The environmental issue caused by atmospheric hexachlorocyclohexanes (HCHs) has been a worldwide concern due to their long-range transport potential. Tree bark is an excellent passive sampler for monitoring atmospheric pollutants. In this study, bark samples from agricultural regions across China were collected and analyzed to elucidate the contamination status of atmospheric HCHs and the enantiomeric composition of chiral α-HCH. Average contents of α-HCH, β-HCH, γ-HCH, δ-HCH, and ∑HCHs in bark were 1.16, 2.51, 1.67, 0.368, and 5.71 ng/g (dry basis), respectively. Jing-Jin-Tang region was identified as the "hot-spot" of bark HCHs in China. Their residues were likely from the combined sources of historical applications of technical HCHs and lindane through long-distance transport. HCH contents were found inversely correlated with annual precipitation and temperature, but positively correlated with PM10 or PM2.5 due to the bioaccumulation of both vapor- and particle-phase HCHs by tree bark. Most bark samples preferentially accumulated (+)-α-HCH, and the enantiomeric fractions (EFs) of α-HCH were positively correlated with α-HCH concentrations and the elevations of sampling locations. Compared to atmospheric analysis, tree bark analysis and enantiomeric signatures provide valuable time-integrated information on the spatial distribution and transport pathways of atmospheric HCHs on the national scale in China.