Degradation of polybrominated diphenyl ethers in sewage sludge by ozonation and solubilisation of degradation products in the water phase

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Presentation outline

- **Focusing the problem;**
- **Potential side-benefits of sludge ozonation;**
- **Results obtained treating real sewage sludge (primary and mixed digested) by ozone**:
  - **Process performance through gross-parameters monitoring**
  - **removal of PolyBrominated Diphenyl Ethers (PBDEs);**
  - **Organic bromine distribution between liquid and solid phase;**
  - **by-products formation/degradation and toxicity;**
- **Conclusions.**

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FOCUSING THE PROBLEM

- **Management of sludge produced in the wastewater treatment plants represents a global environmental and economic issue:**
  - **The volume of the sludge extracted from primary and secondary settling tanks is about 2% of the volume of treated wastewater;**
  - **Sludge treatment and disposal entails very high capital and operating costs, which can account for as high as 50 % of the total costs of wastewater treatment plant;**
- **Presently, an outlet for sludge disposal is its use in agriculture as a fertilizer.**
- **According to 86/278 Directive, sludge has to be used taking primarily into account the nutrient needs for plant growth, and that the quality of the soil and the surface- and ground-waters is not impaired.**

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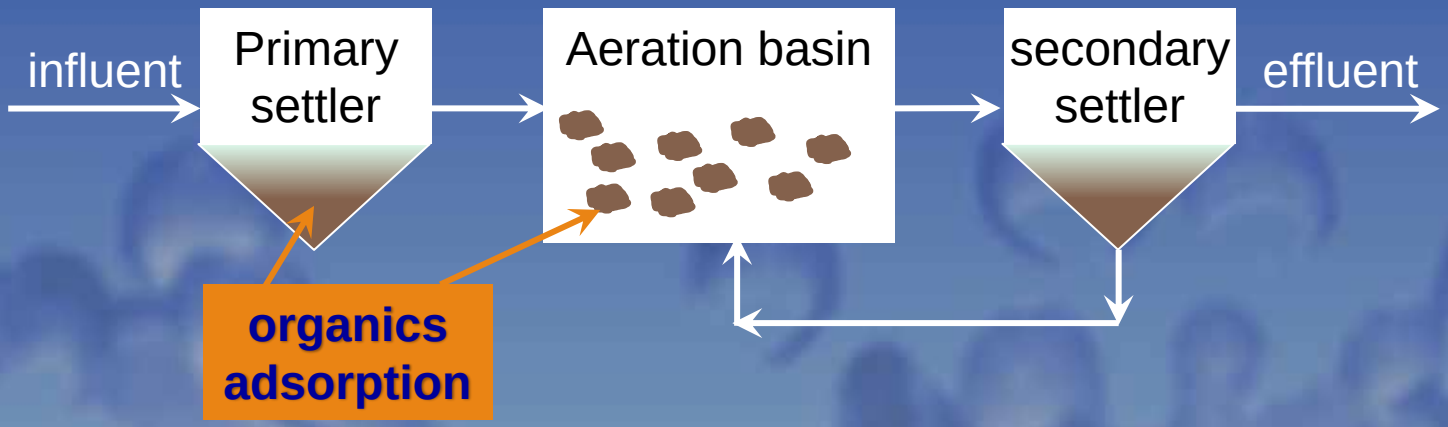
Organic pollutants in sludge: how is it possible to limit their presence?

- During operation of wastewater treatment plants sorption of hydrophobic organics onto sludge flocs occurs.



- Brominated flame retardants enter sewage treatment plants and are mainly partitioned onto sludge due to their hydrophobic properties. They are then accumulated on sludge causing pollution of the sites where sludge is ultimately disposed of.

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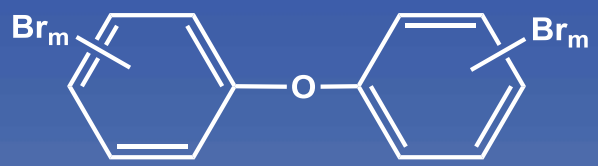
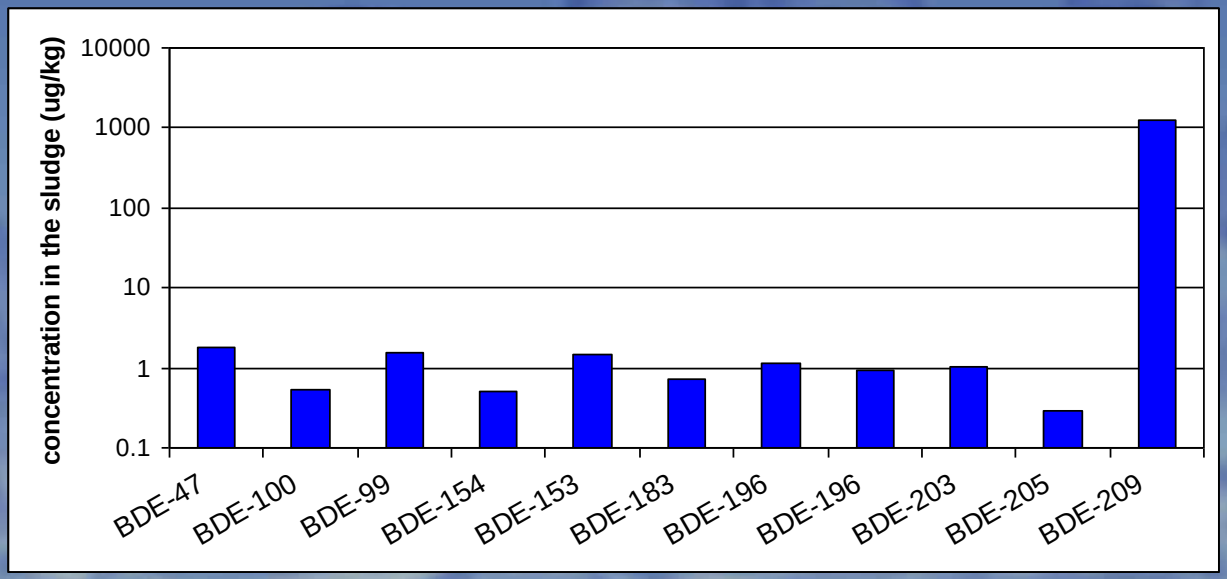
Organic pollutants in sludge: PolyBrominated Diphenyl Ethers (PBDEs)

