Phosphorus Material Flow and its Recovery from Wastewater and Solid Waste

Masaki Takaoka[1*], Kazuyuki Oshita[1], Xiu Cui Sun[1], Kazutsugu Matsukawa[2], Taku Fujiwara[2]

1:Department of Urban & Environmental Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto, 615-8540

2: Faculty of Agriculture and Agricultural Science Program, Graduate School of Integrated Arts and Sciences, Kochi University, Otsu 200, Monobe, Nankoku-shi, Kochi,783-8502

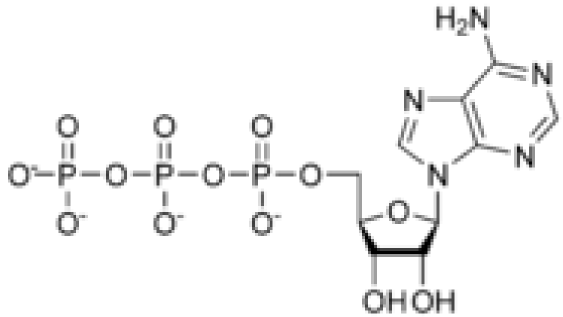
UNEP-DTIE-IETC, Regional Workshop on Waste Agricultural Biomass
March 2-5th, 2010 at Global Environment Centre Foundation in Osaka

Content

- Current status of Phosphorus (P) Resources and Material Flow
- Recovery from Wastewater
- **Recovery from Sewage Sludge**
- Recovery from Livestock Manure
- Ongoing Research

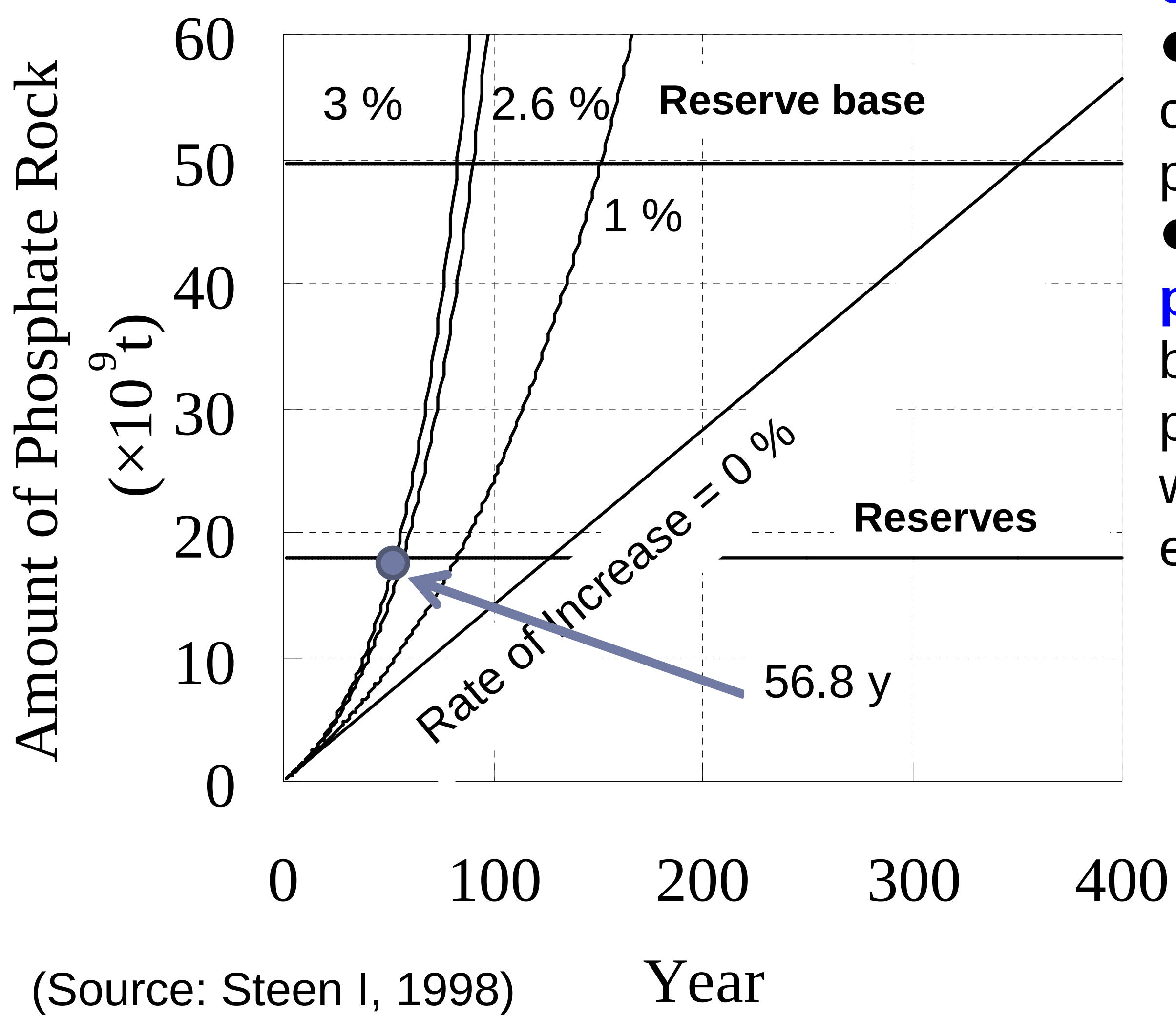
Phosphorus

- Essetial element for plant growth as well as Nitrogen(N) and Pottasium(K)
- Important component in ATP (**A**denosine **Trip**hosphate)



