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Phytoremediation of POPs-contaminated soils: solutions and development potential in Kazakhstan

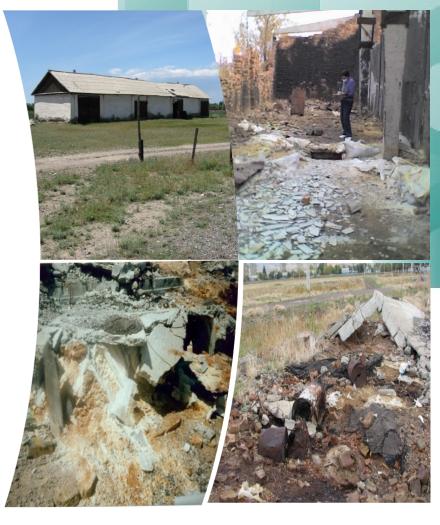
Nurzhanova A., Mamirova A.



The problem of obsolete pesticides in Kazakhstan (case study of Almaty region)

Table 1 - Inventory of obsolete pesticides in Almaty region

	# of storehouses	Pesticide amount, kg				
Districts		Ministry of Ecology of Kazakhstan, 2005	IPBB, 2010	IPBB, IGG&C, 2018-2020		
Karasay	6	1 350	600 NA			
Talgar	7	121 449	31 150	450		
Zhambyl	5	13 245	100 700	NA		
Enbekshikazakh	9	25 000	7 970	NA		
Uygur	7	3 250	3 830	NA		
Balkhash	7		500	NA		
Ile	3	17 550	107 150	NA		
Eskeldi	12	60 000	100 750	NA		
Kerbulak	8	0		NA		
Koksu	0	0 0		NA		
TOTAL	64	436 049	352 650	450 (disposed 2019)		

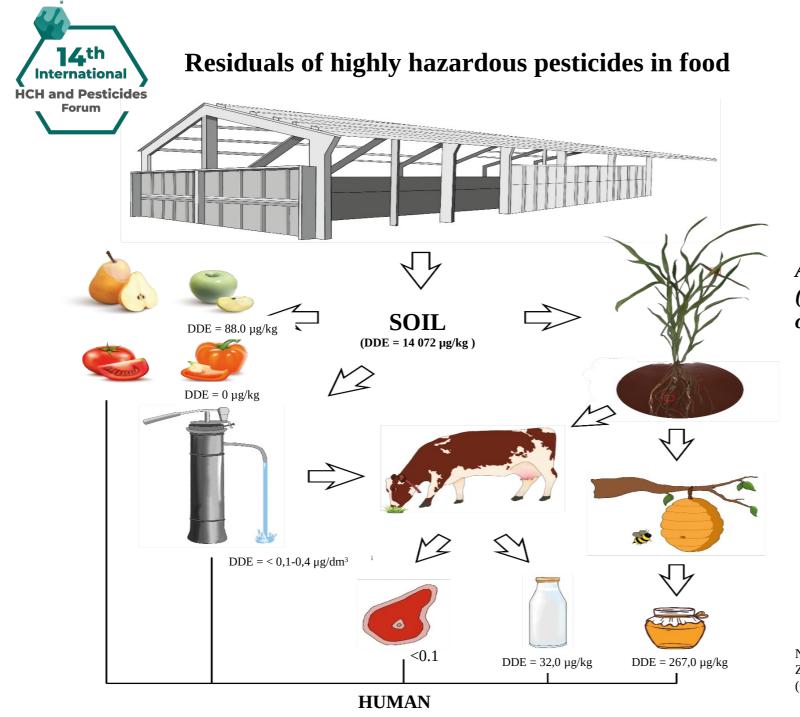


350 kg of banned pesticides (sayfos, metaphos) out of 352 t of obsolete pesticides, 21 % are pesticides in packaging, remaining 79 % are mixed unknown pesticides.