BDE congener	number of bromine atoms
BDE-47	4
BDE-99	5
BDE-100	5
BDE-153	6
BDE-154	6
BDE-183	7
BDE-196	8
BDE-197	8
BDE-203	8
BDE-205	8
BDE-209	10



PBDE (209 isomers)



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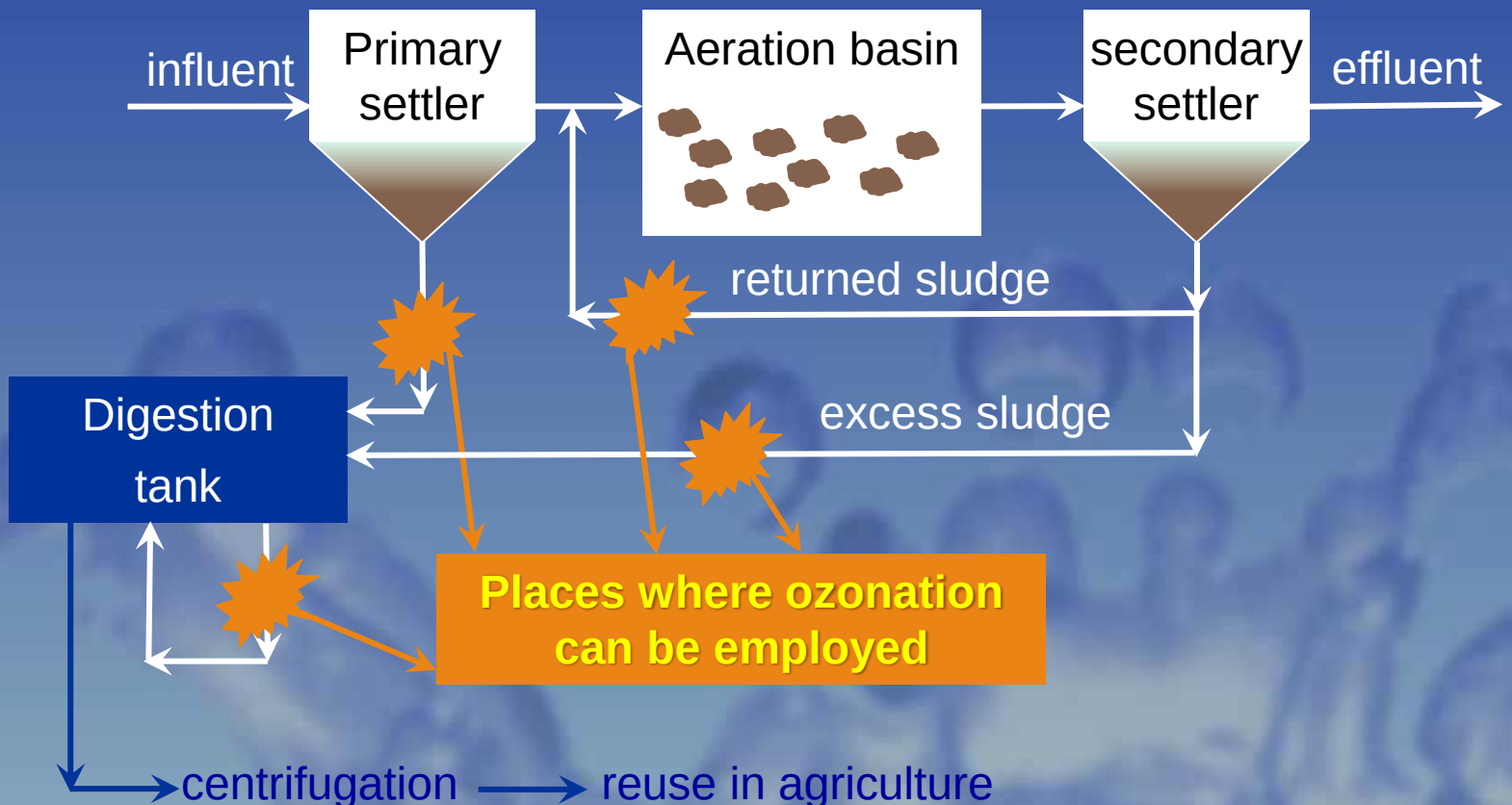
Application of ozonation for sludge reduction