- Causing substance of eutrophication
- Low mobility and circularity
- Uneven distribution (Morocco:42%, China:26%, America:7%)

Estimate of Phosphate Rock Depletion



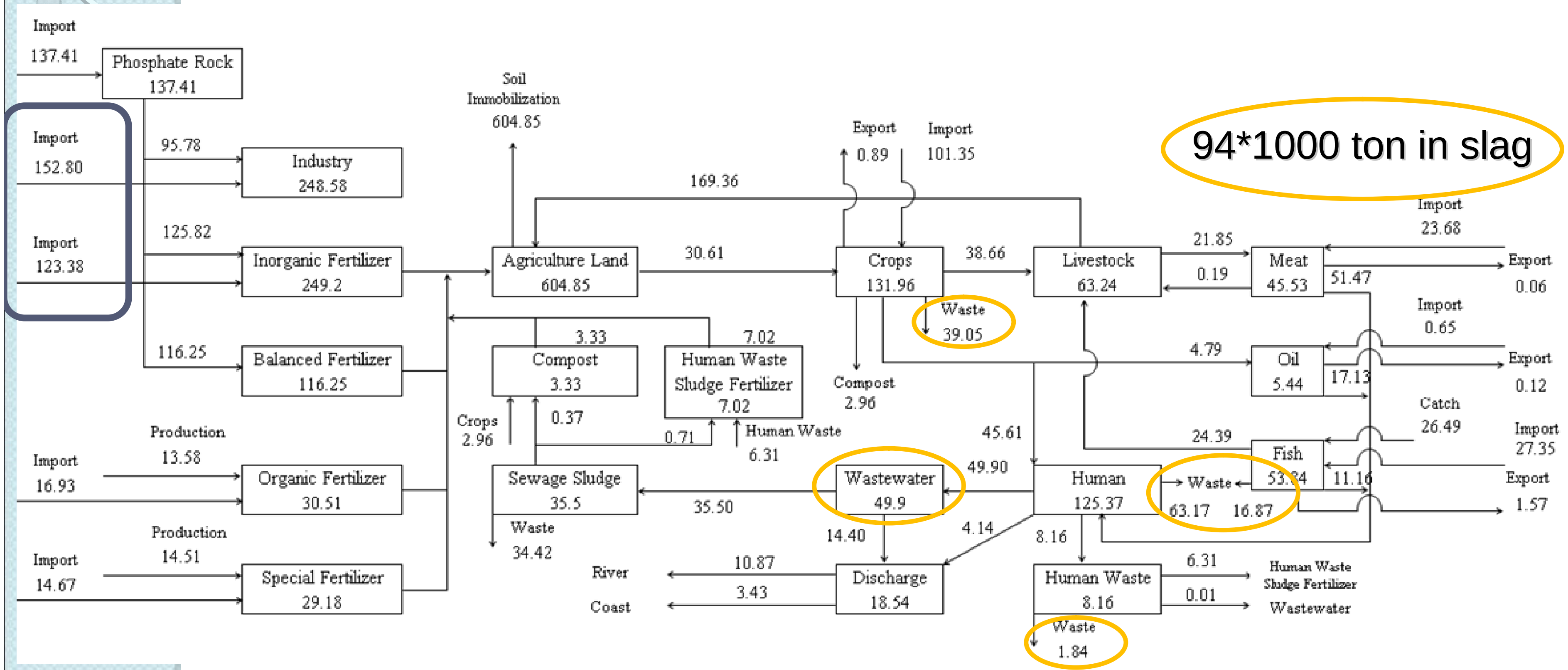
(Source: Steen I, 1998)

- **Phosphorus (P)** is an **exhaustible resource**.
- Japan depends on foreign countries for most of its phosphorous supply.
- As **high-grade phosphorus mines** are being **depleted**, phosphorous recovery from waste streams becomes even more important.

To establish P cycle

Fertilizer → food → human → wastewater/waste → Fertilizer/product

Phosphorus Material Flow in Japan(2000)



Inflow to wastewater: 50,000 ton

The recovery potential from waste streams : about 260,000 ton-P/year, almost equivalent to the amount of phosphorus in **imported fertilizers**.

(Source: Kato etal, 2003, Matsubae etal, 2008)