	Number of storage facilities						
Districts	Total	Without contamination	Contaminated, MPC <100	Contaminated, MPC >100			
Karasay	6	0	0	6			
Talgar	7	1	1	5			
Zhambyl	5	1	2	2			
Enbekshikazakh	9	0	2	7			
Ile	3	1	1	1			
Uygur	7	4	3	0			
Balkhash	7	2	4	1			
Kerbulak	8	8	0	0			
Eskeldi	12	4 6		2			
Koksu	0	0	0 0				
Total	64	21	19	24			

The soil around 24 former pesticide storehouses is contaminated with organochlorine pesticides and concentrations of these compounds exceed the limits of Kazakhstan's maximum permissible concentrations (MPC) (for organochlorine pesticides MPC is $100 \mu g/kg$). The most common contaminants were α -HCH, β -HCH, 4,4-DDE, and 4,4-DDT. The depth of soil contamination was 30 cm.



According to the World Health Organization (WHO), everyone's health depends 25-30 % on the condition of the natural environment

Nurzhanova A., Jansugurova L.B., Zhapbasov R.Zh., Vsevolodov E.B., Zhubanova A.A. et al. Cadaster of obsolete pesticides in Almaty Region (Case Study of Talgar District) - Almaty: Kazakh University, 2022 - 116 p.



DDT degradation methods

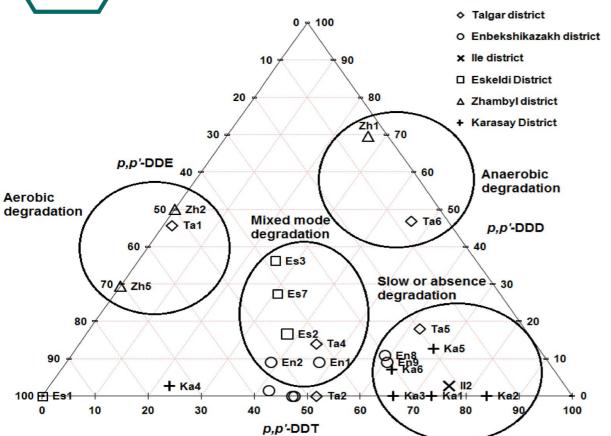


Fig. 1. Three-fold diagram illustrating p,p'-DDT degradation pathways in soil samples from various locations within Almaty Region, Kazakhstan.

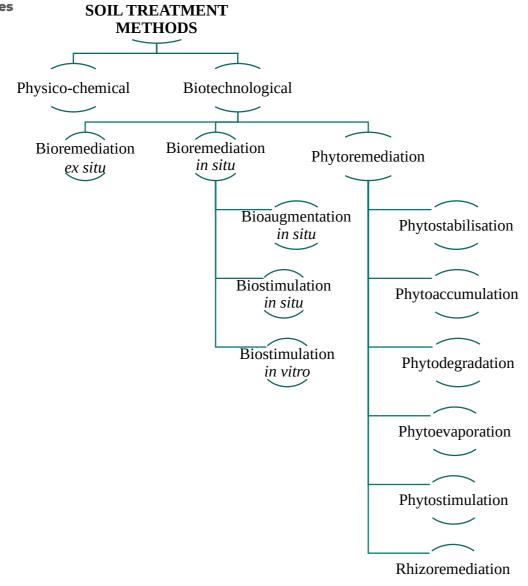
In Zhambyl and Talgar districts, points near DDT-DDE degradation axis indicate **aerobic degradation** of metabolites, points near DDT-DDD axis, on the contrary are associated with **anaerobic degradation pathway**.

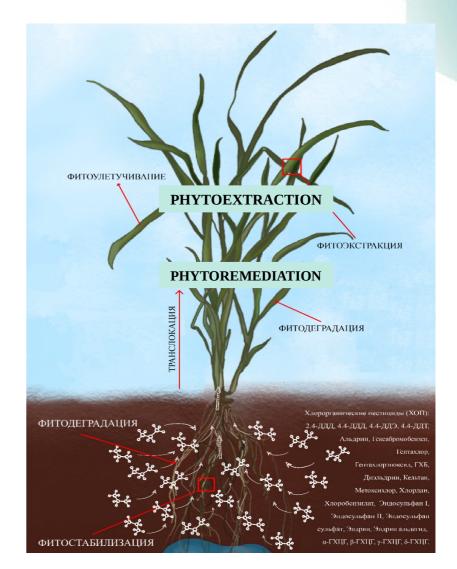
In the territory of Karasay, Ile, and Enbekshikazakh districts, DDT dominates in the soil, which reflects slow or even no degradation.



