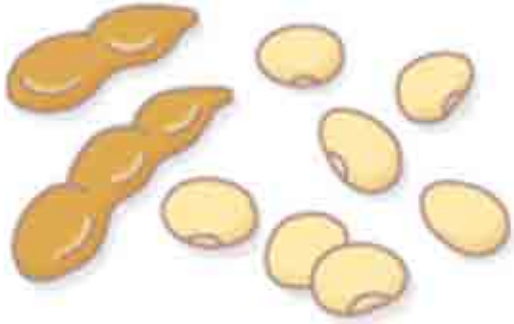


Phosphate Rock reserves (thousands of metric tons)

Morocco, China, South Africa and the U.S. hold 83% of the world's easily exploitable phosphate rock and contribute two thirds of the annual phosphorus production.

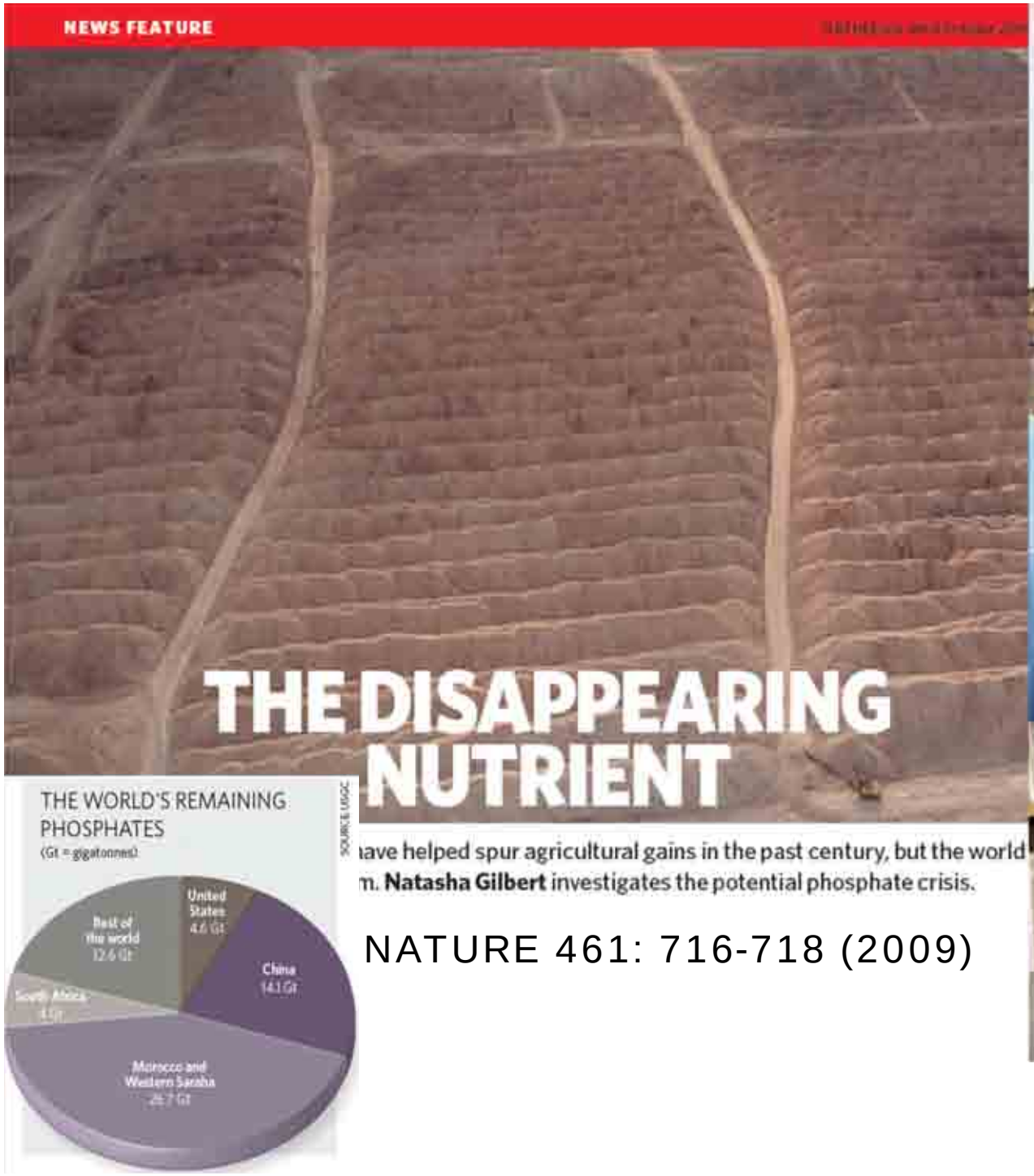
D.A. Vaccari, Scientific American, 54-59, June (2009)

Trend in other country



Brazil was phosphorus exporting country

But now they are importing phosphorus due to bio-fuel production



NATURE 461: 716-718 (2009)

Prof. D.A. Vaccari

SCIENTIFIC AMERICAN
54-57 June (2009)

P RECYCLING: JAPAN AS A CASE STUDY

I. Why does Japan need P recycling?

II. What are the potential resources for P recycling?

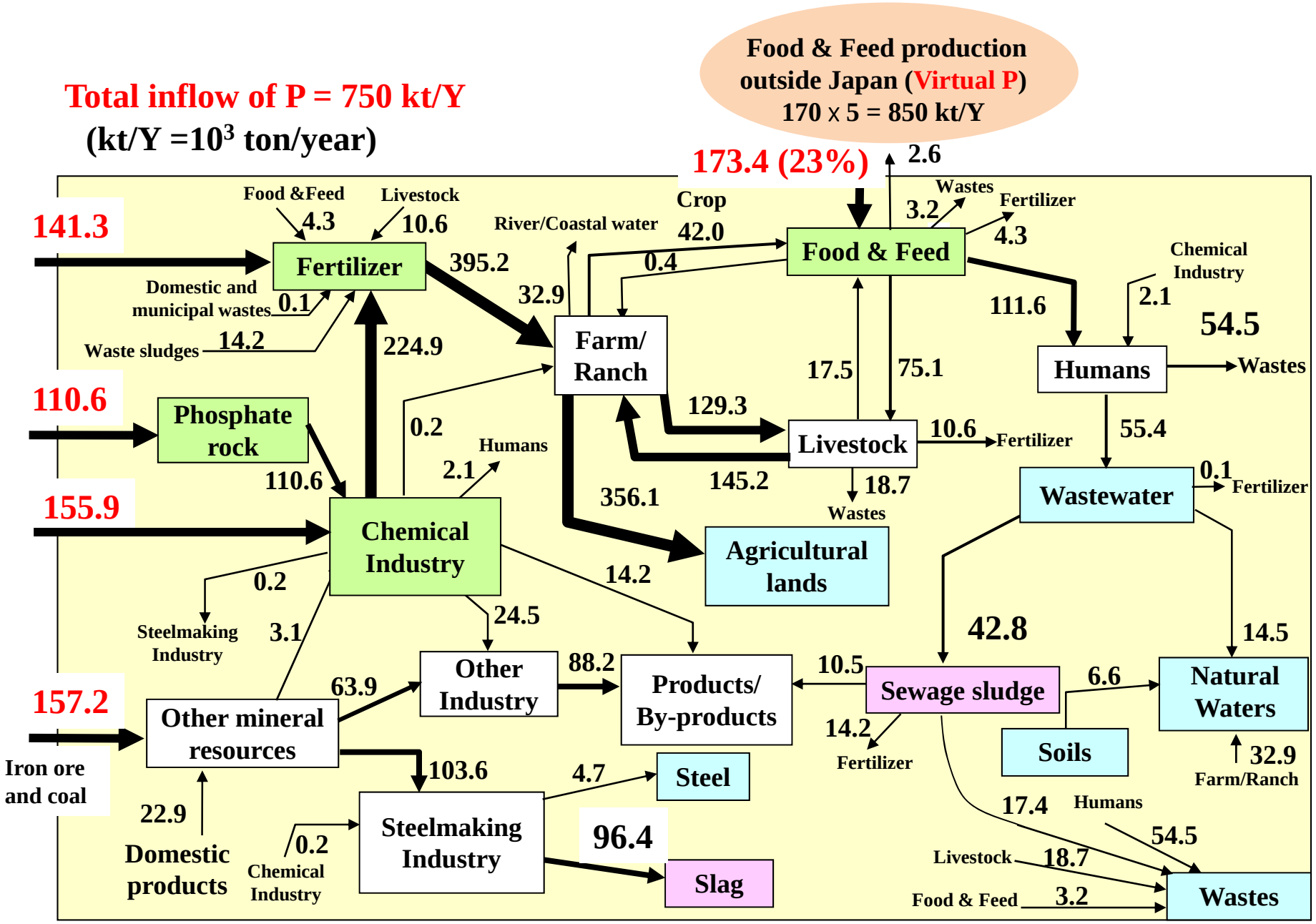
III. Development of P recycling as a new green industry

IV. Emerging technologies and business models

V. Key issues for fully realizing P recycling

VI. P Recycling Promotion Council of Japan

NATIONAL PHOSPHORUS FLOW IN JAPAN



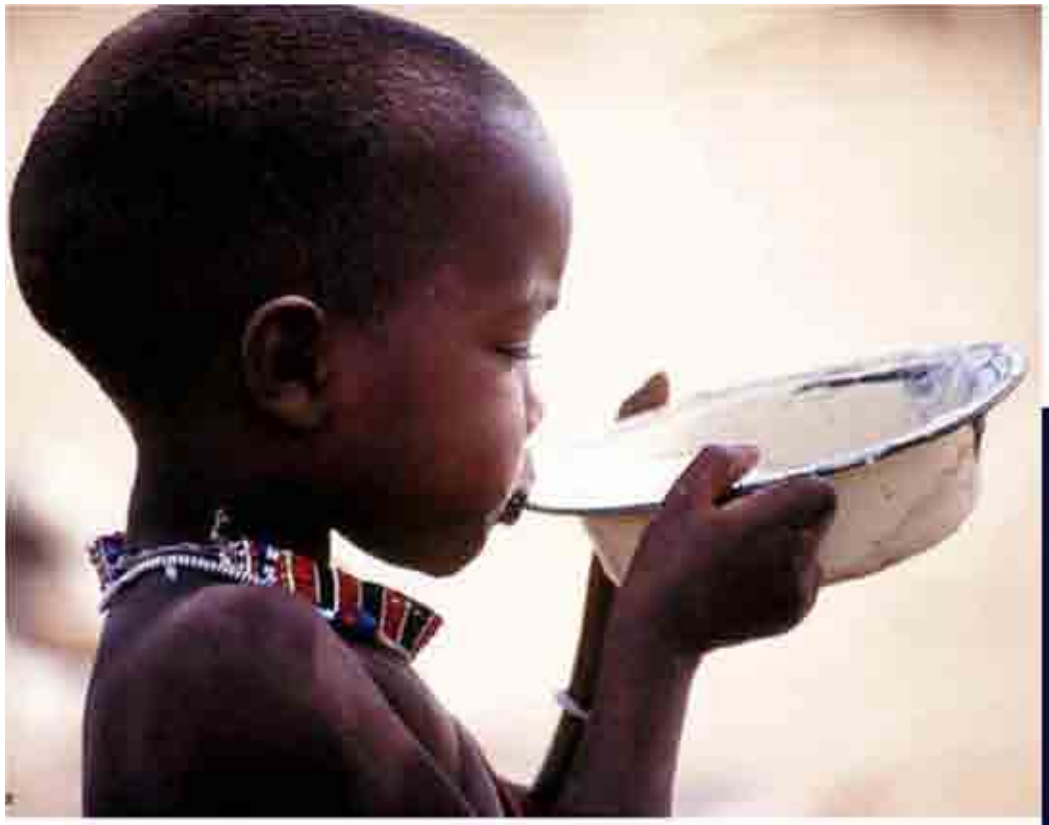
Yokoyama, et al., ISIJ International, 47: 1541-1548 (2007); modified by H. Ohtake