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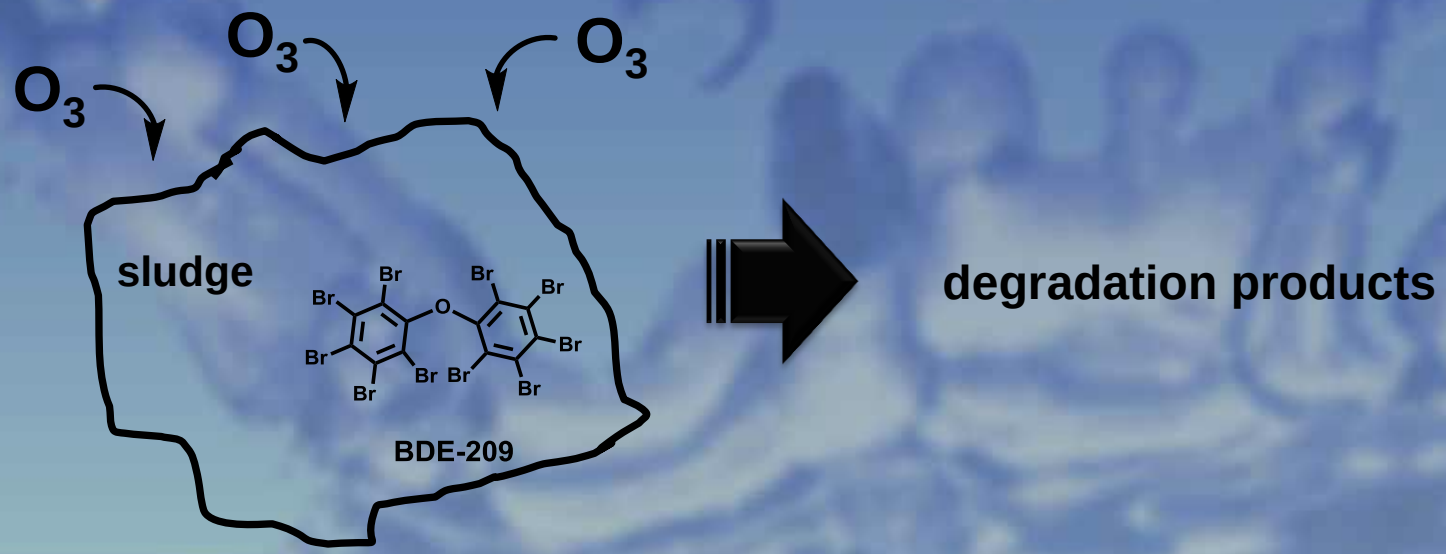
Main goals of the performed investigation

- Experiments on ozonation of sewage sludge to degrade brominated flame retardants on primary and mixed-digested sludge.
- Identification of degradation products and degradation pathway.



Composition of influent/effluent wastewater (primary step)

	TSS, mg/L	VSS, mg/L	VSS/TSS	COD, mg/L	TN, mg/L	N-NH_4, mg/L	N-NO_2, mg/L	N-NO_3, mg/L	P tot, mg/L	IC, mg/L	DOC, mg/L
influent (total)	254 ± 37	221 ± 29	0.87 ± 0.03	408 ± 48	52 ± 7	45.2 ± 4.5			7.5 ± 2.0		
influent (sol.)				116 ± 42	45.8 ± 8.1	39.8 ± 3.7	0.03 ± 0.01	0.14 ± 0.08	5.3 ± 2.1	87.4 ± 6.4	34.2 ± 10
effluent (total)	120 ± 31	109 ± 24	0.91 ± 0.06	309 ± 47	44.1 ± 4.3	38.1 ± 7.0			5.5 ± 2.1		
effluent (sol.)				127 ± 55	35.7 ± 5.0	32.8 ± 7.2	0.03 ± 0.01	0.20 ± 0.06	3.6 ± 0.9	84.5 ± 9.9	39.6 ± 14

Bari-west wastewater treatment plant

250,000 PE

Average flow rate = 0.6 m^3/s, pH = 7.5-7.9

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Ozonation of mixed-digested sludge: gross parameters

ozone dose g_{ozone}/g_{TSS}	TSS g/L	VSS g/L	VSS/TSS	COD g/L	TN mg/L	N-NH_4 mg/L	N-NO_2 mg/L	N-NO_3 mg/L	P tot. mg/L	IC mg/L	TOC mg/L
total (liquid + solid phase)											
0	24.3	16.9	0.695	28.6	589	560			316		
0.014	23.2	16.6	0.716	24.6	593	532			298		
0.038	21.2	14.5	0.684	26.4	587	532			297		
0.061	19.8	13.6	0.687	26.6	579	539			317		
0.105	19.6	13.1	0.668	26.5	593	574			311		
liquid phase											
0				0.44	462	323	3.03	0.45	4.6	543	176
0.014				1.5	498	343	2.77	0.94	5.5	358	539
0.038				2.6	521	385	1.28	3.25	12.2	356	1045
0.061				3.8	584	385	1.86	14.4	13.7	335	1395
0.105				4.5	601	399	1.75	24.4	20.7	290	1886

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Ozonation of primary sludge: gross parameters

ozone dose g_{ozone}/g_{TSS}	TSS g/L	VSS g/L	VSS/TSS	COD g/L	TN mg/L	N-NH_4 mg/L	N-NO_2 mg/L	N-NO_3 mg/L	P tot. mg/L	IC mg/L	TOC mg/L
total (liquid + solid phase)											
0	30.3	23.7	0.78	55	1240	280			390		
0.014	29.3	22.4	0.76	51	1230	283			345		
0.038	27.1	20.6	0.76	48.6	1130	297			326		
0.061	26.9	19.8	0.73	48	1186	313			319		
0.105	22.1	16.0	0.73	38.8	1210	294			374		
liquid phase											
0				1.5	171	98	<dl	<dl	24.2	132	468
0.014				4.4	296	133	<dl	1.1	25.5	77	1404
0.038				5.8	563	168	1	2	25.9	69	1985
0.061				6.6	695	201	2	28	35.4	27.4	2361
0.105				7.9	802	224	1	59	46.5	26.2	3038