Biological methods of soil remediation

Phytoremediation is a promising technology in balance with the ecosystem.





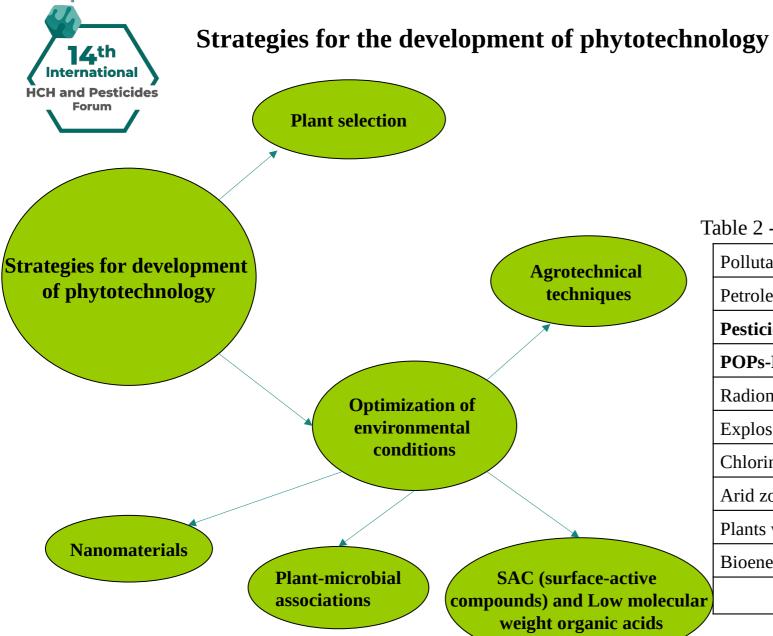


Table 2 - Phytoremediation plants of Kazakhstan's flora

Pollutants	woody	perennial	annual
Petroleum hydrocarbons	9	18	5
Pesticides	5	10	5
POPs-Pesticides	3	7	11
Radionuclides	8	26	3
Explosives	0	3	2
Chlorinated solvents	4	3	1
Arid zones	19	0	0
Plants with large biomass	9	0	0
Bioenergy species	2	4	3
Total	65	102	40



Advantages and disadvantages of phytotechnology

USE OF CONTAMINATED SOILS

PHYTOREMEDIATION

The process of soil remediation from xenobiotics for further use.

PHYTOMANAGEMENT

The process of growing energy crops on contaminated sites to **produce clean biomass.**

PHYTORE	MEDIATION	PHYTOMANAGEMENT			
Advantages	Disadvantages	Advantages	Disadvantages		
Eco-friendliness Economic efficiency	Access to land use in the long run	Use of marginal and contaminated sites	Lack of quality standards for input raw materials		
Can be applied to a wide	Long time	Profitability	Strict requirements for the output product		
range of contaminants	Continuous monitoring and control	Eco-friendliness	· ·		
		Can be combined with phytostabilisation			



Phytoremediation of soil polluted with pesticides

Table 3 - Organochlorine pesticides concentrations in soil before phytoremediation