P Removal from Wastewater

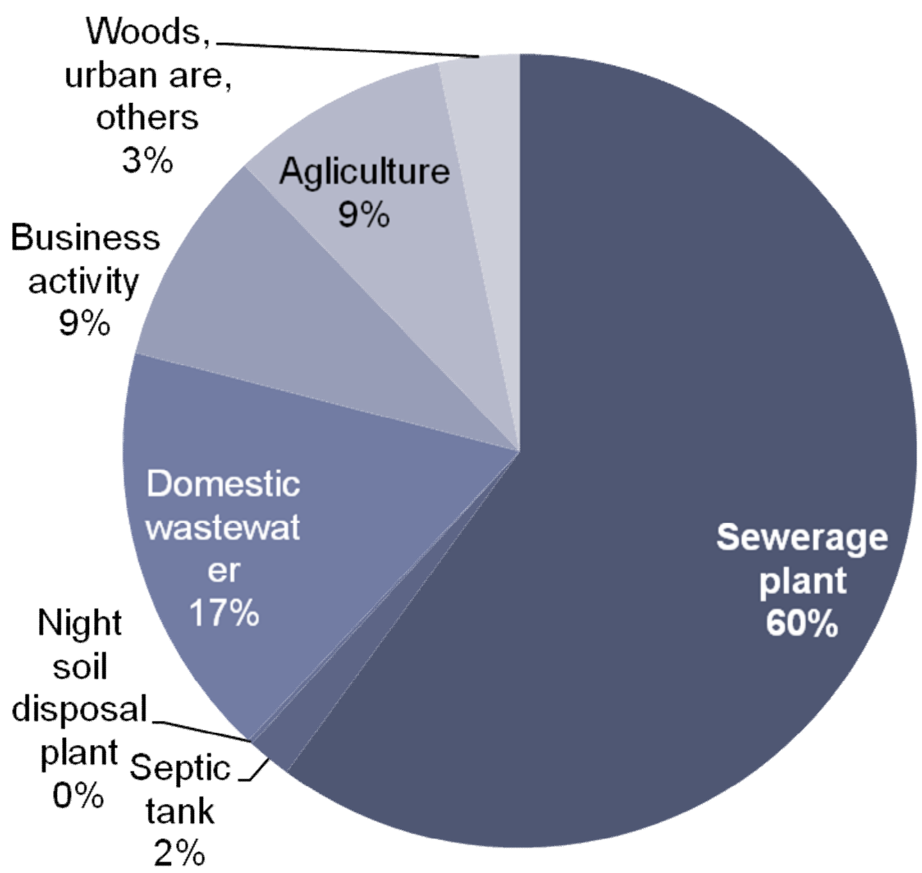
Various **advanced wastewater treatment** system for P removal have been introduced in wastewater treatment plant due to **prevention of eutrophication** in closed water area since 1970s.

Phosphorus removal methods from **wastewater** have been developed (coagulation, AO, A2O process, MAP, Crystallization, adsorption, etc.).

Accumulation of P in **sludge**

Recovery from **sewage sludge**

Input ratio of P to Tokyo bay (1999)



P Recovery from Wastewater

Technology	Process	Characteristics	P Form
MAP Method	**Magnesium Ammonium Phosphate (MAP, Struvite)** is generated through crystallization among **PO_4^{3-}, NH_4^+, Mg^{2+}.** Chemicals are added to wastewater including high phosphorus concentration such as **digester supernatant**, and they are stirred, mixed with aeration.	**Easy operation**. Needless to pretreat. Low running cost. NH_4^+ is simultaneously removed. $NH_4^+$is required. **Not suitable for low phosphorus concentration water**.	**MAP**
HAP Method	**Hydroxyapatite (HAP)** is generated through crystallization among **PO_4^{3-}, Ca^{2+}, OH^-**. Chemicals are added to wastewater including low phosphorus concentration such as **secondary effluent**, and they are sent to crystallization reactor.	**Few by-product.** Low running cost. Already operated in full scall. **Degassing and Filtration are required.** Difficulty to maintain seeding grain.	**HAP**

(Source: Kato etal, 2007)

P Recovery from Wastewater

Technology	Process	Characteristics	P Form
Electrolysis	After immersing **iron electrode** under wastewater and passing DC electricity, **Fe^{2+}** is eluted from positive electrode, being oxidized to **Fe^{3+}** by dissolved oxygen, and **phosphate is precipitated reacting with Fe^{3+}.**	**Simple equipment**. Already applied to household digestion tank. Possibility to small-scall facilitied. **Maintainance of electrode is required** avoiding iron hydroxide layer generation on its surface.	**$FePO_4$**
Adsorption	**Secondary effluent** is sent to packed tower filled with **Zr, activated alumina adsorbent** and phosphate is removed. The adsorbent is reused.	**Few sludge generation**. There are adsorbent which has reletively large adsorption capacity to phosphite, hypophosphite, polyphosphate. **Easily affected by coexisting materials.**	**Phosphoric Acid, Calcium Phosphate**

(Source: Kato etal, 2007)

