White Phosphorus

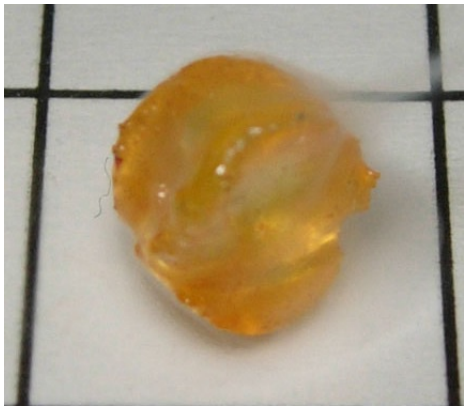
Molecular Structure	P_4
Molecular Weight	124 amu
Melting Point	44° C
Boiling Point	280° C
Appearance	Waxy Transparent Colorless (pure)
Moh's Hardness	0.5
Density	1.8 g/cm^3

Physical Properties Relevant to the Fate and Transport of P_4

Vapor Pressure	(0° C)	0.005 torr
	(20° C)	0.03 torr
	(40° C)	0.13 torr
Solubility in Water	(15° C)	2.4 mg/L
	(36° C)	4.7 mg/L
Henry's Constant	2.1×10^{-3} atm-m^3/mole	
K_{ow}	1,200	
Auto ignition Temperature	20 to 40° C	

Oxidation States and Toxicity

+5	P_4O_{10}; H_3PO_4	Low toxicity (irritant)
+3	P_4O_6; H_3PO_3	High toxicity
+1	H_3PO_2	↓
0	P_4	
-2	P_2H_4	
-3	PH_3 (phosphine)	



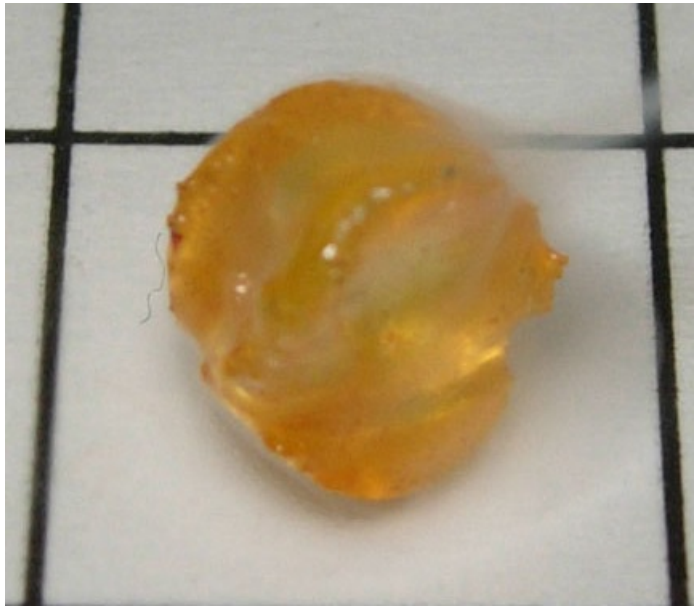
Reaction with Oxygen

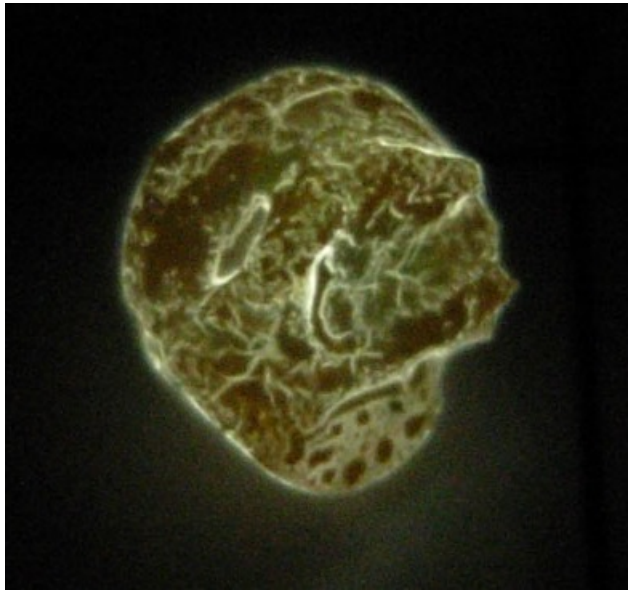
P_4 (solid) → P_4 (vapor) → (+ O_2) → Complex mixture of suboxides → P_4O_{10} and polymeric phosphates

Example: (P_4O_6)

- The many oxidation states of phosphorus results in a large number of possible products.
- The "smoke" is from the formation of phosphorus pentoxide (P_4O_{10}), which is extremely hygroscopic and condenses water vapor from the atmosphere.
- Polymeric phosphates form a white coating on solid P_4 that is stored under water and form "crusts" in P_4 contaminated soils.
- In the absence of oxygen, P_4 will turn to vapor and diffuse through soil, where it may sorb to organic matter.