SIGNIFICANCE OF P RECYCLING IN JAPAN

WORLD P CONSUMPTION = ~17,000 KT/Y

INFLOW OF P	=	**750** (4.4%)
VIRTUAL P	=	**850** (5.0%)
TOTAL	= ~	**1,600 KT/Y**

~ 9% OF WORLD P CONSUMPTION



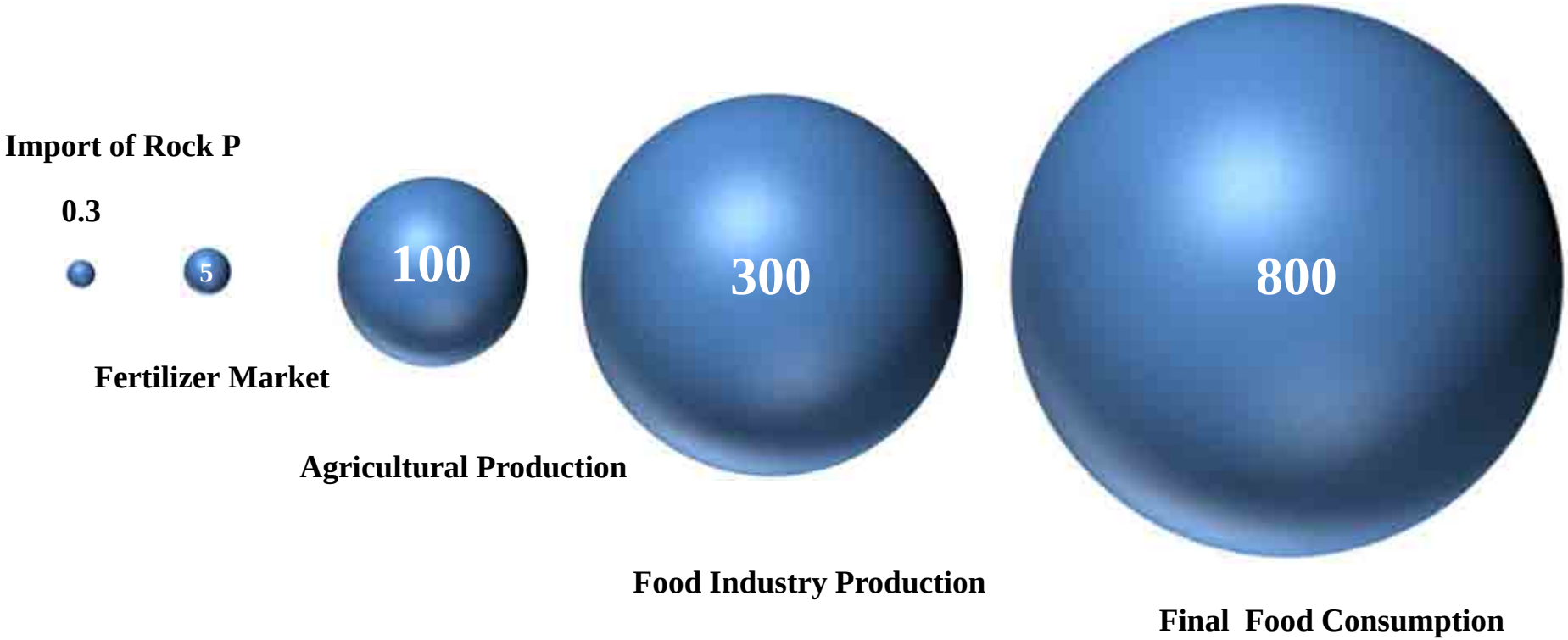
Morocco is the world-largest producer of high-quality rock phosphate. Nevertheless, the people in Morocco are facing difficult problems on the phosphate availability.

Japan is consuming approximately 10% of the world-consumption of rock phosphate.

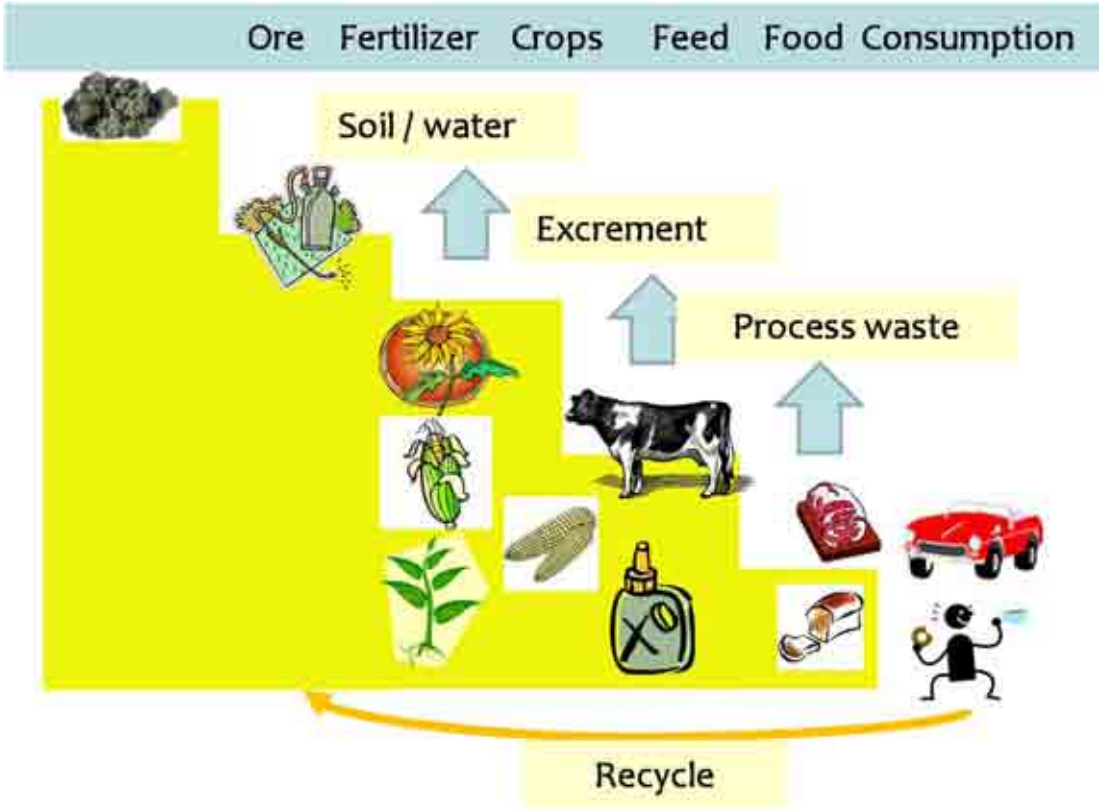
We have a responsibility for achieving phosphorus recycling for the green growth of the world.

THE SIZE OF MARKETS RELEVANT TO FOOD IN JAPAN

billion $/Y



The nature of phosphorus flow



- Most of all the phosphorus products start from ore.
- Once phosphorus flow into our society, phosphorus is in gradually loss by stages

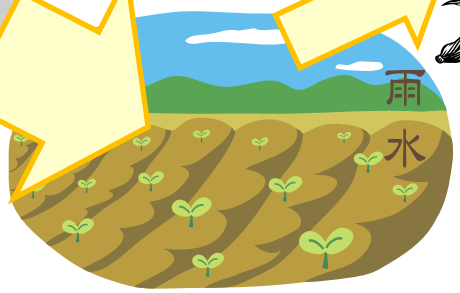
Food consumption derives the phosphorus ore demand.

Input	Loss
Fertilizer	Soil and Water
Feed	Excrement
Crops	Inedible Part, Food waste
Phosphorus compounds	Waste water, sludge

Virtual Phosphorus Ore Requirement (VPOR)

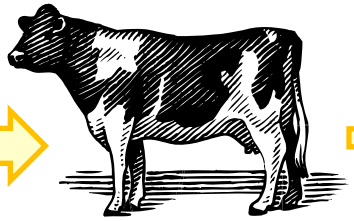
15.8 kg of phosphorus

7 t of maize,
11 t of corn silage,
and 450 kg of soy bean

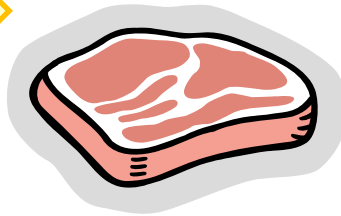


0.6 ha of farmland

550 kg



250 kg



One unit of cattle consumes 7 t of maize, 11 t of corn silage, and 450 kg of soy bean in 394 days produce 250 kg of beef from 550 kg of grown cattle (Subak, 1999).