Sewage Sludge as Biomass Resource

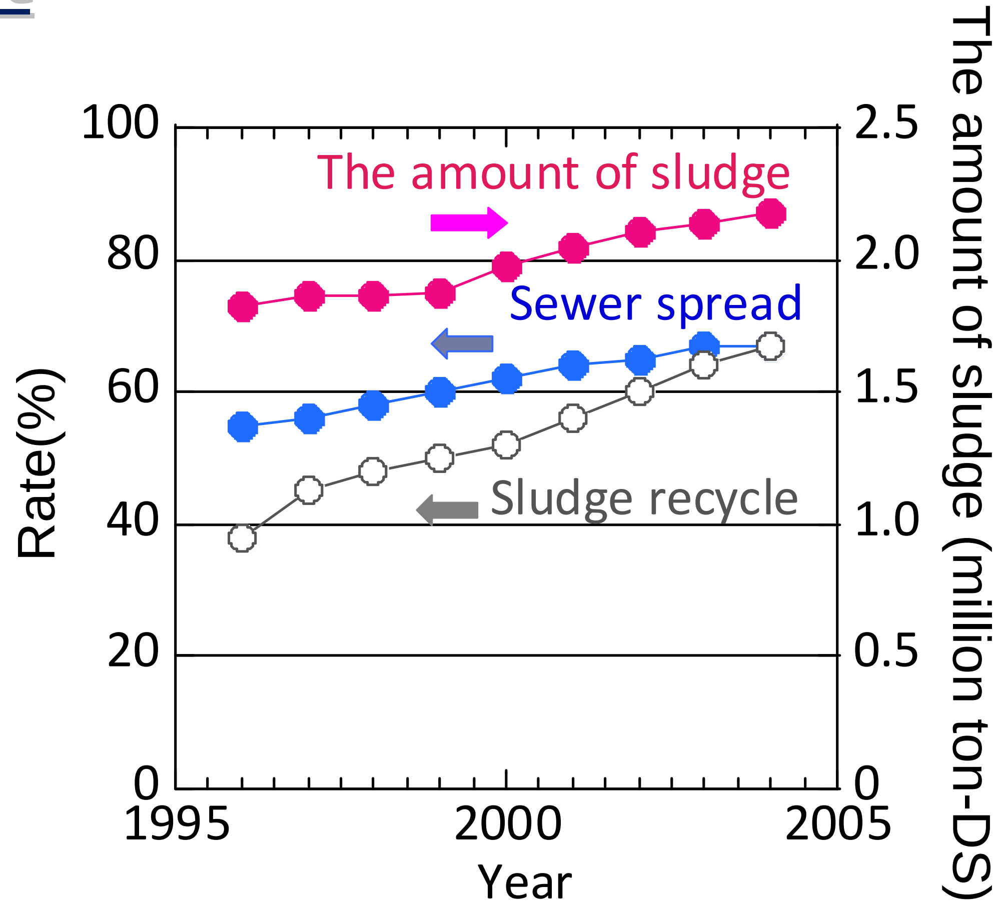
Source:
MOE home page

- Huge amount of waste, but both a **biomass resource** and a form of **renewable energy**.

- Technological development for **the efficient use** of sewage sludge and **the resource recovery** from sewage sludge is required as part of **establishing a sound material-cycle society and preventing global warming**.

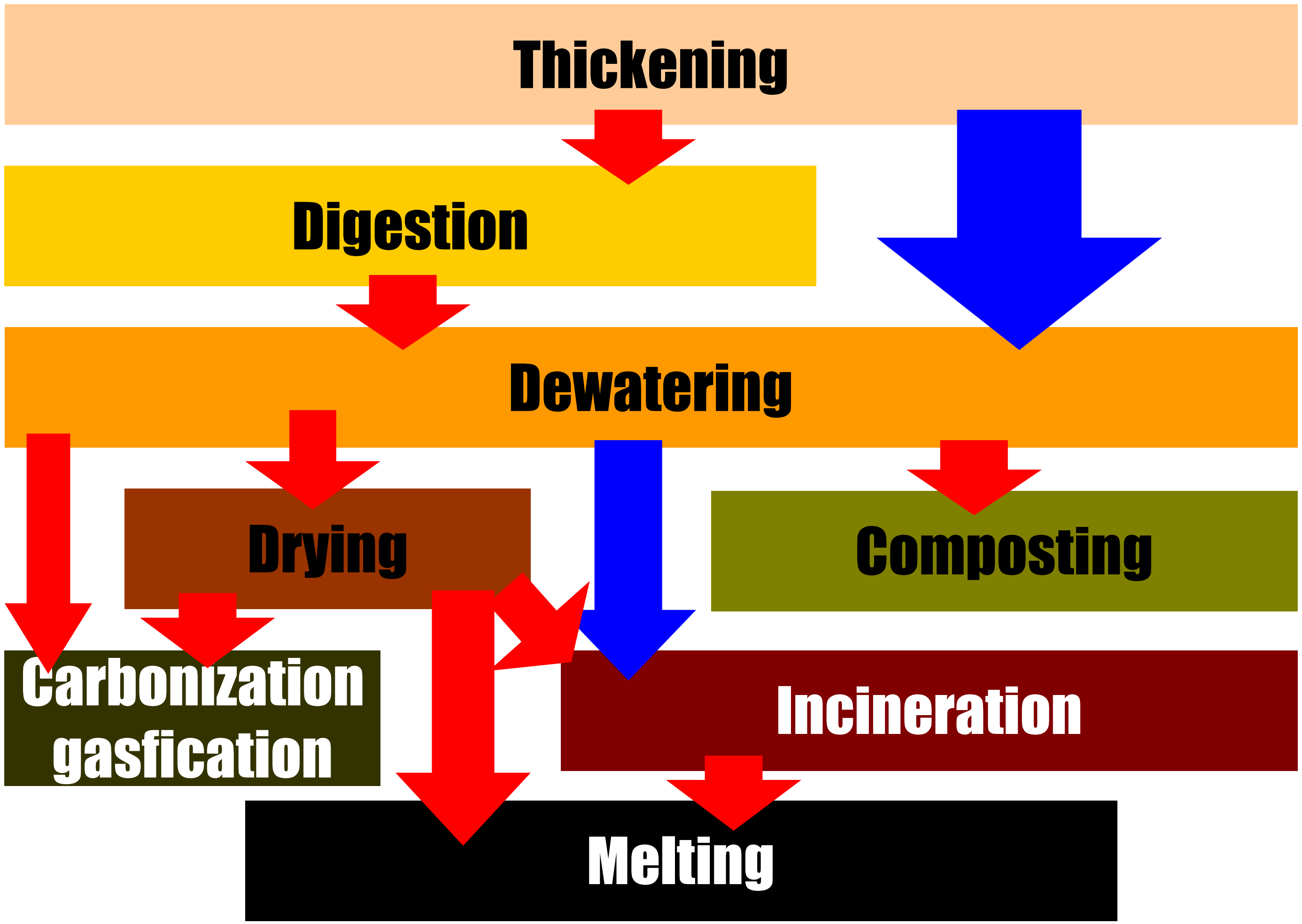
Changes in volume of sewage sludge generated and its treatment

- The volume of sewage sludge in Japan has been increasing with the rise in the number of people using sewage treatment systems.
- The amount of **sewage sludge (dry basis)** was approximately **2.2 million tons** in 2004.
- **Sludge recycle rate** has been increasing rapidly, achieving to **67%** in 2004.