Chemiluminescence





- Images show a piece of solid P_4 vaporizing.
- Chemiluminescence from the formation of PO_2

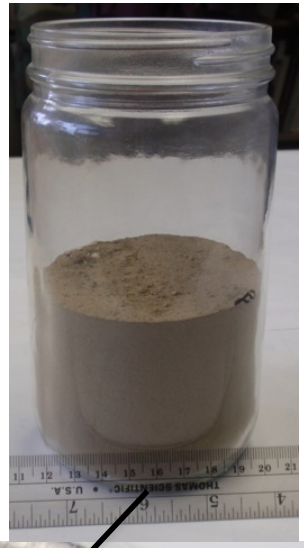
Images from: http://www.periodictable.ru/015P/P_en.html

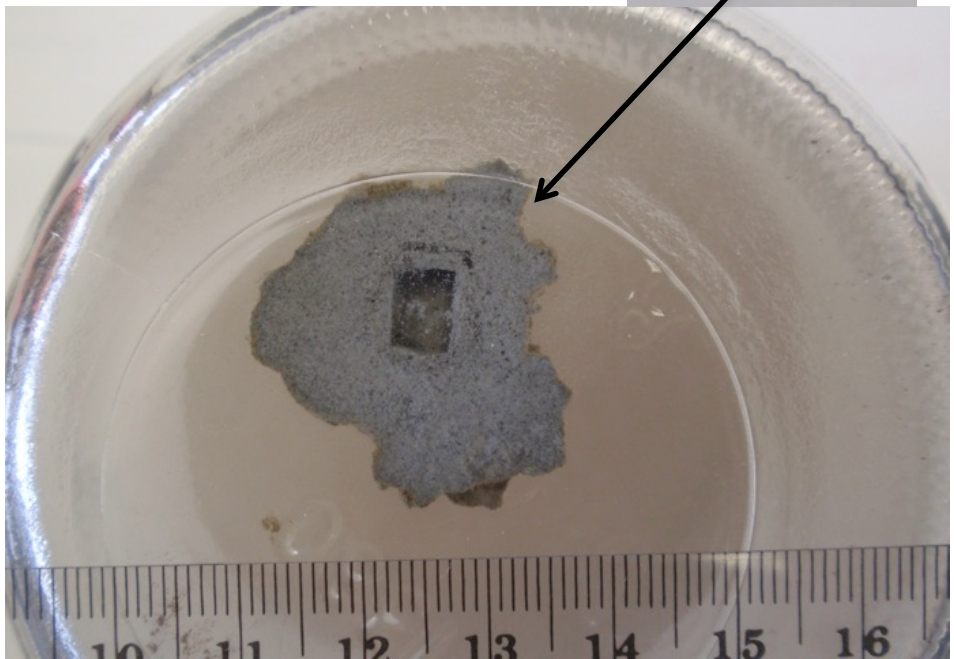
P_4 in Unsaturated Sediment

Example of the formation of oxidation products in the vapor phase when P_4 contaminated sediment was uncovered during sampling in a military impact area.

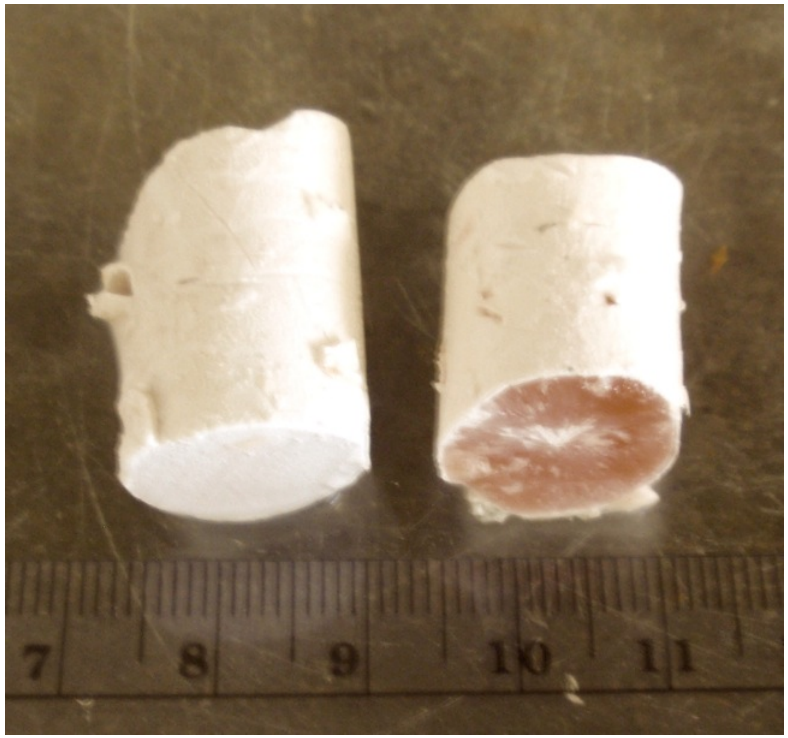
Images of Polymeric Phosphate "Crusts" and "Coatings" From P_4 Oxidation

