In the intense and sometimes exhilarating context of wartime, with death constantly looming, romance often flourishes. This is certainly true of the home front in most wars; near the battlefront, it was usually confined to love affairs between soldiers and nurses or local women. The Spanish civil war was no exception: romances between doctors or frontline volunteers and nurses within the international brigades were numerous. But the war in Spain brought a new dimension: for the first time, there were also a substantial number of female writers and journalists. The American Kitty Bowler, for instance, had a lasting affair with commander of the British battalion Tom Wintringham, while her compatriot Milly Bennett formed a relationship with the Swedish volunteer Hans Amlie.

Of all the affairs, there are three which, because of the richness of available sources and their enduring resonance, constitute a temptation that Amanda Vaill has not resisted. The couples she has chosen are the Spaniard Arturo Barea and his future wife, the Austrian Ilsa Kulcsar; the Americans Ernest Hemingway and Martha Gellhorn; and two great photographers, the Hungarian Robert Capa and the German Gerda Taro, who died at the battle of Brunete. Barea’s vivid autobiography, The Forging of a Rebel, translated into English by the multilingual Kulcsar, is one of a handful of indispensable books on the Spanish conflict. The contemporaneous articles and subsequent fictions of both Hemingway and Gellhorn also offer unique insight into many aspects of the war. The same, and more, is true of the photographs of Capa and Taro. The tenuous link between them is the Hotel Florida, where correspondents, international brigaders and Russian pilots caroused and consorted with the prostitutes dubbed by Hemingway “whores de combat”.

Vaill portrays them beautifully. A real delight of her book is the way she evokes the colours and smells both of starving, besieged Madrid and the well-fed opulence of Valencia on the distant Mediterranean coast. Best of all are her
characterisations. The life of the sparkling and adventurous Gellhorn, before and after the Spanish civil war, is well drawn – although to describe her early writing as "chick-lit" strikes an incongruous note. Through her mother Edna, Gellhorn had become a friend of Eleanor Roosevelt and a frequent visitor to the White House. She had been a close friend, and maybe the lover, of HG Wells. Gellhorn already idolised Hemingway the writer when she bumped into him in Sloppy Joe's bar in Key West. Over the next months, she was seduced by his talent and the fact that he shared her determination to be part of the anti-fascist struggle in Spain. He was turned on by the sexual allure of a leggy blonde with the highest political and social connections – as Vaill comments: "Martha always moved easily between picket line and the receiving line."

Their relationship – which dominates the book – comes across as rather empty. Having made his conquest and boasted about it like a teenager, Hemingway preferred drinking with his cronies, and she didn't like sex. Vaill portrays Hemingway as dishonest and insecure, obsessed with friendship and loyalty and truth, yet as untrustworthy as a rattlesnake. She notes how in his writing he would respond to perceived slights by making the person's "fictional avatar do something or say something that he could legitimately despise ... leaving himself free to treat that person badly. Like a papal indulgence purchased in advance of the sin." Although some of the correspondents who travelled with Hemingway in the last months of the war regarded him as a brave and generous friend, here we have the pugnacious, malicious bully familiar from the classic biography by Carlos Baker. Vaill shows a Hemingway who liked to think of himself as a combatant. She might have relished the comment of the English brigadista Jason Gurney, who saw the writer as "full of hearty and bogus bonhomie. He sat himself down behind the bullet-proof shield of a machine-gun and loosed off a whole belt of ammunition in the general direction of the enemy. This provoked a mortar bombardment for which he did not stay."

Barea and Kulcsar met in the censorship office in Madrid, and played key roles in ensuring that truth prevailed over propaganda in the news about the struggle of the second republic against Franco and his Axis allies. Indeed, Barea was responsible for saving the photographs used in the posters immortalised by the slogan: "If you tolerate this, your children will be next." Vaill enriches Barea's autobiographical account with the backstory of Kulcsar's early life in the same Austrian communist cell as Stephen Spender and Kim Philby. This is all the more valuable since Kulcsar is the only one of the protagonists without a substantial biography.

Vaill is excellent throughout on her six protagonists, but elsewhere is undone by a lack of specialist knowledge. There is an underlying cold war tone about the book that echoes the oft-repeated myth that the Spanish Republic was the puppet of Moscow. Here it derives partly from her reliance on the false testimonies of two Soviet defectors: Alexander Orlov's The Secret History of Stalin's Crimes and Walter Krivitsky's I Was Stalin's Agent.

Vaill presents Krivitsky as former head of Soviet military intelligence in Spain, but recent research by Boris Volodarsky has revealed that Krivitsky was never in Spain and all the facts from his book were actually invented by his ghost writer, Isaac Don Levine. Orlov reinvented himself 18 years after his defection to justify his presence in the US, to fool the FBI and to write well-paid articles for Life magazine.

Accordingly, there is an excessively sinister light cast on the roles of Russians and on the Republic's security services. Inevitably, the Republic, like any wartime state, had an apparatus for counterespionage to root out saboteurs and fifth-columnists. In this context, Vaill makes much of the notorious case of José Robles, a friend of the novelist John Dos Passos. Robles was arrested, she tells us, by "extra-legal" police and later executed for allegedly passing information to his brother, a pro-Francoist army officer in the fifth column. Into the story comes the brother of the famous artist Luis Quintanilla. Vaill presents Pepe Quintanilla as "head of Madrid's secret police" and an executioner. She uses a series of sources – The Starched Blue Sky of Spain by the novelist Josephine Herbst, Hemingway's play The Fifth Column, Baker's biography of Hemingway – all of which, for different reasons, present an undeservedly hostile picture of him. Historical accuracy was not a priority for any of them. In her 1960 memoir, Herbst quoted Hemingway as telling her that Pepe was "head of the department of justice"; in act two...
of Hemingway's play, the character "Antonio" is presented as the "thin-lipped security chief". Then, assuming that "Antonio" was Pepe, Baker described him as "the thin-lipped executioner of Madrid".

Hemingway got this idea from a lunch with Pepe attended by himself, Herbst and the journalist Virginia Cowles. At that lunch, if we are to believe Cowles's account, Pepe gave a blood-curdling version of the fight against the fifth column, perhaps enjoying the impact he felt it was having on the two women. In fact, Pepe was head of neither the department of justice nor of republican counterespionage. He was not an executioner but an administrator. He certainly had access to inside information about the Robles case, but his real job was secretary to the real chief of the republican counterespionage services, who headed the so-called special brigades (not "extra-legal"), one of which arrested Robles.

There is an irony in Vaill's comment that "in her zeal to make a point, Martha made up facts to go with it". Vaill herself puts thoughts into her characters' heads and frequently "extrapolates" from fictional and other accounts as if they were documentary evidence. This leads to some striking insights but sends the curious reader to check the sources only to be driven back with heavy losses by the book's infuriating note system. More often than not it's a wild goose chase.

There are also many small factual mistakes such as placing Gibraltar 20 miles from Málaga (really more than 100) and presenting one of the most celebrated photographs of the war, by Agustí Centelles, as if it was taken in 1936. The photo was of a school bombed in Lleida on 2 November 1937 and portrays a woman weeping over the body of her dead husband. This book should be read for its sensitively told stories of three love affairs, but not for authoritative views on the Spanish civil war.

• Paul Preston's latest book is The Spanish Holocaust (HarperPress). To order Hotel Florida for £18.49 with free UK p&p call Guardian book service on 0330 333 6846 or go to guardianbookshop.co.uk.