Source:
MLIT home page

Chart of Sewage Sludge treatment in Japan



Sewage Sludge Disposal and Utilization

Unit: DS-ton at March 2005

Sludge Form 処理性状	Final Status 最終形態								Total 合計	
	Disposal by Sanitary Landfill 埋立処分	Utilization of Green Form 緑農地利用	Utilization of Construction Material 建材資材利用		Fuel 燃料化等	Marine Restration 海洋還元	Stock 場内ストック	Others その他		
			Cement セメント化	Other Than Cement セメント化以外						
Liquid Sludge 液状汚泥	12	25	0	0	0	0	0	7	44	0.0%
Dewatered Sludge 脱水汚泥	66,333	35,823	59,051	746	1,169	0	218	204	163,544	7.3%
Composted Sludge コンポスト	363	224,010	267	3,689	52	0	0	0	228,381	10.3%
Dried Sludge 乾燥汚泥	6,144	32,822	1,559	149	10,632	0	11	4,304	55,621	2.5%
Carbonized Sludge 炭化汚泥	0	1,600	966	256	78	0	0	7	2,968	0.1%
Ash 焼却灰	563,082	11,418	632,186	352,075	334	0	5,783	634	1,565,511	70.3%
Melted Slag 溶融スラグ	1,050	2,637	4,429	172,755	0	0	28,005	2,427	211,303	9.5%
Total 合計	637,044 28.6%	308,334 13.8%	698,458 31.4%	529,670 23.8%	12,265 0.6%	0 0.0%	34,017 1.5%	7,583 0.3%	2,227,371	100%

55%

(Source: MLIT Homepage)

P Recovery from Sewage Sludge

Technology	Process	Characteristics	P Form
Hydrolysis, Physicochemical Treatment	**Sulfuric acid** is added to centrifuged sludge hydrolyzing at 150° C, pH1~2, and organic matters and Heavy Metals are precipitated. **Iron salt** is added to **supernatant recovering $FePO_4$**, and excess iron is reused as flocculant.	Organic matters in sludge can be used as carbon resource for denitrification. **Reducing sludge volume**, sludge treatment cost. **Flocculant cost and hydrolysis heat** is required.	**$FePO_4$**
Chemical Addition	NaHS is added to pre-coagulated sludge generated in primary sedimentation tank using ferric chloride, and FeS and phosphoric acid is generated. And calcium salt is added to its supernatant recovering calcium phosphate. Acid is added to FeS recovering H_2S	Reducing Organic load, electricity, tank volume can be reduced through pre-coagulation. ONLY calcium salt and acid is not reusable. H_2S gas is toxic and its control is required. Including many processes.	**Calcium Phosphate**

(Source: Kato etal, 2007)

P Recovery from Dewatered or Carbonized Sludge

Technology	Process	Characteristics	P Form
Compost of Dewatered sludge	Dewatered sludge is dried by drum drying, and its dried sludge is used as fertilizer and low-grade fuel.	Recovered materials excludes ash dust, and are particulate, drying by combustion of generated gas. Suitable for dewatered sludge including 15~40 % of moisture content.	**Fertilizer**
Acid Treatment for carbonized sludge	**Sulfuric acid** is added to carbonated sludge, extracting phosphorus, aluminium, and heavy metal at 90° C. And **alkali** is added to extract, **selectively recovering phosphorus** and heavy metal.	Phosphorus, Al, Fe, Mn can be removed. Adsorptive capacity increased 10 times than without acid treatment. Aluminium in recovered material may affect plant growth.	**Calcium Phosphate**
Heating Treatment for carbonized sludge	NaOH is added to carbonated sludge including Si, Al, Ca, calcinating at 800° C, generating sodium phosphate and zeolite.	Carbonated sludge can be heated as fuel, recovering at lower temperature than sewage sludge ash. Application of zeolite is unclear.	**Sodium Phosphate**