- Feedstuffs also require crop acreage and nutrients.
- One unit of cattle requires 0.6 ha of farmland and 15.8 kg of phosphorus to produce its feedstuff.
- Feedstuff requirement for other meat production refers to inventory data derived from a Japanese Input Output Table

Details are in Matsubae et al, Chemosphere, 2011

Virtual Phosphorus Ore Requirement

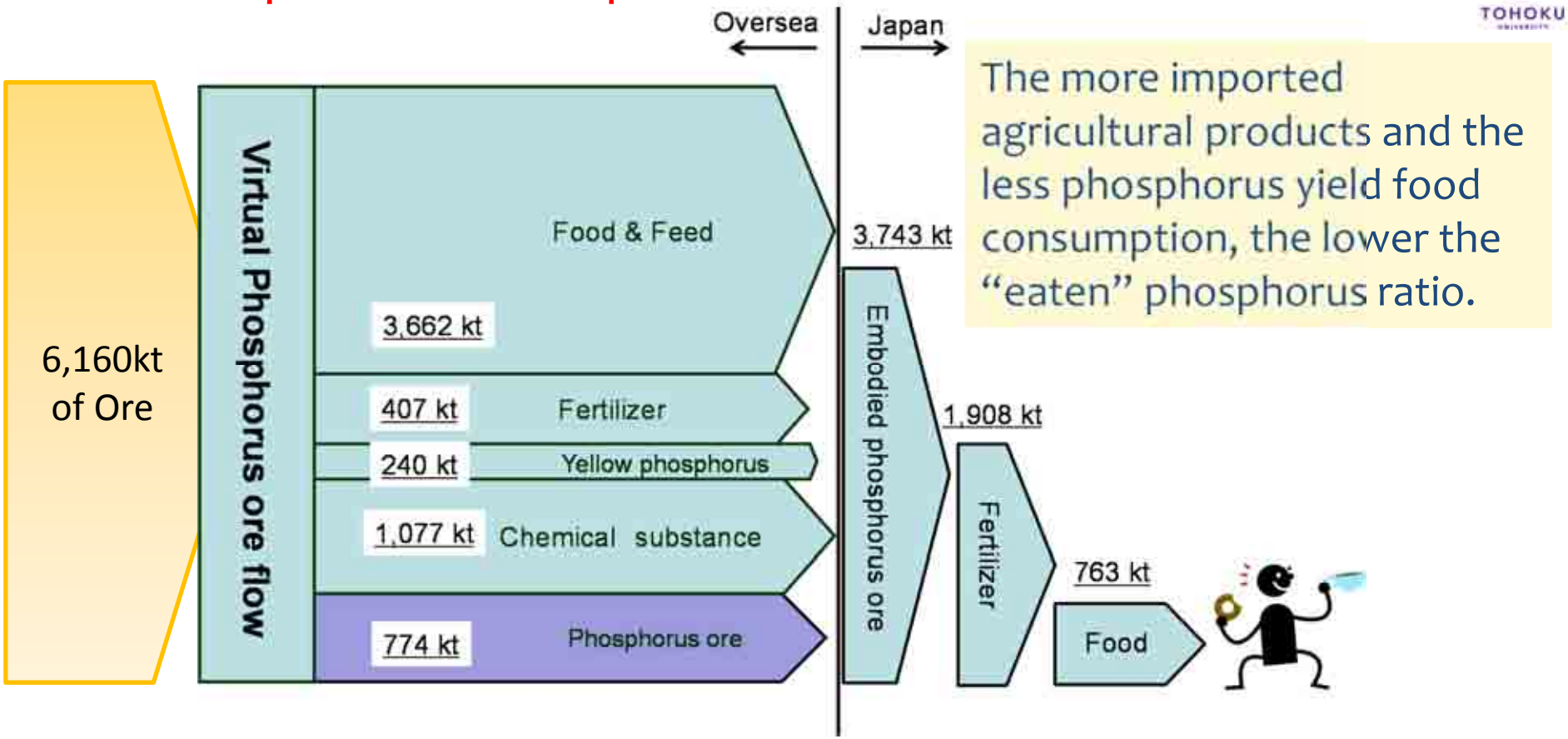


Fig. The Virtual Phosphorus Ore Flow in Japan(2005)

- Approximately half of imported embodied phosphate ore was transformed into fertilizer, and utilized to produce agricultural products.
- "Eaten" phosphate ore was 20% of imported virtual phosphorus ore and 12% of all the virtual phosphorus ore demand of Japan.

Matsubae, Kajiyama, Hiraki, Nagasaka, Chemosphere, 2011

P RECYCLING AS GREEN INDUSTRY

Food Industry

Food

Vegetable oil refinery process

Consumer

Water reclamation

Eutrophication control

Sewage

Wastewater treatment

Biosludge

Ash

P recovered

Fertilizer Industry

P fertilizer

Food and Feed

Agriculture

Farmland

Ash

Manure

P-free ash

Recycle Industry

Cement Industry

The P content of clinker needs to be lower than 0.5%.

High-tech Industry

Automobile

Semiconductor

Liquid crystal

P Recycling for Industry

Yellow P manufacturing

Yellow P

Phosphoric acid manufacturing

High-quality phosphate

P slag

Iron ore

Coke

Steel Industry

Steel-making slag

P-free slug

P-free slag can be returned to a steel manufacturing process.

Steel-making Industry

Phosphate production by a wet process

Phosphoric acid manufacturing

Phosphate

Chemical Industry

P recovered

P recycle through yellow phosphorus regeneration

P RECOVERY IN HIGH-TECH INDUSTRY

Surface treatment chemicals

Automobile

HONDA
The Power of Dreams

TOYOTA

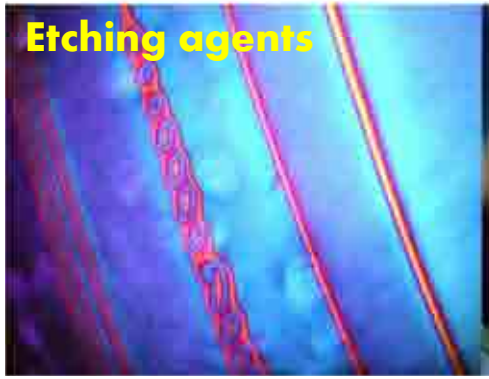
$Zn_2Fe(PO_4)_2 \cdot 4H_2O$

Rechargeable battery

$LiFePO_4$

Panasonic
ideas for life

Quality phosphoric acid is used in high-tech industries.



Etching agents

Flame retardants

Liquid crystal panel

DIRECT HYDRATION OF ETHYLENE TO ETHANOL

Catalyst: phosphoric acid
300°C 60 atm. *JAPAN SYNTHETIC ALCOHOL CO.,Ltd.*

P RECOVERY IN FOOD AND FERMENTATION INDUSTRY

Waste and wastewater from edible oil refining process contain high levels of P.

P emission: 10-20 tons P per year

J-OIL MILLS

Ever-increasing disposal costs have offered incentives to P recycling.

P RECYCLING AS GREEN INDUSTRY

90 ktonP/Y

Food and Feed

Agriculture

Fertilizer Industry → **P fertilizer** → Farmland ← Ash ← Manure

Import from Australia, Brazil, and India

P recovered

P slag

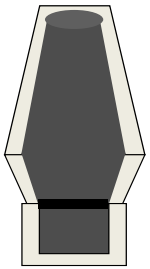
Iron ore
Coal
→ **Steel Industry** → **Steel-making slag**

P-free slug

P-free slag can be returned to a steel manufacturing process.

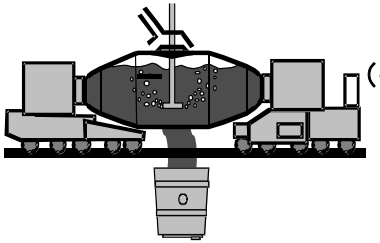
Steel-making Industry

P RECYCLING IN STEEL-MAKING INDSUTRY



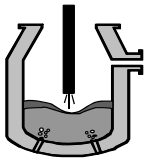
P 0.12 w%

(~1500℃)



P 0.02 w%

(~1400℃)



(~1600℃)

P 2-3 w%

Iron making | **Hot metal pretreatment** | **Basic oxygen steel making**

Steel-making slag

P RECYCLING AS A SUCCESSFUL BUSINESS

Phosphorus and the Titanic

K. Felkins, H.P. Leighly, Jr., and A. Jankovic:

The Royal Mail Ship Titanic: Did a Metallurgical Failure Cause a Night to Remember? Journal of Metals, 50 (1) (1998), pp. 12-18.

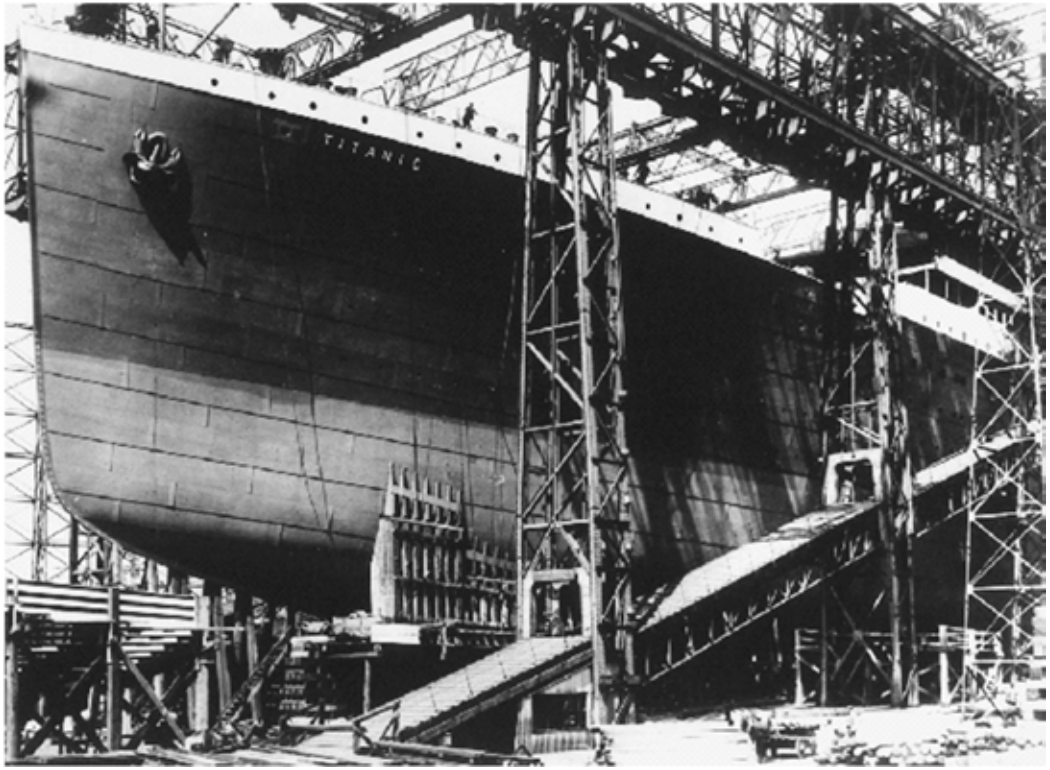


Figure 1. The Titanic under construction at the Harland and Wolff shipyard in Ireland. (Photo courtesy of the Titanic Historical Society.)