Pesticides	MPC, μg/kg		Amangeldy	Belbulak	Beskainar	Kyzylkairat		
	KZ	EU	Amangeluy	Delbulak	Deskalllar	Kyzyikaii at	< LOD	
2.4-DDD	100	10.0	487	176	848	14 072		
4.4-DDD	100	10.0	654	198	824	11 434	< MPC	
4.4-DDE	100	10.0	784	576	34 215	777	\MC	
4.4-DDT	100	10.0	1 237	62	6 274	10 023		
α-НСН	100	220.0	7.30	< LOD	7.33	45.1	> MPC (< 5)	
β-НСН	100	92.0	6.5	< LOD	13.4	25.5		
ү-НСН	100	0.01	97.0	9.50	251	488	> 5 × MPC	
Endrin	1	2.9	859	23.9	32548	4485	_	
Aldrin	2.5	7.0	12.2	< LOD	64.0	230	> 40 × MDC	
Chlordane	100	4.3	30.1	4.1	< LOD	48.1	> 10 × MPC	
Chlorobenzilate	20	-	277	25.7	4 067	32 061		
Dibutyl chlorendate	-	-	511	154	1 285	2 134	> 50 × MPC	
Dicofol	100	-	11.9	< LOD	14.7	21.9		
Dieldrin	0.5	7.0	42.3	22.0	194	< LOD	>100 × MPC	
Endosulfan α	100	0.003	83.1	5.06	4.40	< LOD		
Endosulfan β	100	0.003	27.8	< LOD	77.8	253		
Endosulfan sulfate	-	-	654	258	266	119	>500 × MPC	



Miscanthus sinensis

CANNOT

Miscanthus sinensis – energy species

(Area – Altai)

Absorb and accumulate in tissues (BCF < 1) following pesticides **9 OCPs out of 24**

- 2.4-DDD
- 4.4-DDD
- Chlorobenzylate
- α-HCH
- δ-HCH
- Heptachlor epoxide
- Endosulfan α
- Endrin
- Dibutyl chlorendate

OCPs - organochlorine pesticides

CAN

- **Bioconcentrate** (BCF >1) **15 OCPs out of 24** 4.4-DDE, 4.4-DDT, Methoxychlor, γ -HCH, Aldrin, Heptachlor, Endosulfan β , Endrin aldehyde, and Hexabromobenzene
- Hyperaccumulation 6 OCPs out of 15 Dicofol, β -HCH, Dieldrin, Chlordane, Endosulfan sulfate, and HCB
- Phytostabilization (TLF < 1) 3 OCPs out of 15
 4.4-DDE, Dicofol, and Chlordane
- Phytoextraction (TLF > 1) 5 OCPs out of 15
 β-HCH, γ-HCH, Heptachlor, Hexabromobenzene, and HCB)
- Evenly distributed in plant tissues (TLF ~ 1) 7 OCPs
 out of 15
 4.4-DDT Methoxychlor Aldrin Dieldrin Endosulfan

4.4-DDT, Methoxychlor, Aldrin, Dieldrin, Endosulfan β , Endosulfan sulfate, and Endrin aldehyde



RESEARCH PERSPECTIVES







Screening for growthstimulating properties





Microorganisms

Miscanthus ×

Reproduction of the target microorganism



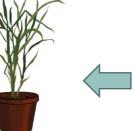
Soil remediation







Miscanthus





Planting on contaminated soil

Inoculation of plant rhizomes

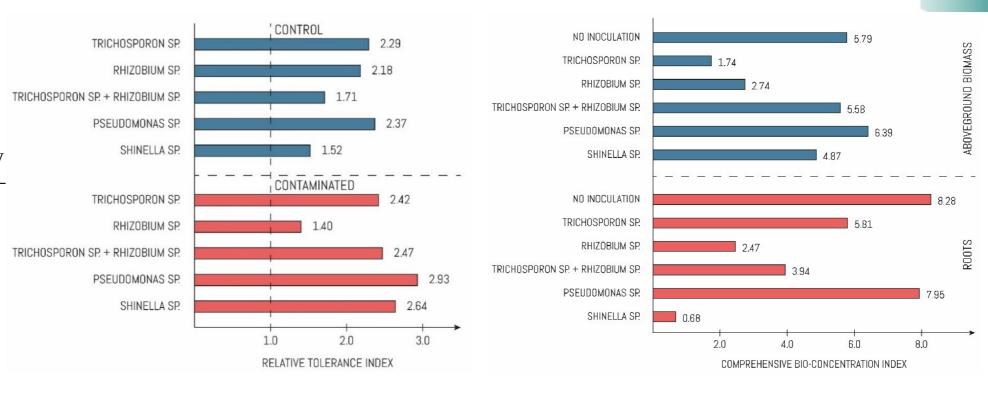
Phytoremediation of soil polluted with trace elements (heavy metals)



