complex. In their reduced form, the electron carriers that function in the acceptor region of PSI are all extremely strong reducing agents. These reduced species are very unstable and thus difficult to identify. Evidence indicates that one of these early acceptors is a chlorophyll molecule, and another is a quinone species, phylloquinone, also known as vitamin K_1.

Additional electron acceptors include a series of three membrane-associated iron–sulfur proteins, also known as **Fe–S centers**: **FeS_X**, **FeS_A**, and **FeS_B** (see Figure 7.27). Fe–S center X is part of the P700-binding protein; centers A and B reside on an 8-kDa protein that is part of the PSI reaction center complex. Electrons are transferred through centers A and B to **ferredoxin** (**Fd**), a small, water-soluble iron–sulfur protein (see Figures 7.19 and 7.27). The membrane-associated flavoprotein **ferredoxin–NADP$^+$ reductase** (**FNR**) reduces NADP$^+$ to NADPH, thus completing the sequence of noncyclic electron transport that begins with the oxidation of water.

In addition to the reduction of NADP$^+$, reduced ferredoxin produced by PSI has several other functions in the chloroplast, such as the supply of reductants to reduce nitrate and the regulation of some of the carbon-fixation enzymes (see Chapter 8).

Cyclic electron flow generates ATP but no NADPH

Some of the cytochrome b_6f complexes are found in the stroma region of the membrane, where PSI is located. Under certain conditions, **cyclic electron flow** is known to occur from the reducing side of PSI via plastohydroquinone and the b_6f complex and back to P700. This cyclic electron flow is coupled to proton pumping into the lumen, which can be used for ATP synthesis but does not oxidize water or reduce NADP$^+$ (see Figure 7.16B). Cyclic electron flow is especially important as an ATP source in the bundle sheath chloroplasts of some plants that carry out C_4 carbon fixation (see Chapter 8). The molecular mechanism of cyclic electron flow is not well understood. Some proteins involved in regulating the process are just being discovered, and this remains an active area of research.

Some herbicides block photosynthetic electron flow

The use of herbicides to kill unwanted plants is widespread in modern agriculture. Many different classes of herbicides have been developed. Some act by blocking amino acid, carotenoid, or lipid biosynthesis or by disrupting cell division. Other herbicides, such as dichlorophenyldimethylurea (DCMU, also known as diuron) and paraquat, block photosynthetic electron flow (**Figure 7.28**).

DCMU blocks electron flow at the quinone acceptors of PSII, by competing for the binding site of plastoquinone that is normally occupied by PQ_B. Paraquat accepts electrons from the early acceptors of PSI and then reacts with oxygen to form superoxide, O_2^-, a species that is very damaging to chloroplast components.

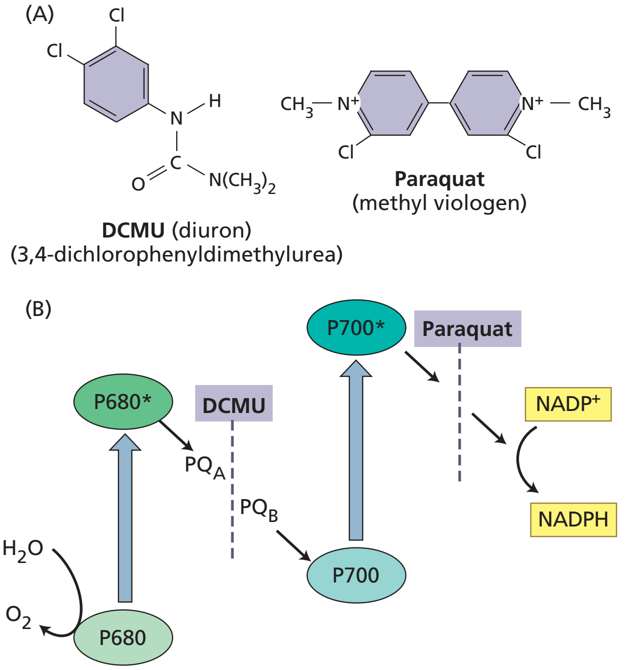

Figure 7.28 Chemical structure and mechanism of action of two important herbicides. (A) Chemical structure of dichlorophenyldimethylurea (DCMU) and methyl viologen (paraquat), two herbicides that block photosynthetic electron flow. DCMU is also known as diuron. (B) Sites of action of the two herbicides. DCMU blocks electron flow at the plastoquinone acceptors of PSII by competing for the binding site of plastoquinone. Paraquat acts by accepting electrons from the early acceptors of PSI.

Proton Transport and ATP Synthesis in the Chloroplast

In the preceding sections we learned how captured light energy is used to reduce NADP$^+$ to NADPH. Another fraction of the captured light energy is used for light-dependent ATP synthesis, which is known as **photophosphorylation**. This process was discovered by Daniel Arnon and his coworkers in the 1950s. Under normal cellular conditions, photophosphorylation requires electron flow, although under some conditions electron flow and photophosphorylation can take place independently of each other. Electron flow without accompanying phosphorylation is said to be **uncoupled**.

It is now widely accepted that photophosphorylation works via the chemiosmotic mechanism. This mechanism was first proposed in the 1960s by Peter Mitchell. The same general mechanism drives phosphorylation during aerobic respiration in bacteria and mitochondria (see Chapter 12), as well as the transfer of many ions and metabolites across membranes (see Chapter 6). Chemiosmosis appears to be a unifying aspect of membrane processes in all forms of life.