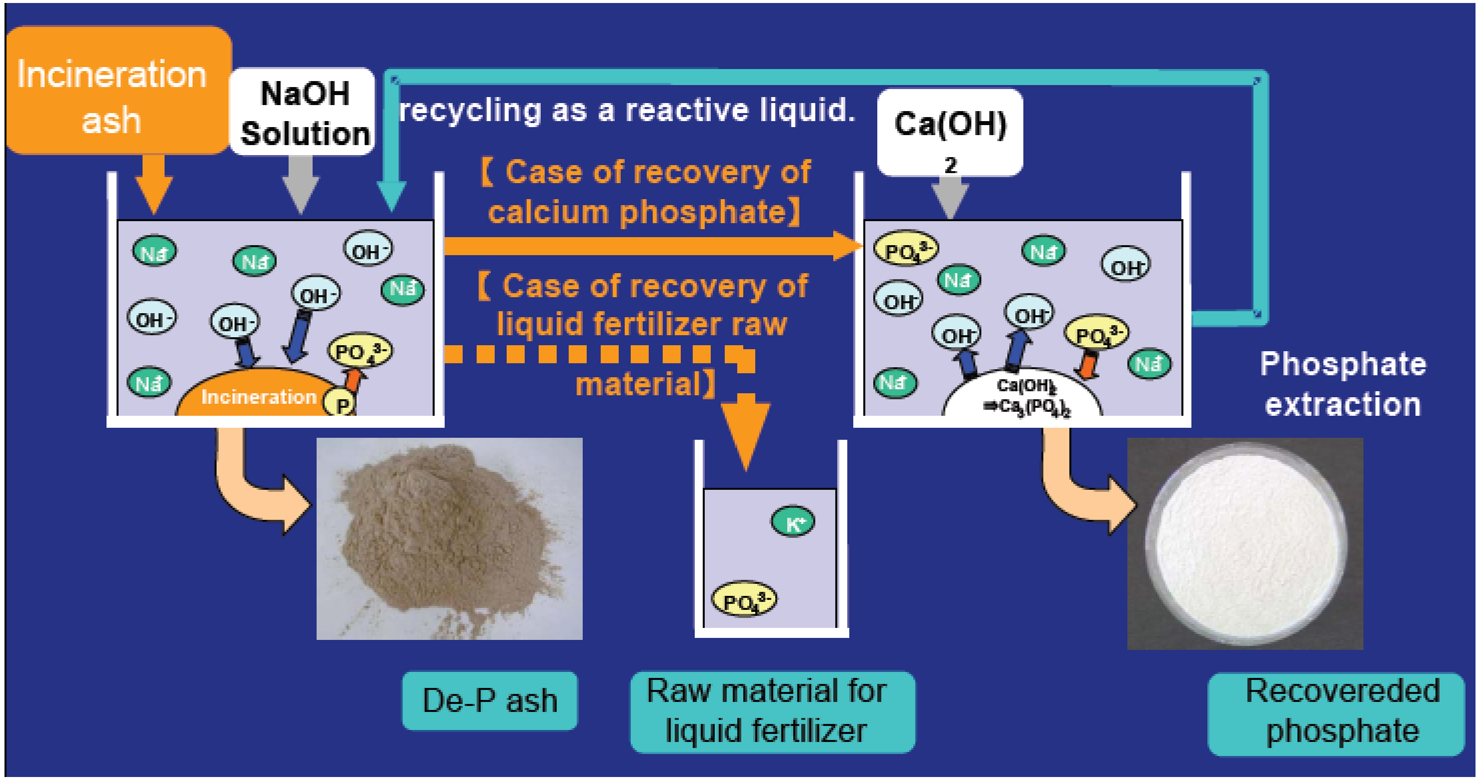
(Source: Kato etal, 2007)

P Recovery from Incineration Ash

Technology	Process Summary	Characteristics	P Form
Acid Treatment	**Sulfuric acid** is added to ash, extracting phosphorus, heavy metals. And its supernatant is ion-exchanged **recovering phosphate, $FeCl_3$,$KHSO_4$**.	Recovered material is used as fertilizer, reducing ash generation. Ion-exchange is noneconomic.	**Phosphoric Acid**
Alkali Treatment	**NaOH** is added to ash, extracting phosphorus and alminum. And **$Ca(OH)_2$** is added to its supernatant recovering **HAP (Ca Aggregation)** or the supernatant is cooled recovering **sodium phosphate (Na Aggregation).**	**Phosphorus and aluminium can be selectively extracted**, sodium aluminate solution after recovering phosphorus can be used as extraction chemical. Aluminum in recovered material may affect plant growth.	**Calcium Phosphate, Sodium Phosphate**

(Source: Kato etal, 2007)

National Project (Metawater co. ltd.)



(1)mixing incineration ash of sewage sludge with the alkaline reaction solution in a reaction tank to extract the phosphorus contained in incineration ash of sewage sludge in a liquid

(2) separating the phosphorus-extracted liquid from the treated ash by solid-liquid separation: adding a calcium component to the separated phosphorus-extracted liquid

(3) withdrawing a calcium phosphate crystal from the calcium component-added phosphorus-extracted liquid.

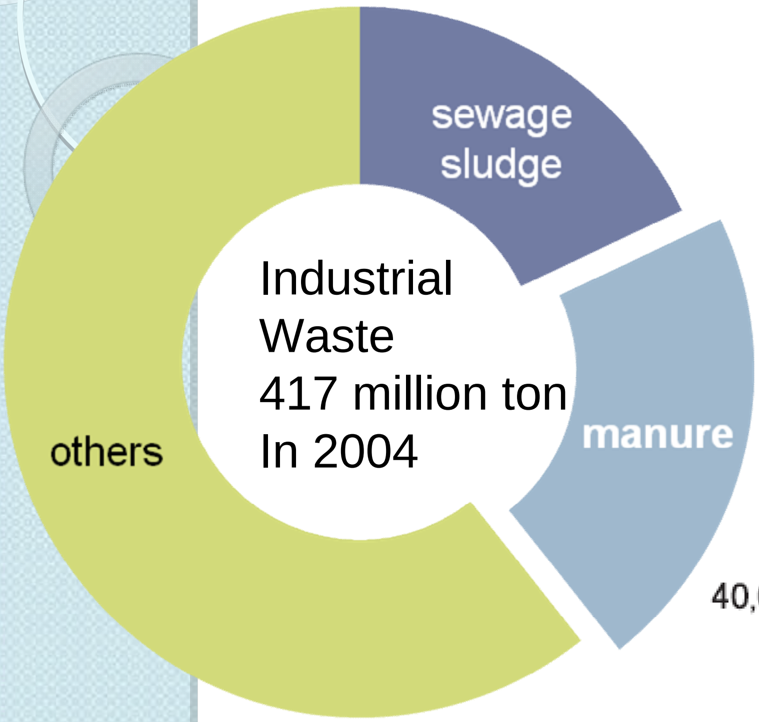
(Source: SPIRIT21 LOTUS Project, 2007)