Phosphorus and the Titanic

Table The Composition of Steels from the *Titanic*, and ASTM A36 Steel									
	C	**Mn**	**P**	**S**	**Si**	**Cu**	**O**	**N**	**MnS: Ratio**
***Titanic* Hull Plate**	0.21	0.47	0.045	0.069	0.017	0.024	0.013	0.0035	6.8:1
ASTM A36	0.20	0.55	0.012	0.037	0.007	0.01	0.079	0.0032	14.9:1

The presence of relatively high amounts of phosphorous, oxygen, and sulfur has a tendency to embrittle the steel at low temperatures.

There is a high probability that the steel used in the Titanic was made in an acid-lined open-hearth furnace, which accounts for the fairly high phosphorus and high sulfur content.

P RECOVERY FROM STEEL-MAKING SLAG

Approximately 90 kt P/Y is emitted in the form of steel-making slag.

Tragedy of phosphorus in slag

"We are producing high quality steels, not slag", steelmaker said.

P RECOVERY FROM SEWAGE

P recovery and recycling in the sewage treatment sector is most practical and promising.

UNUSED PHOSPHORUS RESOURCE

- Eutrophic lake water and sediments
- Sewage sludge and sludge incineration ash
- Steel-making slag
- Waste from food and fermentation industry
- Waste from chemical industry
- Garbage and kitchen waste
- Agricultural and livestock waste
- Waste from high-tech industry
- Farmland soil
- Low-quality rock phosphate

PHOSPHATE REFINERY

QUALITY, COST, AND MARKET

Yellow phosphorus

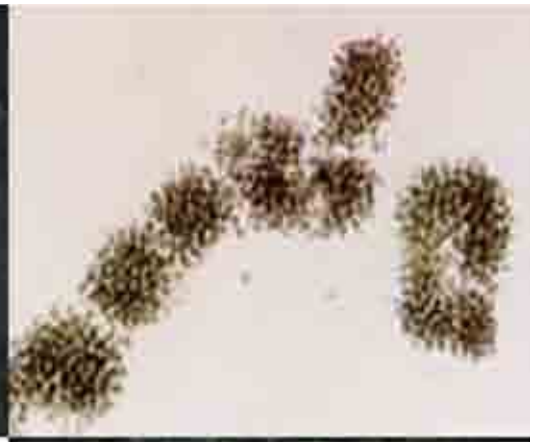
Phosphoric acid

Phosphate Refinery is the technology for recovering phosphorus from unused resources .

SECONDARY PRODUCT	USE APPLICATION
Surface treatment chemicals	Automobile body Steel plate
Etching agent	Computer Cellular phone Liquid crystal TV
Food additive	Antioxidant Flavor enhancer
Frame retardant	Home electronics Textile Printer
Electronics, Battery	Electric Car Battery PC battery
Intermediate of medicine	Antibiotics Medicine
Chemicals, Pesticide	Detergent Shampoo
Fertilizer, Feed additive	Phosphate fertilizer Mixed fertilizer
Food oil refinery agent	Cooking oil Salad oil

P RECYCLING HAS NEVER BEEN REALIZED ON A LARGE SCALE.

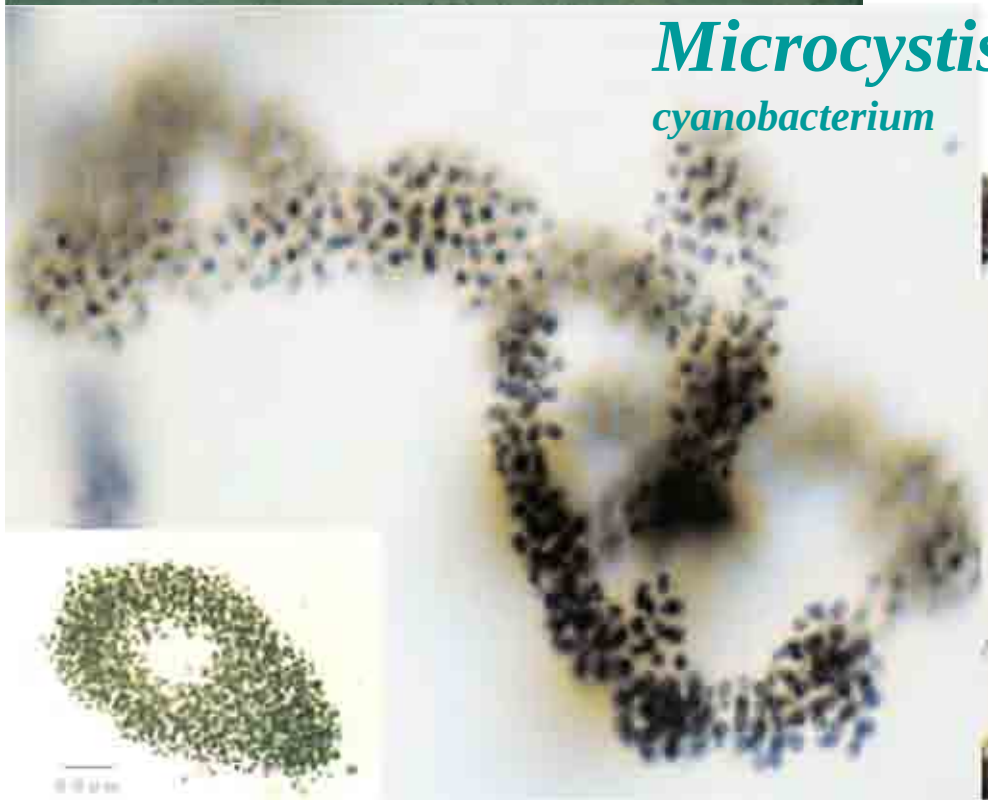
It is very important to show how P recycling becomes a successful business.