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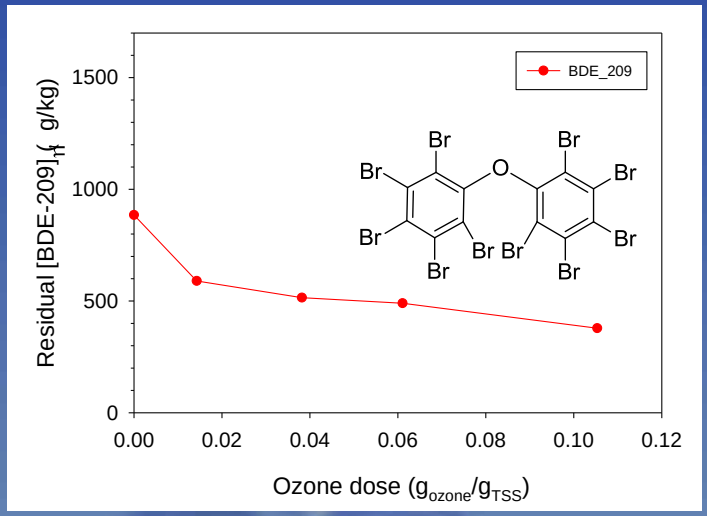
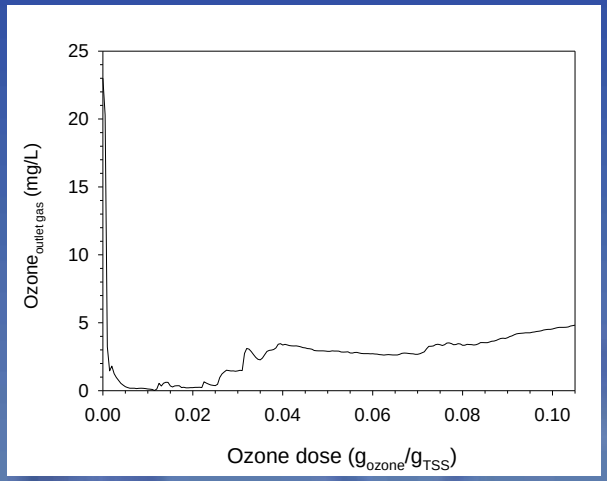
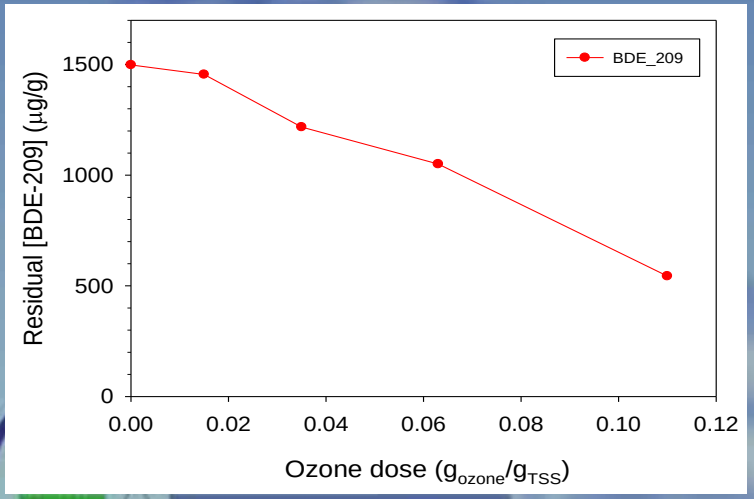
Ozonation of primary and mixed digested sludge: BDE-209 decay and off-gas ozone concentration

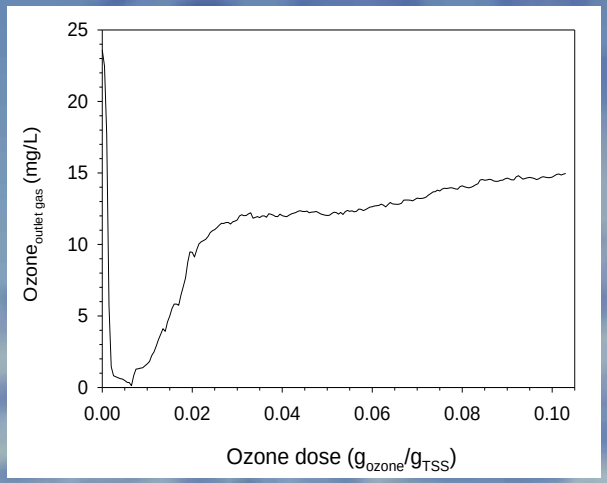




primary sludge

Off-gas ozone concentration profile during ozonation of mixed digested sludge.