P Recovery from Melting Process

Technology	Process	Characteristics	P Form
Melting Treatment	**Coke** is added to ash, melting in **reduction atmosphere** at 1250~1500° C, volatilizing **yellow phosphor**, then recovering liquid yellow phosphor with cooling or phosphorus oxide with combusting yellow phosphor gas.	Recovered yellow phosphor **is high grade** (99.94 %) . Generated slag and metal can be used as materials. Arsenic is simultaneously volatilized. **More arsenic in recovered material** is included than in industrial yellow phosphor.	**Yellow Phosphor, Phosphoric Acid**
	MgO, CaO, SiO_2 are added to ash, melting them, **generating slag** as well as **fused phosphate**.	Recovered slag can be used as **citrate soluble phosphorus fertilizer**. Heavy metal concentration meets standard of fertilizer control law. Citrate solubility of P_2O_5 and MgO is inhibited due to Al_2O_3 in ash.	**Fused phosphate**

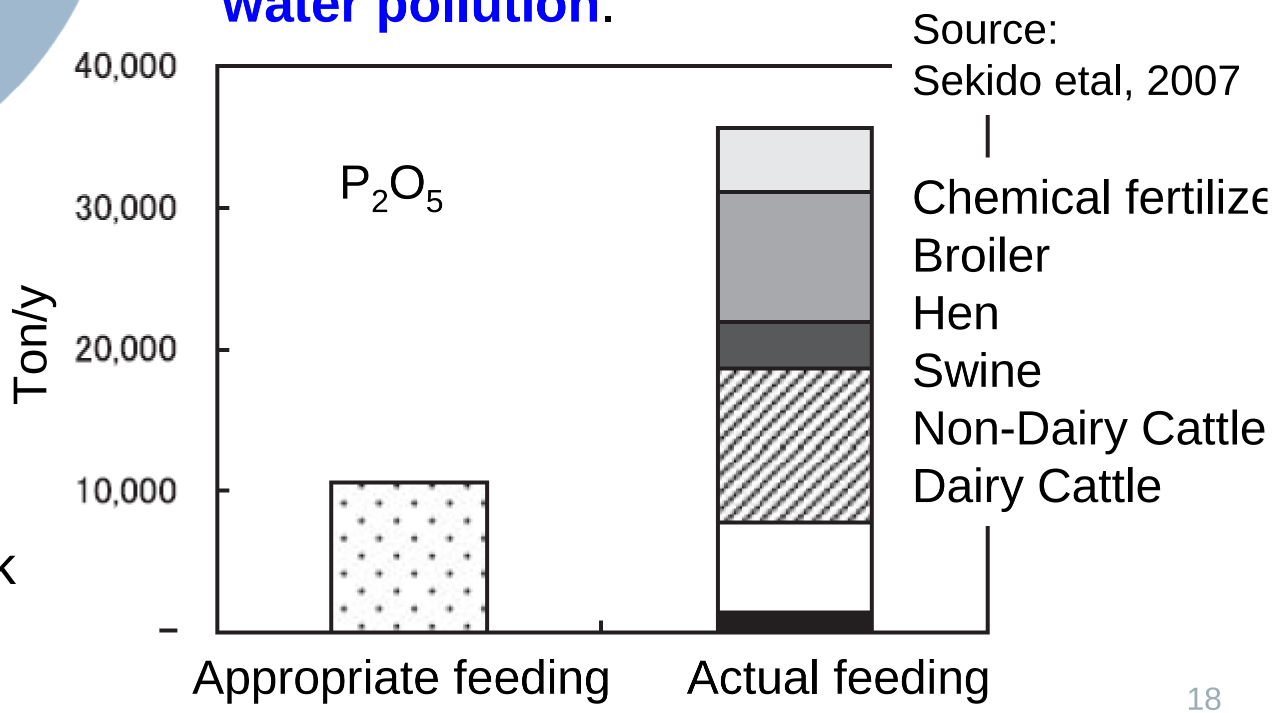
(Source: Kato etal, 2007)

Manure as Biomass Resource



■Largest amount of waste, 90% is recycled as **manure-derived organic fertilizer.**

■But, in some part of Japan, actual P input in farming land is **more than three times** of appropriate feeding amount. This causes **underground water pollution**.



■To **stop excess feeding** of manure-derived organic fertilizer and **share it with other farming area**, it is necessary to **recover phosphorus** from livestock manure and make easy handling fertilizer.

