Long-term relationships among pesticide applications, mobility, and soil erosion in a vineyard watershed

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Agricultural pesticide use has increased worldwide during the last several decades, but the long-term fate, storage, and transfer dynamics of pesticides in a changing environment are poorly understood. Many pesticides have been progressively banned, but in numerous cases, these molecules are stable and may persist in soils, sediments, and ice. Many studies have addressed the question of their possible remobilization as a result of global change. In this article, we present a retro-observation approach based on lake sediment records to monitor micropollutants and to evaluate the long-term succession and diffuse transfer of herbicides, fungicides, and insecticide treatments in a vineyard catchment in France. The sediment allows for a reliable reconstruction of past pesticide use through time, validated by the historical introduction, use, and banning of these organic and inorganic pesticides in local vineyards. Our results also revealed how changes in these practices affect storage conditions and, consequently, the pesticides' transfer dynamics. For example, the use of postemergence herbicides (glyphosate), which induce an increase in soil erosion, led to a release of a banned remnant pesticide (dichlorodiphenyltrichloroethane, DDT), which had been previously stored in vineyard soil, back into the environment. Management strategies of ecotoxicological risk would be well served by recognition of the diversity of compounds stored in various environmental sinks, such as agriculture soil, and their capability to become sources when environmental conditions change.

pesticides | glyphosate | DDT | lake sediment | soil erosion

Viticulture is an important type of agricultural land use in many countries, including France. During the last several decades, the use of many chemical substances to control disease, insect damage, and weed competition in vineyards, which was practiced with few studies examining the behavior of these substances in various environmental compartments, has become a primary focus of interest for the European Union (1, 2). France accounts for ∼30% of European consumption of pesticides and remains the region's leading consumer, with 20% of the nation's pesticides used in viticulture despite the fact that this sector represents only 3% of agricultural land (3).

It is now widely accepted that the routine use of pesticides (herbicides, fungicides, and insecticides) has adverse effects on the health of ecosystems and humans. Many of these substances are highly toxic and have been progressively banned as their toxicity has been proven. Many substances also are now subject to European regulation (4). Unfortunately, in many cases, these pesticides and/or their degradation products are stable molecules that may persist for several years, or even decades, in soils and sediments (5, 6), from which they can propagate into the environment through various dynamic processes (7, 8). In many vineyards, soil erosion, which is often intense as a result of both practices in sloping vineyards (e.g., tillage, herbicide applications) and the climate, has an important effect on the dispersion of pollutants into other environmental compartments (rivers, sediments, groundwater), where they may persist (9–12). Thus, there is a potentially complex interplay between pesticide dissemination, which, among other processes, increases soil erodibility, and soil erosion, which is influenced by pesticides but is also involved in the dynamics of pollutant dissemination. The long-term environmental fate of pesticides has rarely been studied (13), despite the chronology of the products and their direct and indirect interactions. With the aim of understanding these complex relationships, we used a retrospective approach based on well-constrained lake sediment stratigraphy to reconstruct the histories of both pesticide dynamics and soil erosion in a small-scale vineyard watershed that contains a small lake as a final sink for the erosion products.

Lake sediment cores have been used extensively to evaluate and reconstruct historical contaminant trends in aquatic environments in relation to human practices in watersheds (14–18). Vertical profiles of particular contaminants in sediment cores associated with high- resolution sedimentologic and geochemical proxies provide a precise chronology of the long-term evolution of contaminant dynamics in watersheds. In this study, we were able to reconstruct the complex, long-term succession of pesticide applications (herbicides, fungicides, and insecticides) in a watershed. Independently, we reconstructed erosion patterns

Significance

A record of lake sediment spanning approximately 100 years allowed us to reconstruct the long-term succession of herbicide, fungicide, and insecticide treatments in a vineyard catchment in France. This record of pesticide deposition is consistent with the historical onset and banning of these chemical substances by French and European environmental agencies. We also present evidence of the effects of postemergence herbicides, such as glyphosate, on soil erosion and evidence of the release of banned remnant pesticides, such as dichlorodiphenyltrichloroethane (DDT), that are stored in vineyard soil back into the environment. These results indicate that the sink–source dynamics of pesticides, which are crucial in ecotoxicological risk assessment, should take into account the effects of a changing environment on pesticide storage.

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in the same watershed, using geochemical proxies to investigate the potential relationships.