mixed digested sludge

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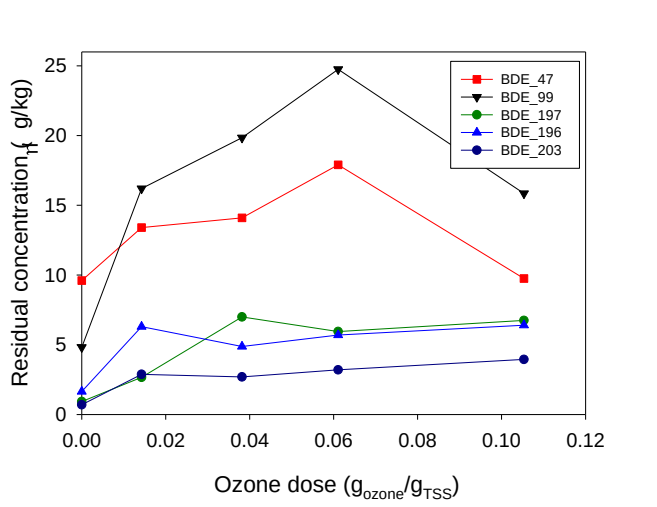
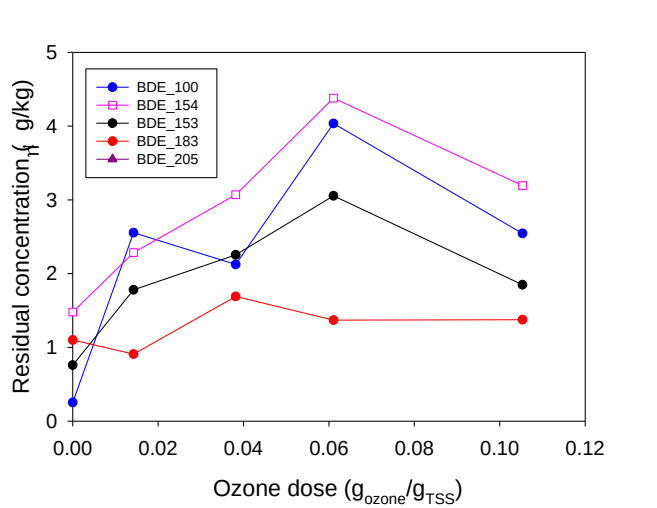
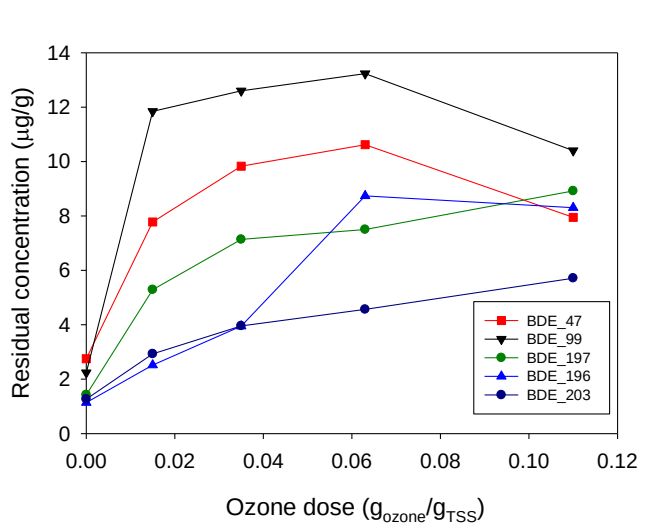
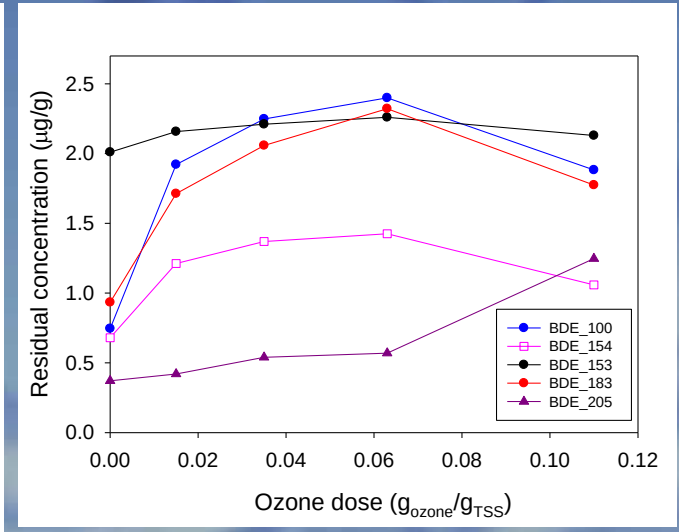
Ozonation of primary and mixed digested sludge: PBDEs decay/formation