P Potential in Livestock Manure

	Feces			Urine		
	Volume (million ton/y)	P conc. (kg/ton-feces)	P amount (1000ton/y)	Volume (million ton/y)	P conc. P(g/ton-urine)	P amount P(1000ton/y)
Dairy Cattle	19.2	0.55	10.5	5.7	6.7	0.0
Non Dairy Cattle	19.8	2.3	46.3	7.2	121	0.9
Swine	8	4.3	34.8	14.9	527	7.9
Hen & Broiler	12.9	3.5	44.5	–	–	–
Sum	59.9		136.1	27.8		8.8

10% of the manure
- ●Wastewater treatment
- ●Methane Fermentation
- ●Incineration
- ●Drying
- ●Carbonization

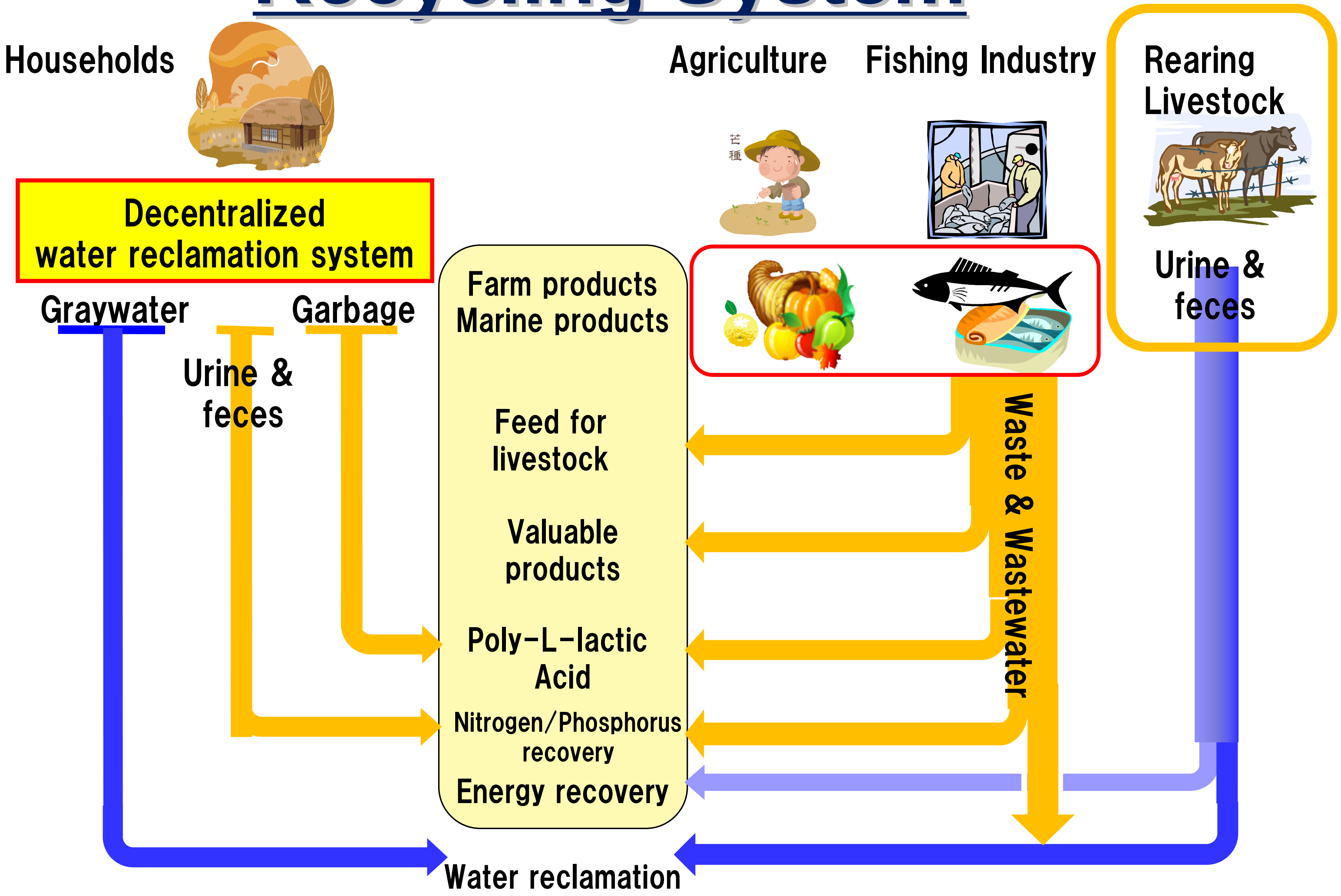
P recovery
from Hen manure
Incineration ash

Ongoing research

- **Global warming :** closely related to consumption of resources and energy the most evident example of the influence of increased environmental load.
- **Effective countermeasures** must be implemented worldwide.
- **Innovative cascading water/bio-resource recycling systems** should be developed to effectively utilize **the diffused biomass in agricultural areas** and minimize the pollution loads discharged into water systems for guaranteeing **the safety and security of both water and food.**

Development of an innovative water management system with decentralized water reclamation and cascading material-cycle for agricultural areas under the consideration of climate change

Cascade WaterBio-Resource Recycling System



Prevention of nonpoint source pollution and **production of valuable products from wastes in agricultural areas** will simultaneously be actualized by development of a cascading water/bio-resource recycling system.

Acknowledgement

- We are very grateful for financial support from
  - Kajima Foundation
  - CREST (Core Research of Evolutional Science & Technology) in Japan Science and Technology
  - Global COE program(Human Security Engineering for Asian Megacities).