Eutrophication

Microcystis aeruginosa

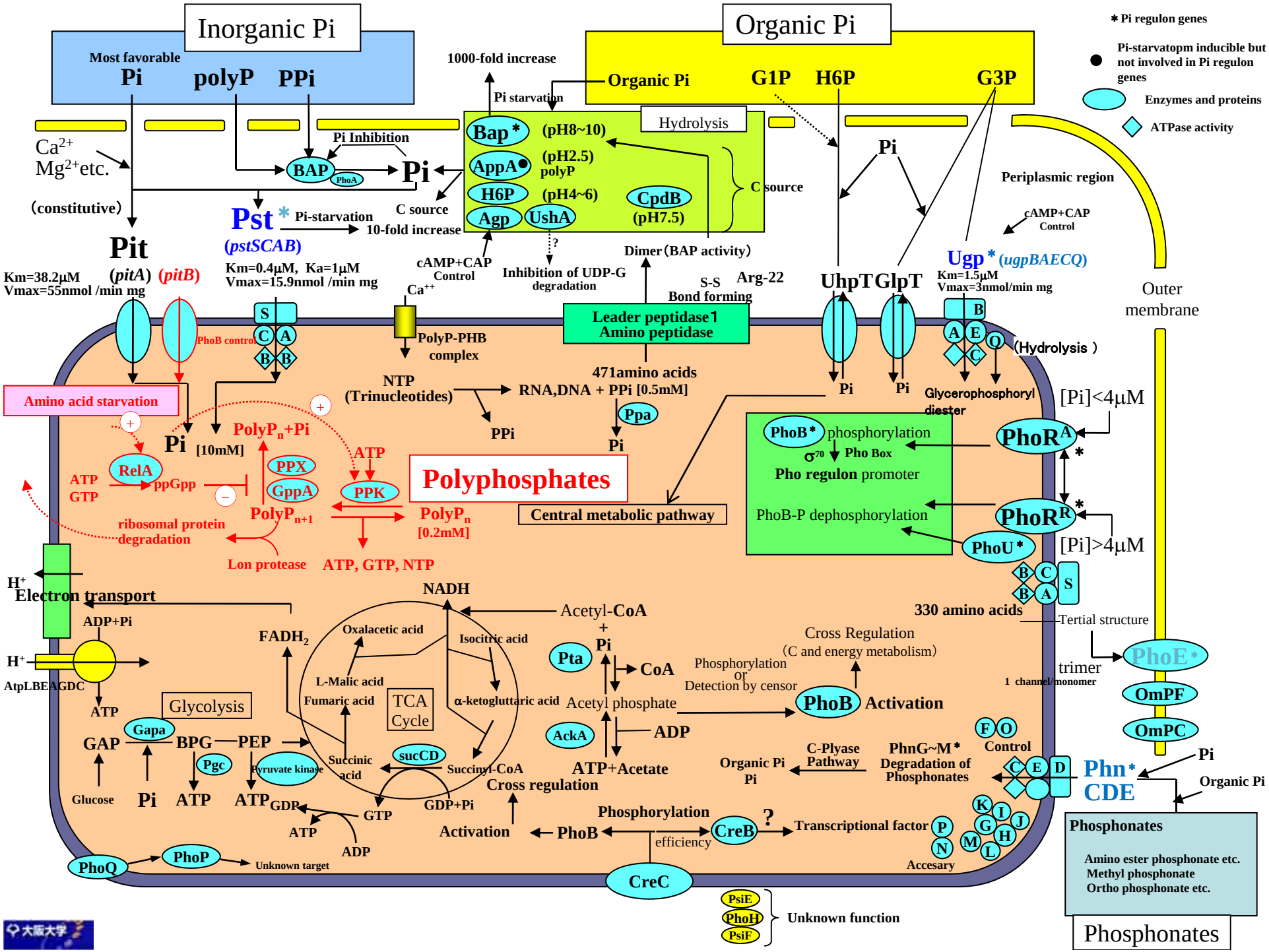
cyanobacterium

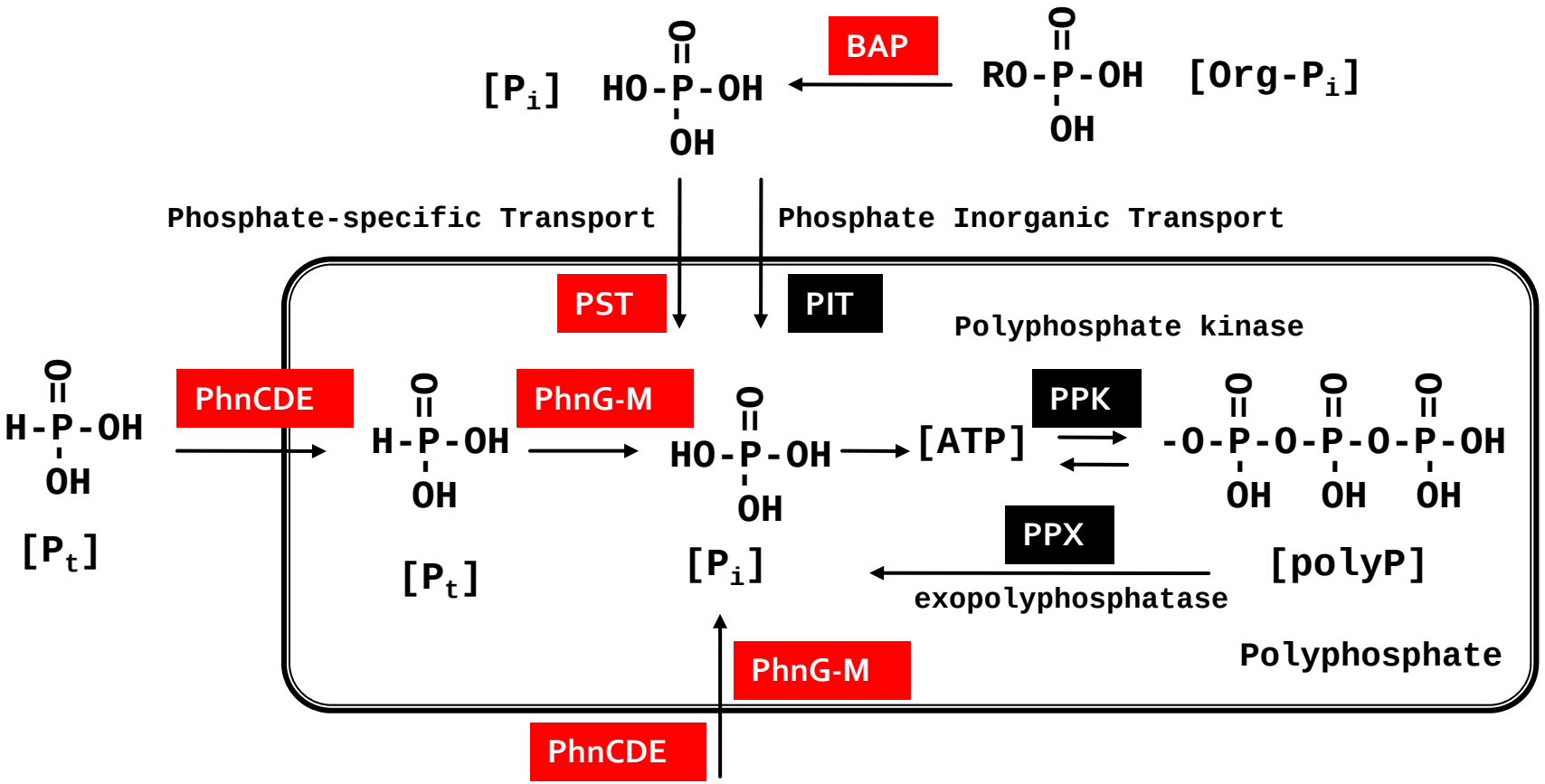


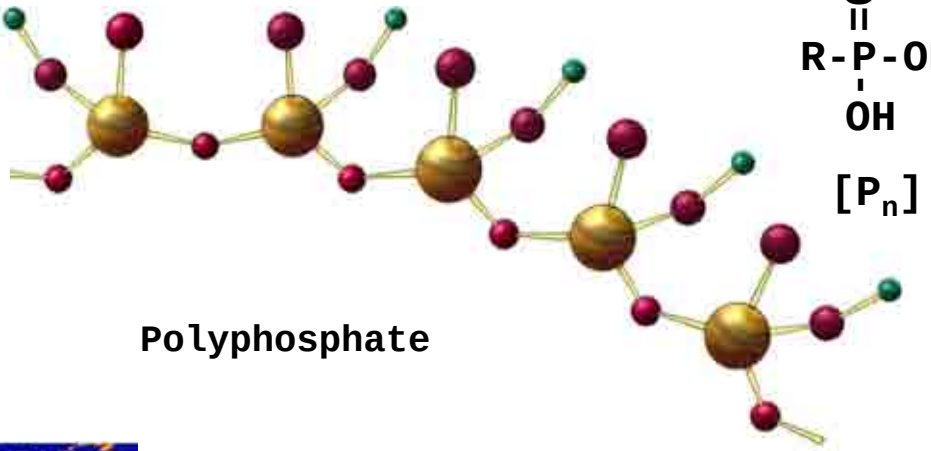
Eutrophication

Dissolved oxygen is consumed when the cells are decomposed by aerobic bacteria, killing economically important fishes and other aquatic organisms. In addition, a toxic substance, called algal toxin, is released from the bloom. This is also a difficult problem in drinking water supply.

Fish Kill


Inorganic Pi
Most favorable
Pi polyP PPi
Organic Pi
Organic Pi G1P H6P G3P
* Pi regulon genes
Pi-starvatopm inducible but not involved in Pi regulon genes
Enzymes and proteins
ATPase activity
1000-fold increase
Pi starvation
Hydrolysis
Bap * (pH8~10)
AppA● (pH2.5) polyP
H6P (pH4~6)
Agp UshA CpdB (pH7.5)
C source
Pi Inhibition
BAP PhoA
Pi
C source
Ca2+ Mg2+etc.
(constitutive)
Pst * Pi-starvation
(pstSCAB)
10-fold increase
Km=0.4μM, Ka=1μM
Vmax=15.9nmol /min mg
Pit
(pitA) (pitB)
Km=38.2μM
Vmax=55nmol /min mg
cAMP+CAP Control
Ca++
Inhibition of UDP-G degradation
Dimer (BAP activity)
S-S Bond forming
Arg-22
Leader peptidase1
Amino peptidase
UhpT GlpT
Ugp * (ugpBAECQ)
Km=1.5μM
Vmax=3nmol/min mg
Periplasmic region
cAMP+CAP Control
Outer membrane
PhoB control
PolyP-PHB complex
(Hydrolysis)
Glycerophosphoryl diester
Amino acid starvation
NTP (Trinucleotides)
RNA,DNA + PPi [0.5mM]
471amino acids
PPi
Ppa
Pi
Pi
Pi
[10mM]
PolyPn+Pi
ATP
RelA
ATP GTP
ppGpp
PPX
GppA
PPK
Polyphosphates
PolyPn+1
PolyPn [0.2mM]
ribosomal protein degradation
Lon protease
ATP, GTP, NTP
Central metabolic pathway
PhoB * phosphorylation
σ70 Pho Box
Pho regulon promoter
PhoB-P dephosphorylation
PhoR A *
PhoR R *
PhoU *
[Pi]<4μM
[Pi]>4μM
H+ Electron transport
ADP+Pi
H+
AtpLBEAGDC
ATP
NADH
FADH2
Acetyl-CoA + Pi
Pta
CoA
Acetyl phosphate
AckA
ADP
ATP+Acetate
Oxalacetic acid
Isocitric acid
L-Malic acid
Fumaric acid
TCA Cycle
α-ketogluttaric acid
Succinic acid
sucCD
Succinyl-CoA
Cross regulation
Glycolysis
GAP Gapa BPG PEP
Pgc
Pyruvate kinase
Glucose
Pi
ATP
ATP GDP
GTP
GDP+Pi
ATP
ADP
Activation
PhoB
Phosphorylation
efficiency
CreB
?
Transcriptional factor
CreC
PhoQ
PhoP
Unknown target
Cross Regulation
(C and energy metabolism)
Phosphorylation or Detection by censor
PhoB Activation
330 amino acids
Tertial structure
trimer
1 channel/monomer
PhoE *
OmPF
OmPC
Pi
Organic Pi
Phn * CDE
C-Plyase Pathway
Organic Pi
Pi
PhnG~M * Degradation of Phosphonates
F O Control
Accesary
PsiE PhoH PsiF
Unknown function
Phosphonates
Amino ester phosphonate etc.
Methyl phosphonate
Ortho phosphonate etc.
Phosphonates





Polyphosphate

Inducible under P_i limitation

大阪大学

K. Imazu et a., Appl. Environ. Microbiol., 64: 3754-3758 (1998).

Science

Role of Inorganic Polyphosphate in Promoting Ribosomal Protein Degradation by the Lon Protease in *E. coli*

Akio Kuroda,[1]* Kazutaka Nomura,[1] Ryo Ohtomo,[2] Junichi Kato,[1] Tsukasa Ikeda,[1] Noboru Takiguchi,[1] Hisao Ohtake,[1] Arthur Kornberg[2]

Inorganic polyphosphate (polyP), a polymer of hundreds of phosphate (P_i) residues, accumulates in *Escherichia coli* in response to stresses, including amino acid starvation. Here we show that the adenosine 5′-triphosphate–dependent protease Lon formed a complex with polyP and degraded most of the ribosomal proteins, including S2, L9, and L13. Purified S2 also bound to polyP and formed a complex with Lon in the presence of polyP. Thus, polyP may promote ribosomal protein degradation by the Lon protease, thereby supplying the amino acids needed to respond to starvation.

PolyP is found in all microbes, fungi, plants, and animals (*1*). In *Escherichia coli*, levels of polyP are low in the exponential phase of growth, but increase more than 100-fold in response to acute stresses such as amino acid starvation and the multiple stresses in stationary phase (*2*, *3*). An *E. coli* mutant deficient in polyphosphate kinase (PPK), the principal enzyme for the synthesis of polyP, shows an extended lag in growth when shifted from a rich to a minimal medium (downshift); addition of amino acids abolishes the growth lag (*4*). Degradation of intracellular proteins is important in providing amino acids for use in the synthesis of the enzymes required for adaptations to starvation (*4*, *5*). The mutant fails to increase protein turnover after the downshift and thus extends the lag (*4*). In yeast and animal cells, the bulk degradation of proteins in response to starvation and cellular differentiation occurs by a ubiquitin-style conjugation system (*6*). However, in bacteria, the mechanisms underlying the regulation of intracellular protein degradation during amino acid starvation remain unknown (*5*).