primary sludge

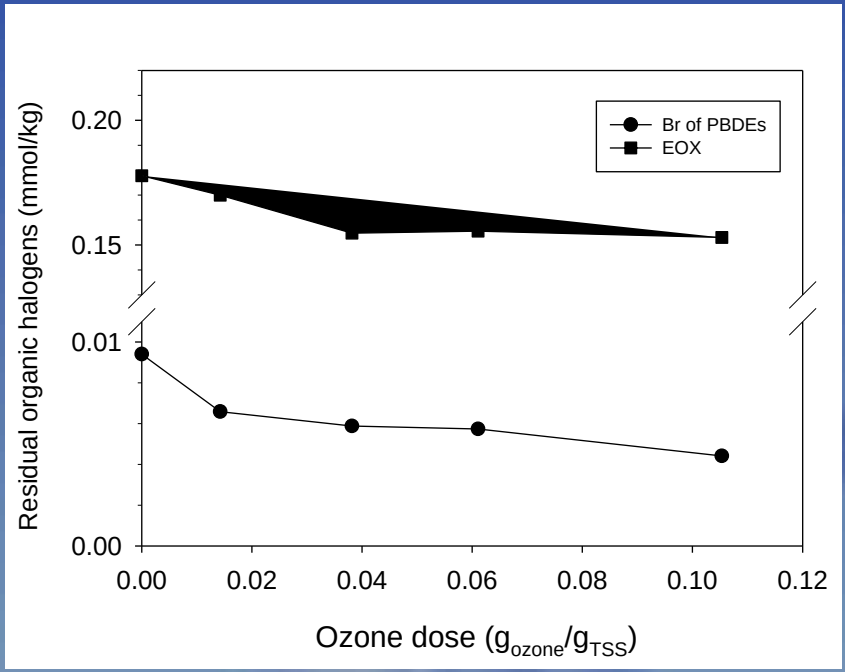




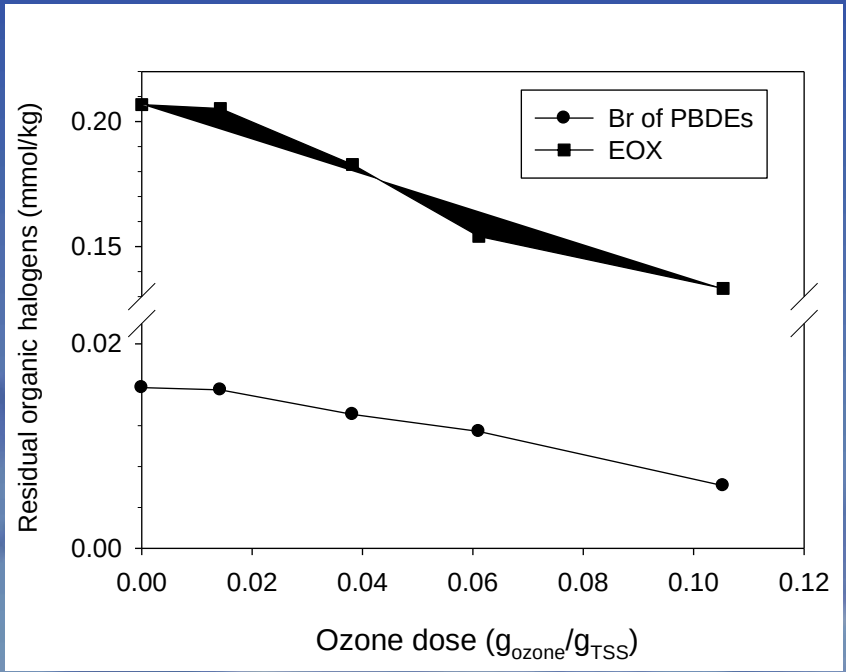
mixed digested sludge

some debromination occurs in the early stage of the ozonation. Then degradation prevails.

Ozonation of primary and mixed digested sludge: organic bromine and total organic halogens decay



primary sludge



mixed digested sludge

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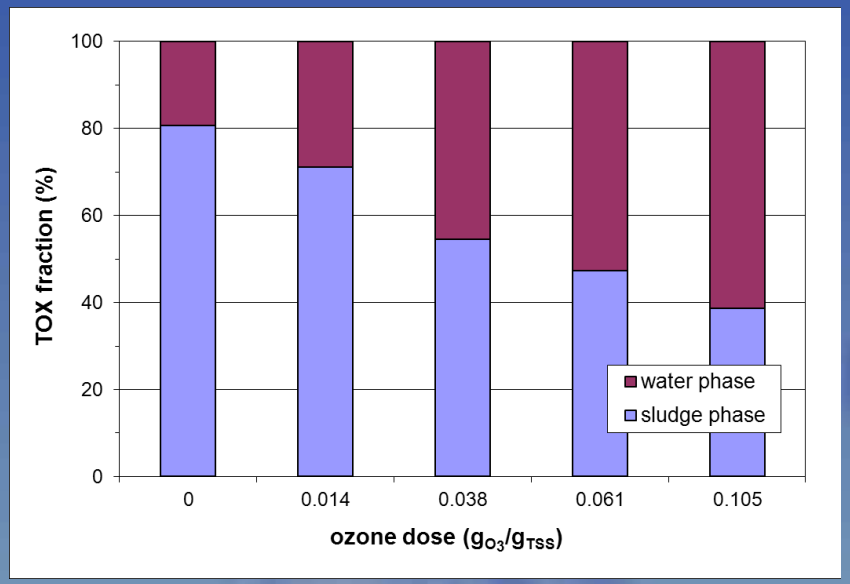
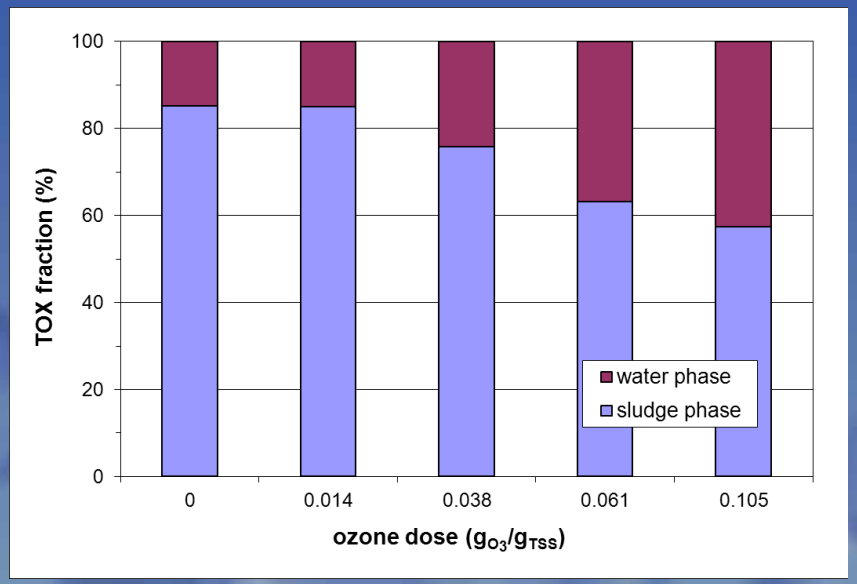
Ozonation of primary and mixed digested sludge: Degradation of total organic halogens in both liquid and solid phase



primary sludge



mixed digested sludge

During ozonation a large fraction of organic bromine is transferred to the water phase.