- A piece of solid P_4 was placed in a jar and covered with sandy soil.
- P_4 sublimed and left a void. A halo of oxidation products formed in the soil pore spaces.





- Solid P_4 stored under water forms a white coating.
- The thin coating can be scraped to reveal P_4.



Crusts and coatings can increase the persistence of solid P_4.

P_4 in Aqueous Solutions

- Oxidation of P_4 in water is analogous to oxidation in the vapor phase.

- Hydrolysis to oxyacids

$$P_4O_2 + 6H_2O \text{ ----------> } 4H_3PO_2$$
$$2P_2O_3 + 6H_2O \text{ ----------> } 4H_3PO_3$$

- Oxidation to orthophosphoric acid H_3PO_4 and polymeric phosphorus oxides

$$H_3PO_2 + O_2 \text{ ----------> } H_3PO_4$$
$$2H_3PO_3 + O_2 \text{ ----------> } 2H_3PO_4$$

P_4 in Alkaline Solutions (High pH)

- Complex reactions with several possible reaction pathways involving disproportionation (both oxidation and reduction) of P_4 and decomposition of water.

- Oxidation products include hypophosphorous acid (H_3PO_2) and phosphorous acid (H_3PO_3).

- Reduced products include phosphine (PH_3) and biphosphine (P_2H_4).

- Decomposition of water produces hydrogen (H_2) gas.

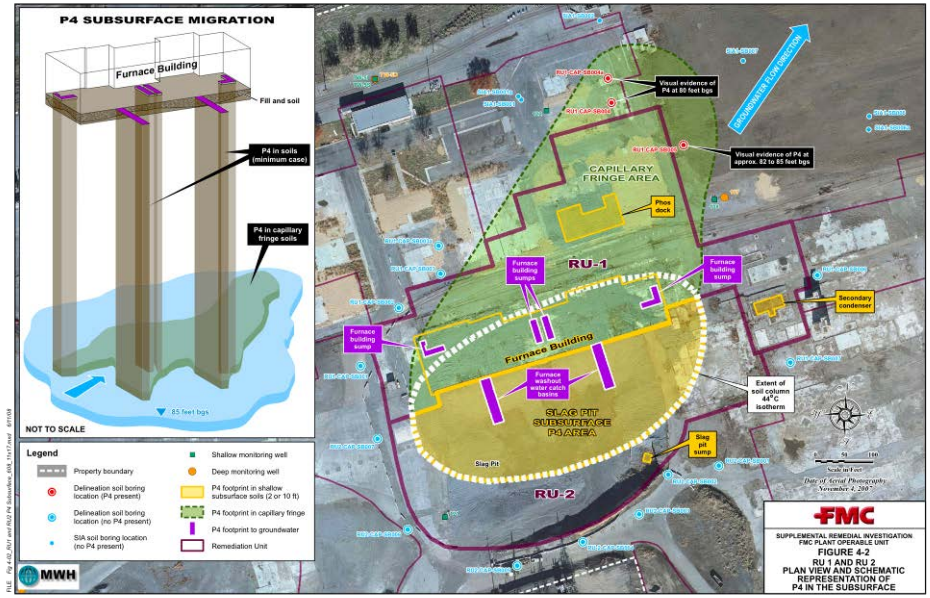
Water Quality Criteria

- In the 1970s and 1980s studies were conducted to determine water quality criteria for the protection of aquatic organisms

- Contamination of water occurred from the release of phossy water that contained colloidal (suspended) and dissolved P_4 from P4 manufacturing facilities (Long Harbour, Newfoundland and Muscle Shoals, Alabama) and from an arsenal (Pine Bluff, Arkansas).

- Water quality criteria for the protection of aquatic organisms: Critical Maximum Concentration estimated to be 1 µg/L (Davidson et al. 1987)

P_4 Subsurface Migration



- Large source of P_4
- P_4 is toxic at very low aqueous concentrations
- Rigorous monitoring will be required to ensure that P_4 does not migrate off-site.