In *E. coli*, more than 90% of cytoplasmic

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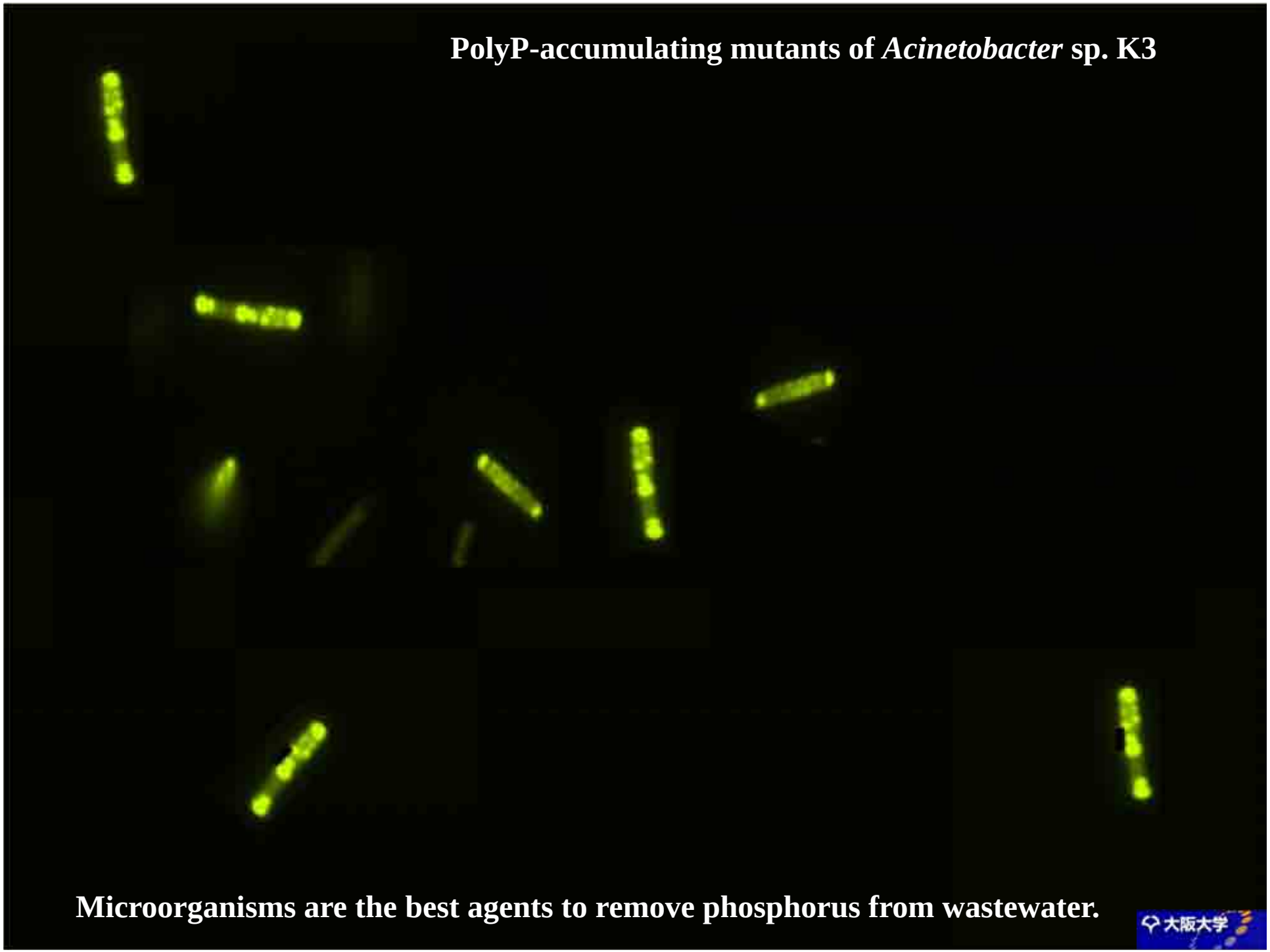
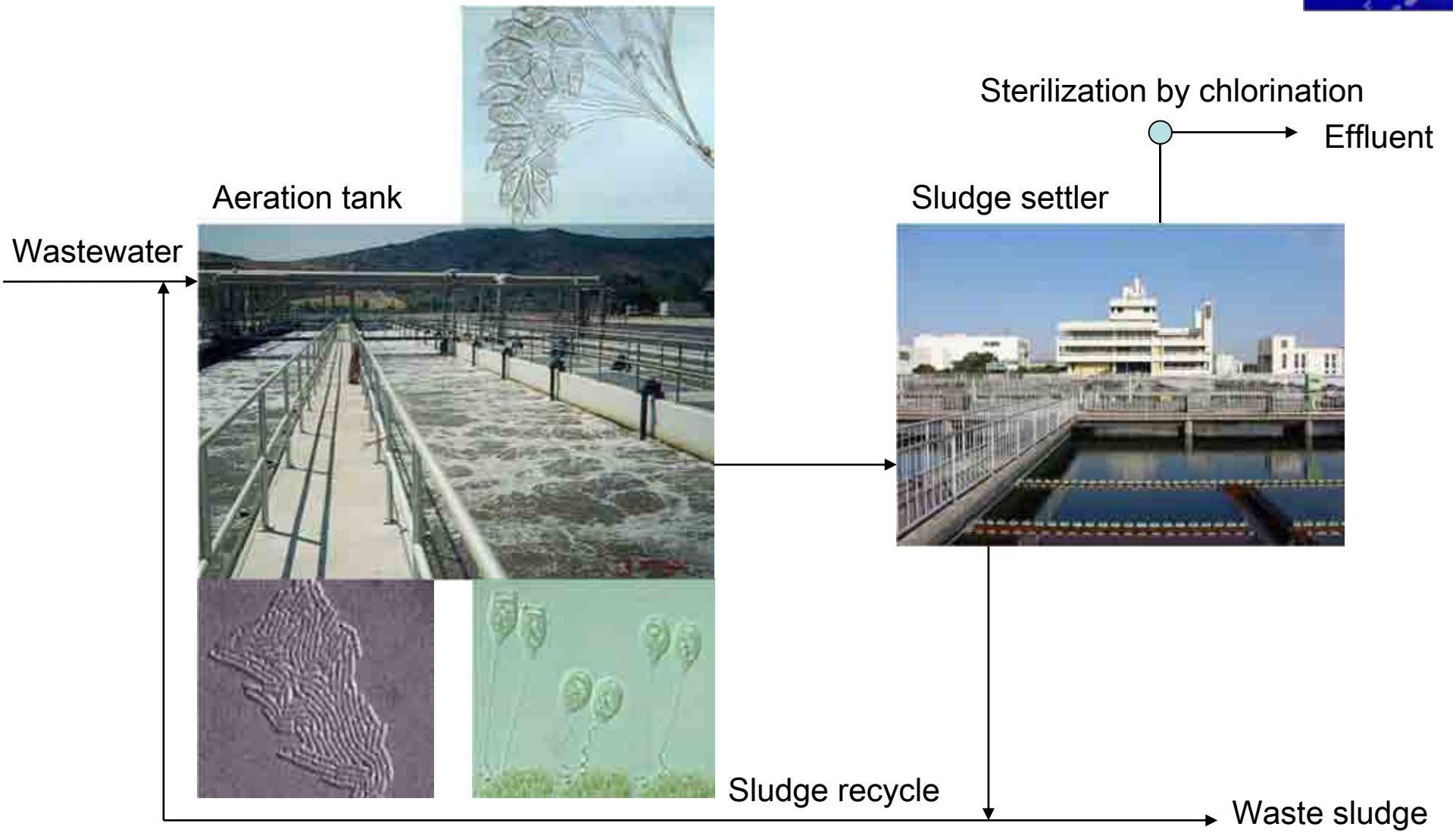
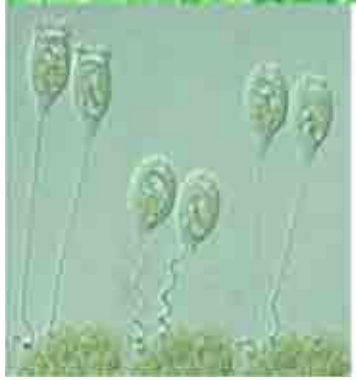
*To whom correspondence should be addressed. E-mail: akuroda@hiroshima-u.ac.jp


PolyP-accumulating mutants of *Acinetobacter* sp. K3
Microorganisms are the best agents to remove phosphorus from wastewater.
大阪大学



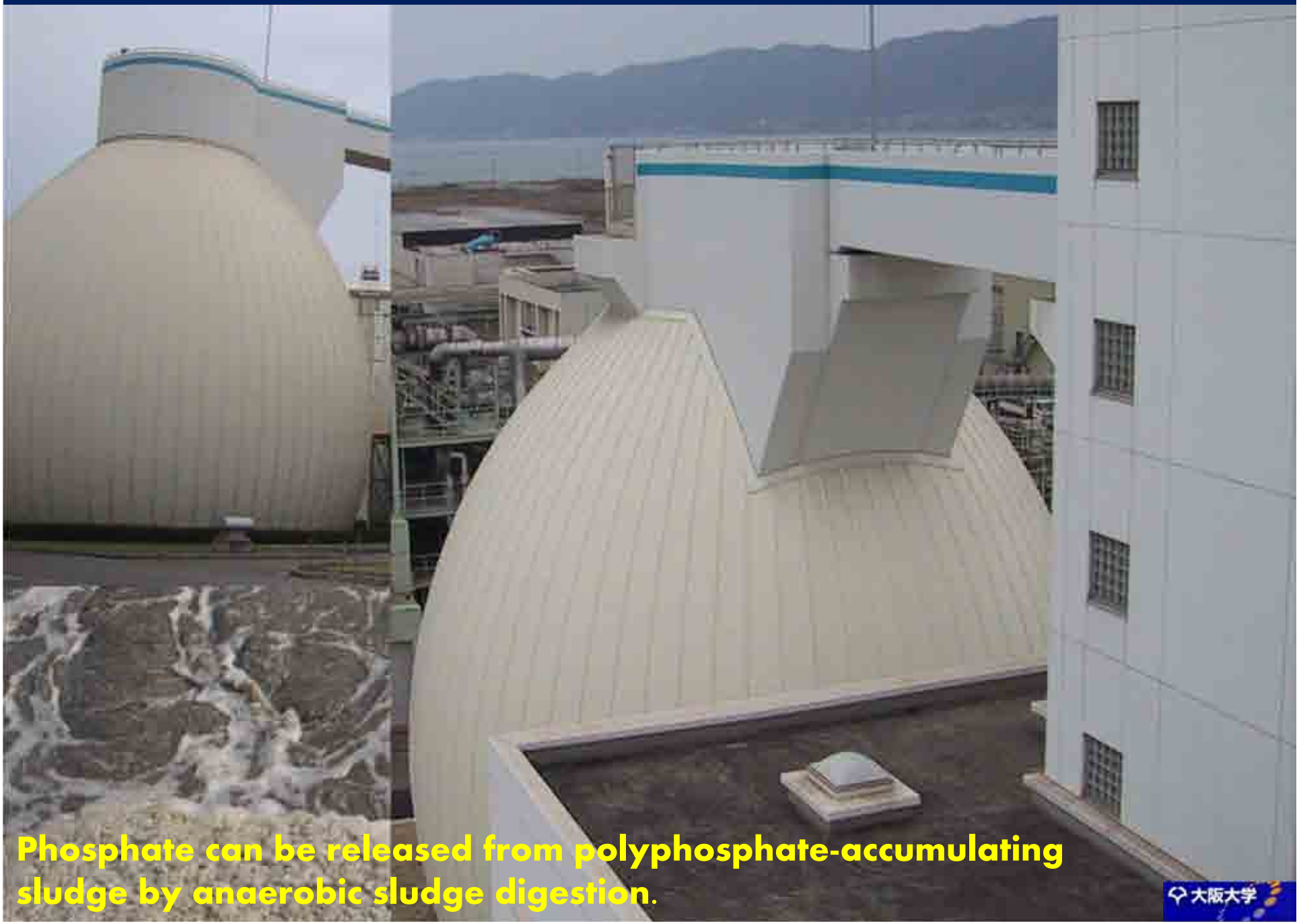
Approximately 50% of organic pollutants are oxidized to CO_2, while the remaining half is converted to activated sludge biomass. It is very important to use waste sludge as renewable resource.

