Calcium plays a critical signaling role in many biological systems. For example, in the postsynaptic neuron, increases in Ca\(^{2+}\) concentration are believed to be essential for the induction of long-term potentiation and long-term depression, changes in synaptic efficacy thought to be the cellular mechanisms underlying learning and memory. Measurements of intracellular Ca\(^{2+}\) have typically relied on the use of fluorescent imaging where the sensors used buffer the Ca\(^{2+}\), obscuring concentration measurements, and have limited spatial and temporal resolution. In postsynaptic spines, the spatial localization of Ca\(^{2+}\)-dependent effectors such as calmodulin, CaMKII and calcineurin make the measurement of Ca\(^{2+}\) concentration in the entire spine less than ideal. Using MCell, a Monte Carlo simulator, to monitor both the influx of Ca\(^{2+}\) into a spine and dendrite and its reactions with intracellular molecules, we have reproduced fluorescent transients measured in neocortical and hippocampal neurons. This has allowed determination of the unperturbed Ca\(^{2+}\) dynamics and suggests kinetics and concentrations of endogenous Ca\(^{2+}\) binding proteins. We have measured Ca\(^{2+}\) concentrations in microdomains throughout the spine showing highly heterogeneous concentrations of free intracellular Ca\(^{2+}\). Furthermore, we show the spatial and temporal activation of different Ca\(^{2+}\)-dependent effectors resulting from asynchronous pairing of pre- and postsynaptic action potentials. To complement experimental studies, we show how computer simulations can offer an alternate and complementary method of assaying intracellular Ca\(^{2+}\) dynamics and reactions.