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Ozonation of primary and mixed-digested sludge: identification of degradation products

Compound classes	solid phase	aqueous phase
hydroxylated-BDE (by HPLC/MS)	not detected	not detected
other by-products (by HPLC/MS)	X	X
other by-products (by HPLC/ICP-MS)	X	X
Br^- (by IC)	not detected	X
Br-organic acids (by IC/MS)	not detected	X

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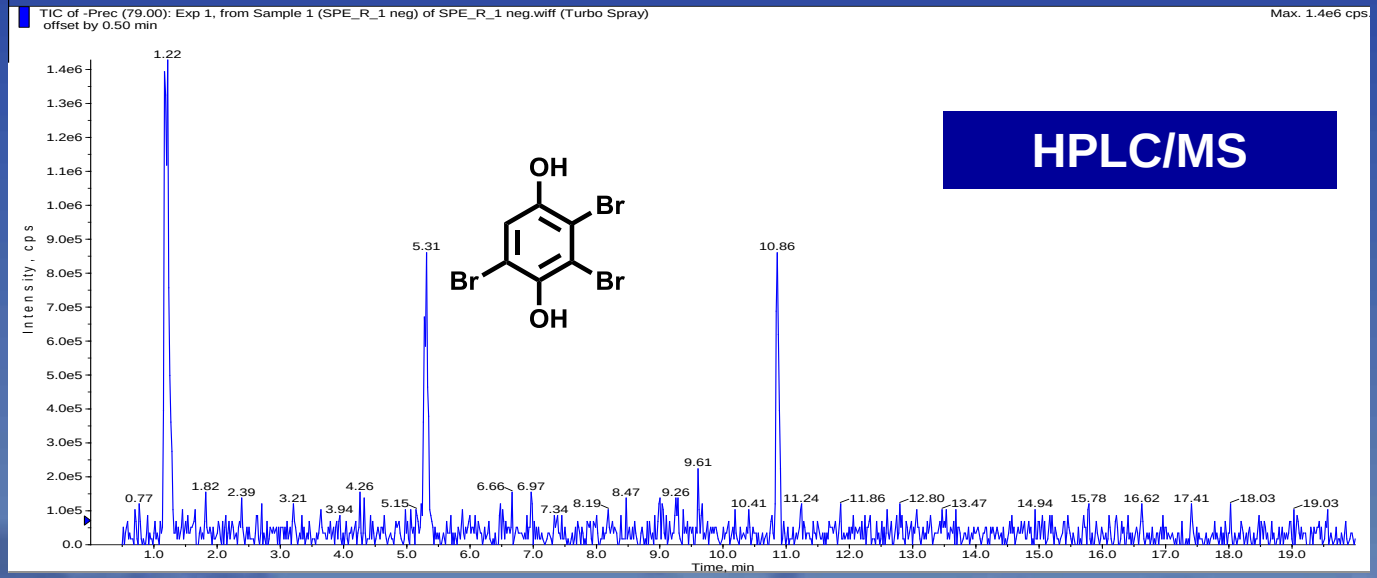
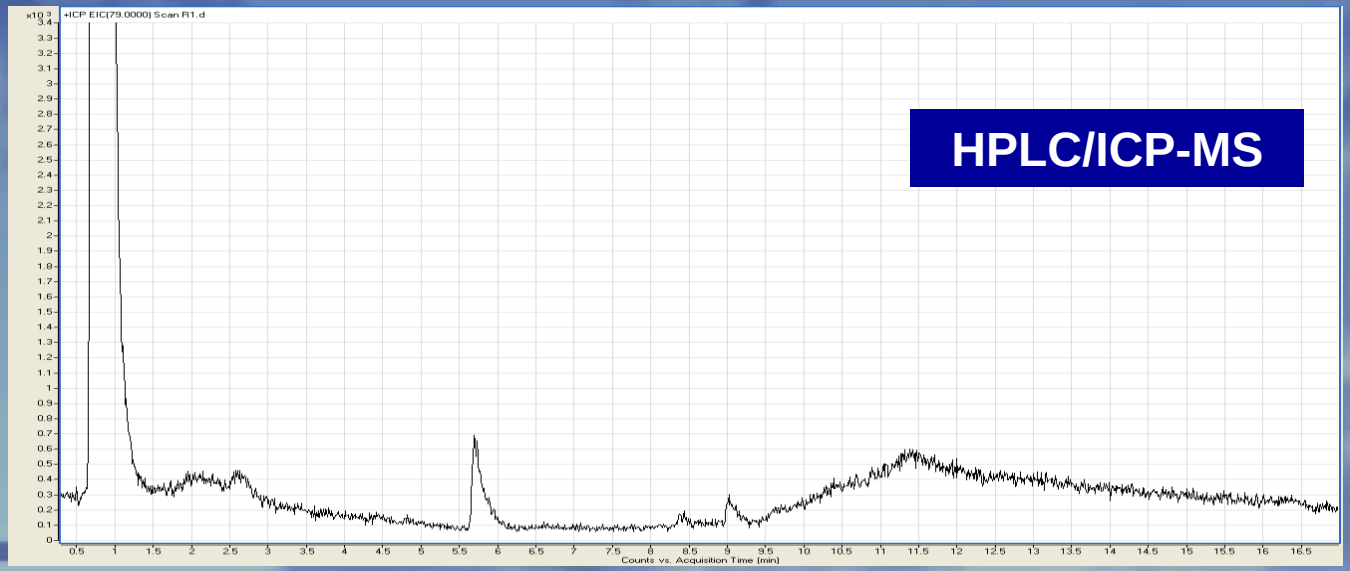
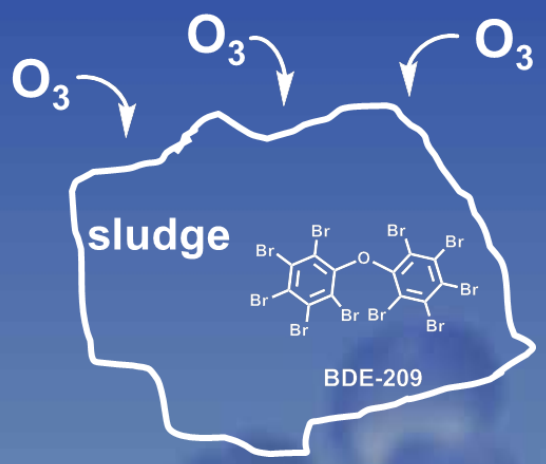
Ozonation of primary and mixed-digested sludge: identification of degradation products