ENHANCED BIOLOGICAL PHOSPHORUS REMOVAL PROCESS



Enhanced biological phosphorus removal primarily relies on the ability of sludge microorganisms to accumulate polyphosphate.

SLUDGE MANAGEMENT



Phosphate can be released from polyphosphate-accumulating sludge by anaerobic sludge digestion.

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P-recovery as struvite

Struvite crystallization reactor


UNITIKA
We Realize It!
UNITIKA LTD.
Dr. Esumi, a pioneer in struvite crystallization process
大阪大学

Struvite often causes difficult incrustation problems in pipelines. The hard crystalline incrustations have to be removed by means of mechanical cleaning techniques.

Struvite (MAP):

Sales price = ¥12 /kg-MAP
Production cost = ¥50 /kg-MAP
at Matsue city

Sales price = ¥21 /kg-MAP
Production cost = ¥500 /kg-MAP
at Fukuoka city

Osaka city and Kitakyushu city have withdrawn from MAP business.

MAP = Magnesium Ammonium Phosphate (Struvite)

SLUDGE INCINERATOR

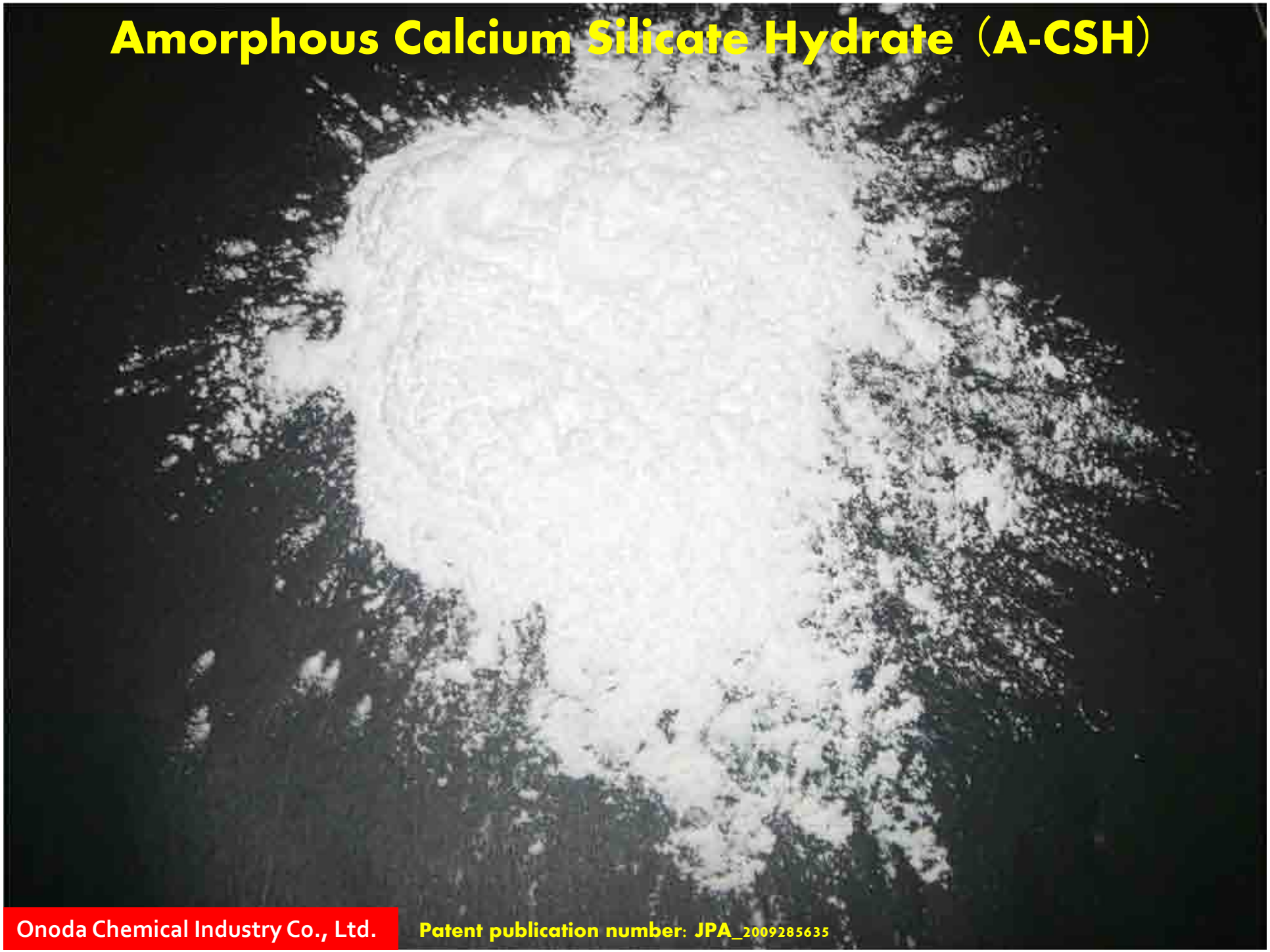
Sludge incineration ash contains P at concentrations similar to rock phosphate.

The full-scale plant for recovering phosphorus from sludge incineration ash started running in April at the city of Gifu, Japan.

From Mr. K. Goto, Gifu City Office

QUALITY, COST, AND MARKET BARRIERS

Amorphous Calcium Silicate Hydrate（A-CSH）



Onoda Chemical Industry Co., Ltd.

Patent publication number: JPA_2009285635

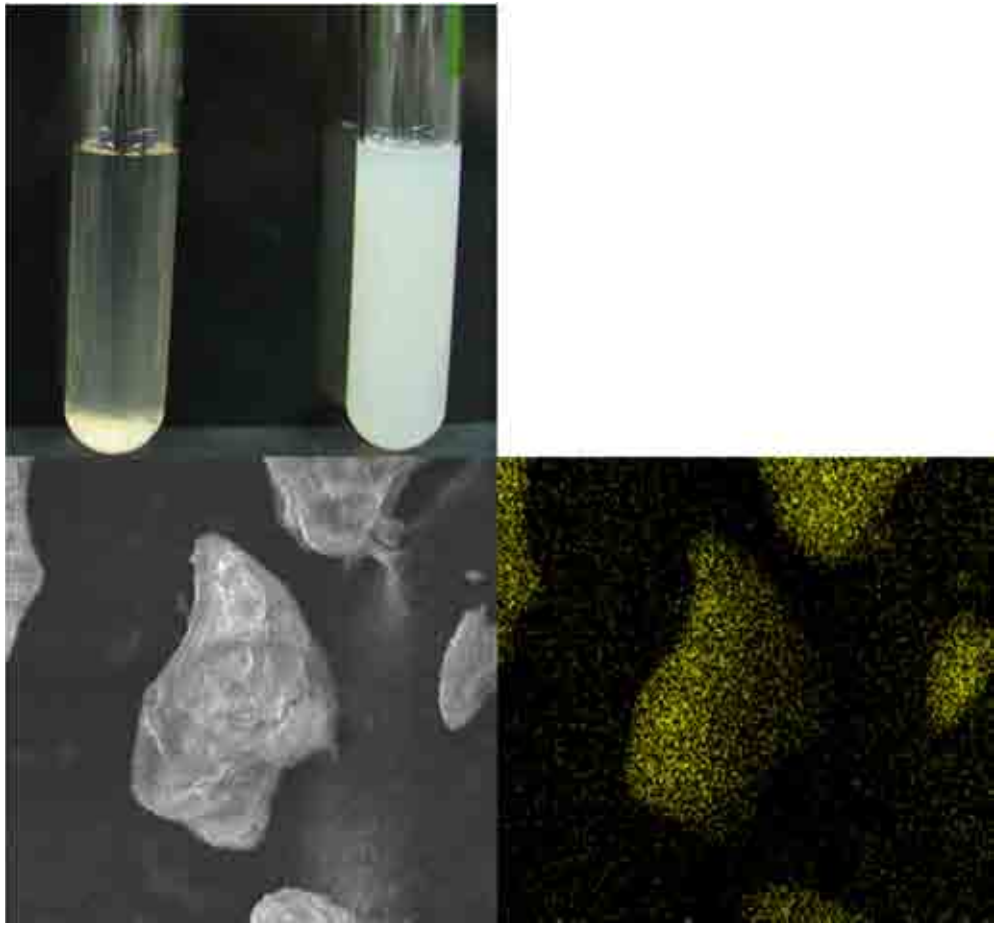
Autoclaved Lightweight Concrete (ALC)