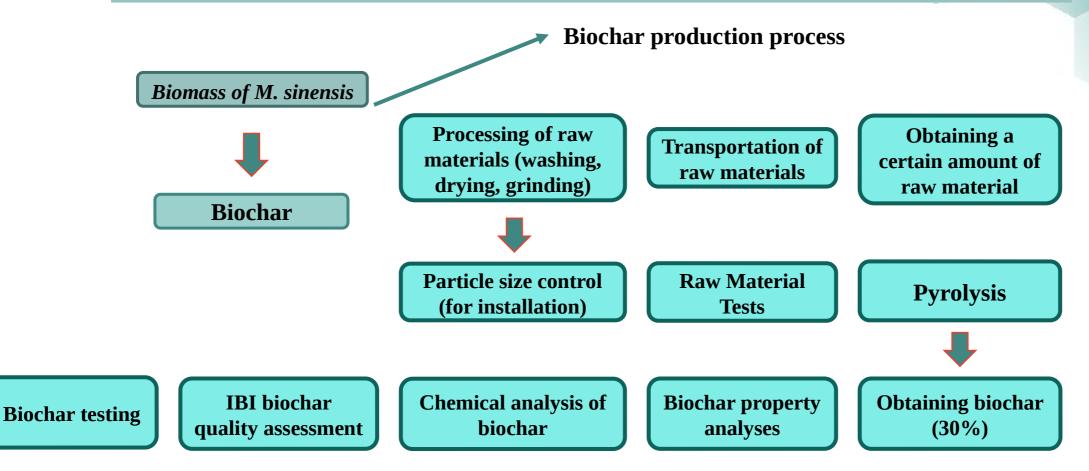
Miscanthus × giganteus is an allotriploid, bioenergetic, highly productive, sterile hybrid (Area – East Asia)

Plant growth promoting rhizobacteria (PGPR)

	N_2	$\mathbf{P}_2\mathbf{O}_5$	Sidayanhaya	IAA	Zn	Pb
PGPR	_	solubilization	Siderophore	synthesis <u>.</u>	tolerance,	tolerance,
	fixation	Solubilization	synthesis	μg mL ⁻¹	mM	mM
Trichosporon sp. CA1	+	+	+	50.2 ± 1.2	4.0	4.0
Rhizobium sp. Zn1-1	+	+	<u>±</u>	12.0 ± 0.2	2.5	0.5
Pseudomonas sp. ChA1-4	+	+	<u>±</u>	31.0 ± 1.1	2.5	0.5
Shinella sp. Zn5-6	+	+	±	19.1 ± 0.1	2.5	0.5



PROSPECTS FOR THE USE OF BIOMASS IN BIOENERGY



Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil (International Biochar Initiative).

New project supported by FAO

"Technical assistance in implementation of laboratory and field trials on bioremediation and phytoremediation of soils contaminated by POPs and heavy metals" 2023 as part of FAO project "Lifecycle Management of Pesticides and Disposal of POPs Pesticides in Central Asian countries and Türkiye"

Destroyed storage facilities of obsolete pesticides in villages of Enbekshi-Kazakh district, Almaty region: **Saimasai**

GPS coordinates: 43°27′19″ N 77°18′53″ E

Ownership: state property, can be used

Suspected soil contamination level based on inventory of 2010 (concentrations of DDT metabolites and HCH isomers): 23 × MPC.

Satellite pictures: since 2002

Tasks:

- 1 Site recultivation
- 2.1 Field trials on bio- and phytoremediation
- 2.2 Microbial preparation application on field scale
- 3 Cultivation of seeds/plants on OCP-contaminated soils in greenhouse







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