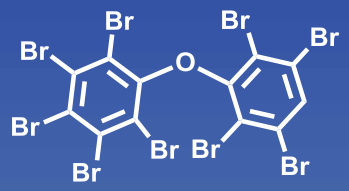




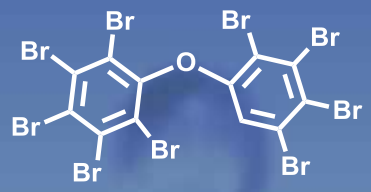
Ozonation of primary and mixed-digested sludge: degradation products identification and degradation pathway



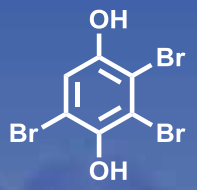
ozonation

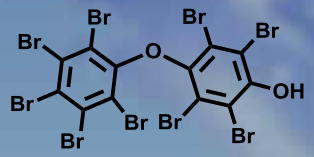


BDE-208

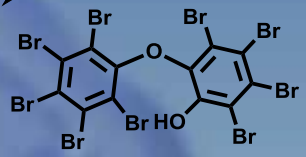


BDE-206





hydroxylated BDE-208



hydroxylated BDE-206

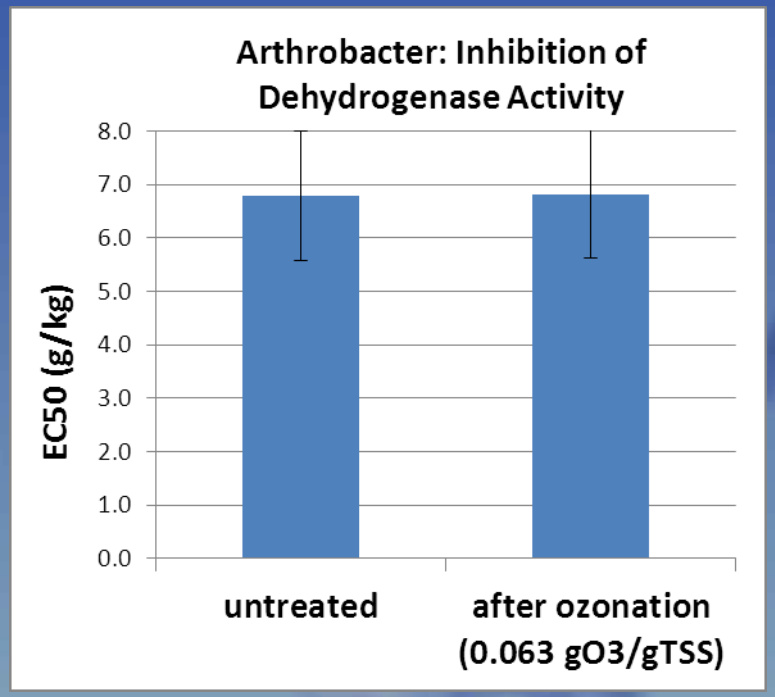
environmental conditions

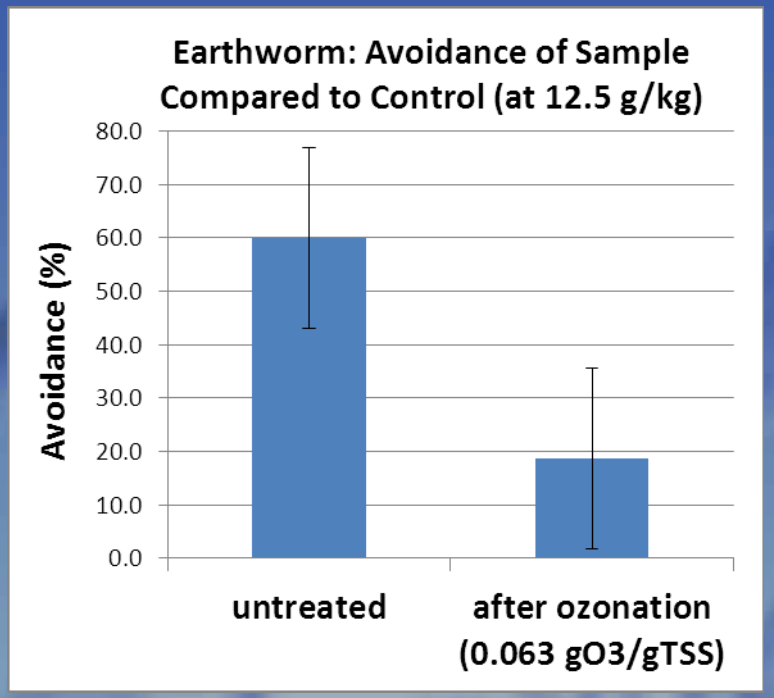
brominate dioxins

$Br^{-}CH_2COOH$

+ other low molecular weght compounds

Ozonation of primary and mixed-digested sludge: toxicity of treated samples





Conclusions

- Ozonation was effective in degrading brominated flame retardant in both primary and mixed digested sludge;
- BDE-209 (the deca-brominated congener present at the highest concentration in sewage sludge) showed a linear degradation rate vs ozone dose;
- A fraction of transformed halogenated organics are transferred to the aqueous phase (for mixed digested sludge up to 41% at 0.105 g_{ozone}/g_{TSS});
- Ozonation leads to formation of polar organics that have a good water solubility and, therefore, get partitioned between the aqueous and the solid phase

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