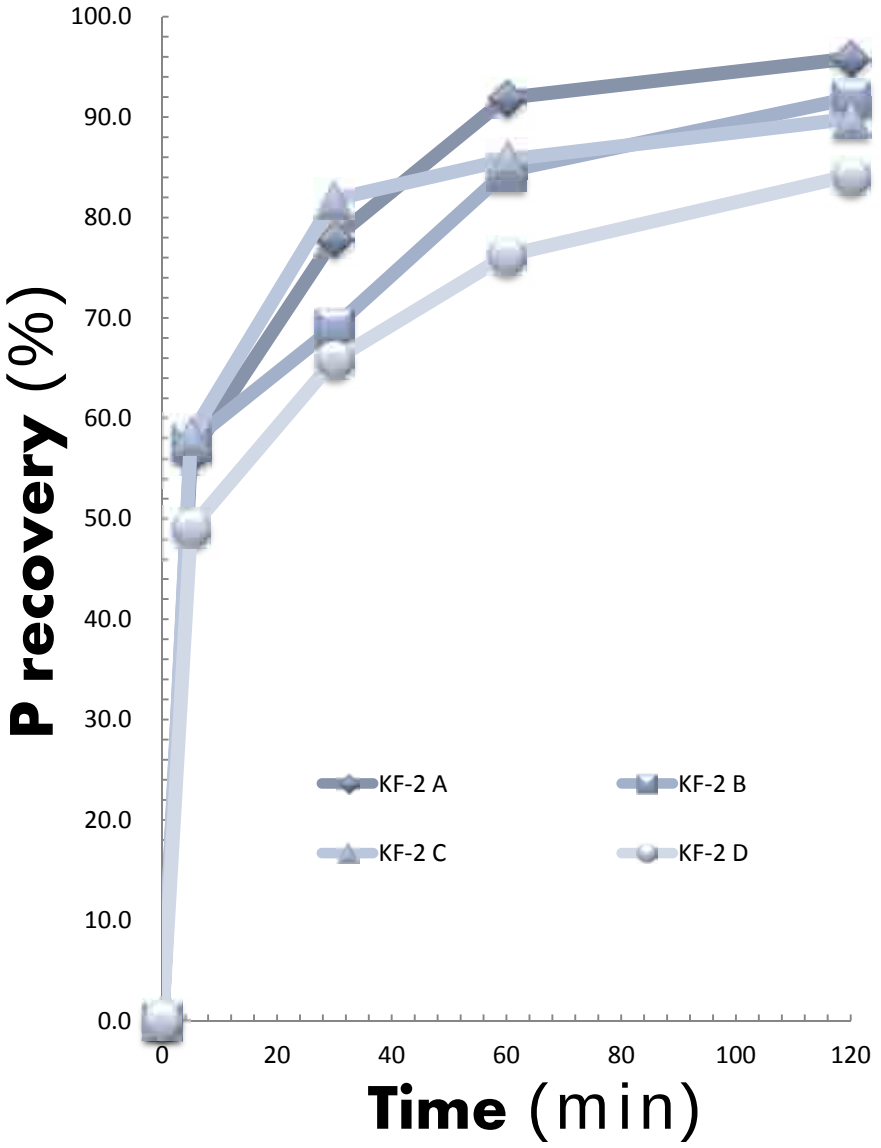
A by-product of the building material industry

Crystalline calcium silicate hydrates are not effective in recovering P.

ALC and tobermorite were added to the liquor at concentrations of 50-times higher than ACSH.

P recovery using A-CSH particles





N and P contents after P adsorption

	Ca/P = 2	Ca/P = 1.5	Ca/P = 1
N	0.13	0.12	0.19
P_2O_5	15.6	18.3	22.0

Onoda Chemical Industry Co., Ltd.

P RECOVERY

Anaerobic sludge digestion

Flow rate: 400 m^3/day

P: 120 mg/l

P = 0.5 ton/day = 180 ton/Y

A-CSH: 400 kg/day

P removal rate: 80%

Mixing tank: 20 m^3

Aeration tank

P: 25 mg/l

Settler

Recovery rate: 470 kg/day

(P_2O_5 18%)

150 tonP/Y

Onoda Chemical Industry Co., Ltd.

P RECYCLING BUSINESS

Sewage → Wastewater treatment plant → Treated water

Wastewater treatment plant → Sewage sludge

Sewage sludge → Anaerobic sludge digestion

Anaerobic sludge digestion → Digestion liquor

Agitating truck

Digestion liquor → Carrying in → P recovery

Plant Engineering company → P recovery

Carrying out → Recovered P

Recovered P → Fertilizer Industry

Fertilizer Industry

Onoda Chemical Industry Co., Ltd.

Plant Engineering company → Production and distribution of A-CSH

Production and distribution of A-CSH → Cement Industry

Cement Industry

BUSINESS MODELS FOR P RECYCLING

Business model 2

Food

Food and Feed

Agriculture

Vegetable oil refinery process

Consumer

Business model 3

Water reclamation

Fertilizer Industry

P fertilizer

Farmland ← Ash ← Manure

P recovered

Eutrophication control

Recycle Industry

Business model 1

High-tech Industry

Sewage

Wastewater treatment

Biosludge

P-free ash

Cement Industry

The P content of clinker needs to be lower than 0.5%.

Automobile

Semiconductor

Liquid crystal

Ash

P Recycling for Industry

Yellow P manufacturing

Yellow P

Phosphoric acid manufacturing

High-quality phosphate

P slag

Phosphate production by a wet process

Iron ore
Coke

Steel Industry

Steel-making slag

P-free slug

Phosphoric acid manufacturing

Phosphate

Chemical Industry

P-free slag can be returned to a steel manufacturing process.

Steel-making Industry

P recovered

P recycle through yellow phosphorus regeneration

Patents have been applied for P recycling.

To realize P recycling, we needed to:

- Narrow knowledge and information gaps between different industrial sectors,
- Promote cooperation between different sectors,
- Innovate P refining technologies,
- Create market for recovered P,
- Establish a nationwide association for P recycling,
- Formulate national strategy for securing of P resources.

P recycling center

- Hotels
- Superstores
- Food manufacturers

Waste water treatment plants (WWTP)

P recovery (Heatphos)

Night soil treatment plant

P recovery (Heatphos)

Recovered P

Industrial Wastes

Industrial Wastes

Ashidagawa WWTP

P recovery (Heatphos)

Recovered P

P recycling center

Biogas
Electricity
Heat energy

Biophosphorites

P industry

Sales

Fertilizer Industry

MLIT
Ministry of Land, Infrastructure, Transport and Tourism

MAFF
Ministry of Agriculture, Forestry and Fisheries

経済産業省
Ministry of Economy, Trade and Industry

Ministry of the Environment
Government of Japan

Model area in P recycling

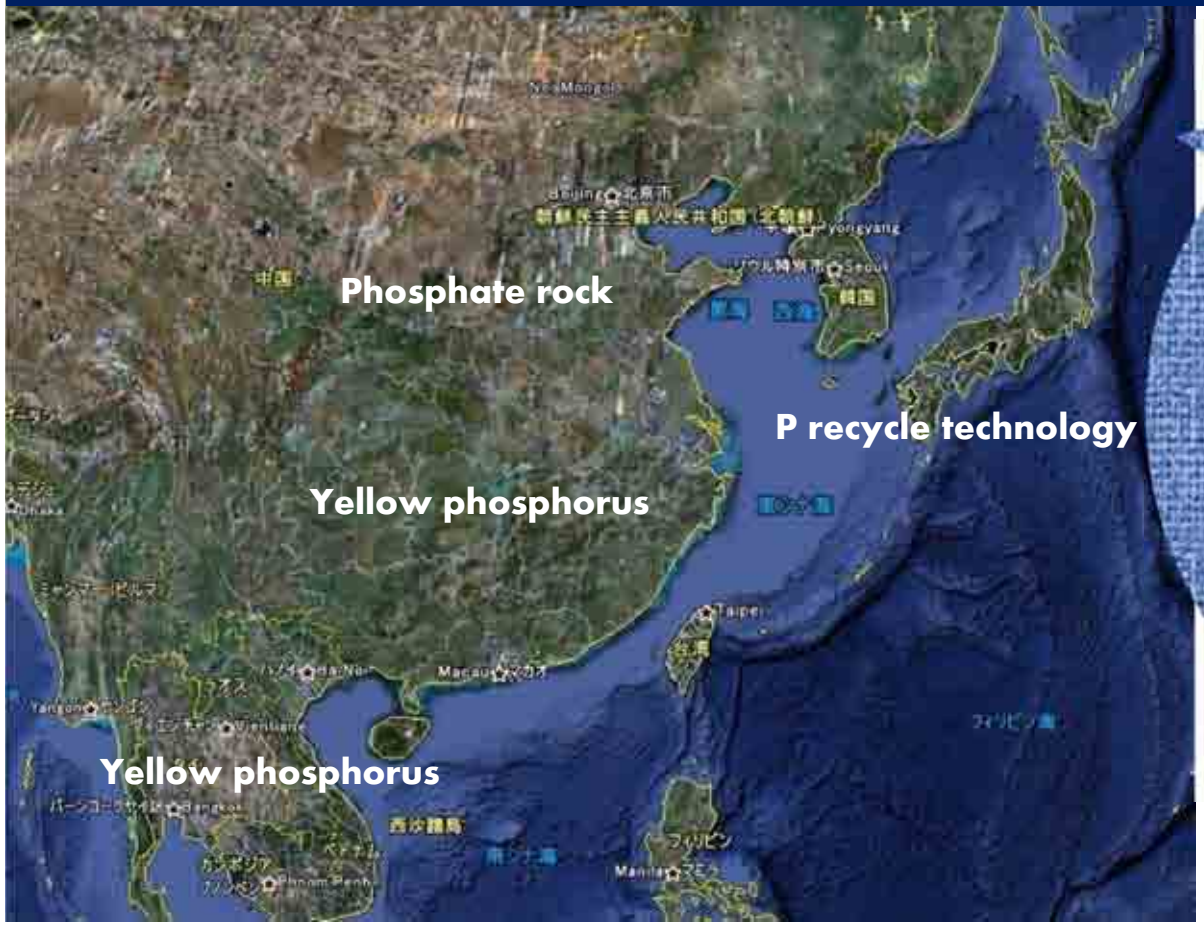
The Phosphorus Recycling Promotion Council of Japan

Industry **Academia** **Government**

TOWA

THE PHOSPHORUS RECYCLING PROMOTION COUNCIL OF JAPAN

INTERNATIONAL COLLABORATION



P depletion is a common challenge not only in Asia, but also in the world. The P recycling technology of Japan can make a great contribution to the crisis prevention in the world.

Transfer of P recycle technology

Efficiency of P use	**China**		**Japan**	**P fertilizer**
P recycling	**Vietnam**			**Food and Feed**
Technology improvement	**Others**			**Industrial P**

Stable supply of P from Asia

International cooperation for P recycling in Asia

EU commission
Sustainable Use of Phosphorus
February 2011

frontiers in life sciences:

sustainable phosphorus summit

phosphorus, food and our future

A summit to define the scale and scope of the P sustainability problem, to develop and communicate possible solutions for achieving sustainable P use, and to raise awareness about the issue, locally and globally.

February 3-5, 2011

Arizona State University, USA

Global TraPs

UNEP YEAR BOOK

EMERGING ISSUES IN OUR GLOBAL ENVIRONMENT

2011

UNEP

Phosphorus and Food Production

60% P recycling by 2015

Global TraPs

Global transdisciplinary processes preparing for sustainably coping with phosphorus from a supply chain perspective

Project proposal for a multiple global transdisciplinary case study on long-term adaptation to the phosphorus challenge

NSSI IFDC

Our book on Phosphorus **1785 JPY**

What's the Looming Crisis of Phosphorus Depletion

By

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