School climate (SC) constitutes a critical factor in school life because it establishes socially acceptable behavior at school, which is able to influence and shape interactions between all school members (i.e., students, teachers, and parents) as well as their development at various levels. In turn, school-centered research recognized the existence of several behavior problems (BP) (e.g., violence, indiscipline, aggression, delinquent antisocial behaviors), which seem to be associated with a decline in SC. Parental involvement (PI) is considered as an essential factor for SC, contributing to promote good students’ educational grades, as well as better social functioning. In the present study we analyzed the mediating effect of PI on the relationship between SC and BP, taking into consideration the school personnel perceptions. A total of 329 school personnel, aged between 29 and 66 (M = 50.78, SD = 7.56), mainly female (79%), were included in the sample. Based on the perception of the school personnel, the results indicated moderate level of PI and SC, as well as the existence of different BP in the school context (e.g., absenteeism, disruptive behaviors and incivilities). PI had a positive important relationship with SC and its dimensions (i.e., environmental–structural and relationships) and a negative significant association with the different BP considered (i.e., disruptive behavior, absenteeism and incivilities). The mediating effect of PI on the relationship of total SC and its dimensions and BP was also demonstrated, concluding that the SC alone did not explain the improvement of behavior, which is verified only when there was PI. These results clarify and reinforce the important role of parents in their children’s school process, whose involvement needs to be widely promoted.