Our study focused on Lake Saint André, which is located in eastern France (45° 29′ 37″ N, 5° 59′ 10″ E) at an elevation of 295 m above sea level. Lake Saint André is a 350-m long by 250-m wide low-altitude lake located in the French Alps 10 km south of the city of Chambéry (Fig. 1). This lake was formed in A.D. 1248 after the Mount Granier landslide caused a 3.5×10^8 m^3 limestone cliff collapse and a gravity slide involving the Valanginian marls in the lower part of the cliff (19, 20). The Lake Saint André watershed is relatively small, with a surface area of 48.5 ha, including 17.4 ha of vineyard in 2009. The vineyards make up 36% of the watershed and drain only this landslide deposit (Fig. 1). This land use has been relatively constant since the beginning of World War II (WWII), although it has slowly and constantly decreased in size until the present day. The area of vineyard land use measured 21.5 ha in 1939, 19.3 ha in 1956, 18.8 ha in 1970, and 18.9 ha in 1990. Lake Saint André is deeper in its northern part, where the maximum water depth is 12 m and from which sediment cores were retrieved (Fig. 1).

Results and Discussion

Lake Sediment. The lake-bottom sediment cores were characterized in terms of their color, grain size, loss on ignition (LOI), and sedimentary structure. The upper 41 cm consists of olive-gray silty clay with constant fractions of carbonate (30%) and organic content (7.5%) (Fig. 2*B*). The grain size distribution of this upper sequence is homogeneous [median (D50) = 12.7 ± 1.8 μm] and exhibits two main populations centered at 0.3 μm (carbonate fraction) and 14 μm (Fig. 2*A*).

The levels of major and trace elements were measured using an X-ray fluorescence (XRF) core scanner (Avaatech) and were subjected to principal component analysis (PCA; Fig. S1) to constrain sediment end-members (21). This PCA of the bulk sediment resulted in the identification of four geochemical end-members: (*i*) Al, Si, K, Fe, Ti, Rb, Ba, and Zr, which are related to terrigenous input from the watershed (aluminosilicates and heavy minerals present in marls); (*ii*) Ca and Sr, which are linked to the carbonate productivity in the lake; (*iii*) S and Mn, which are related to the lake's oxidation state; and (*iv*) a Cu source that may be correlated with periods of significant vineyard-related activities in the watershed, during which a blend of copper sulfate and calcium hydroxide (Bordeaux mixture) was sprayed as a fungicide.

A chronological framework was established via measurements of short-lived radionuclides (22, 23). A logarithmic plot of ($^{210}Pb_{ex}$) activity (Fig. 2*C*) shows a general decrease with three distinct linear trends. According to the "constant flux, constant sedimentation rate" (CFCS) model (22, 24), as applied to each part of the profile, the levels of ^{210}Pb indicate mean accumulation rates of 2.9 ± 0.2 $mm \cdot y^{-1}$ between depths of 41 and 26.5 cm, 5.2 ± 0.6 $mm \cdot y^{-1}$ between 26.5 and 17 cm, and 8.7 ± 1.3 $mm \cdot y^{-1}$ in the upper 17 cm of the core (Fig. 2*C*). The plot of ^{137}Cs data (Fig. 2*D*) displays a peak at a depth of 29.5 ± 1 cm, which apparently correlates with the maximum atmospheric production of ^{137}Cs in 1963 (25). This temporal correlation is supported by the ^{241}Am peak at the same depth, which was a result of the decay of ^{241}Pu in fallout from atmospheric nuclear weapons tests (26). In the upper part of this core, at a depth of 20.5 ± 0.5 cm, a second ^{137}Cs peak corresponds to the time of the Chernobyl accident in 1986 (Fig. 2*D*). The good agreement between the ages derived from the $^{210}Pb_{ex}$-CFCS model, and the artificial radionuclide peaks provide a well-constrained, continuous age–depth relationship (Fig. 2*E*) within the sediment sequence, with two primary sedimentation rate changes in ~1973 ± 5 y and 1994 ± 2.5 y.

Sediment Chronology of Pesticides Use. No significant variations in the grain size distribution or the organic content were observed during the last century. Thus, these two parameters could not have affected the absorption/degradation of pesticides in this sediment sequence (27). On the basis of the age–depth relationship, the down core variations in pesticides were presented in relation to the age and expressed in flux ($ng \cdot cm^{-2} \cdot y^{-1}$) (Fig. 3). Historical vineyard practices were obtained through a survey of winemakers and agricultural technicians working in the study area. Three herbicides (or their metabolites) were identified in

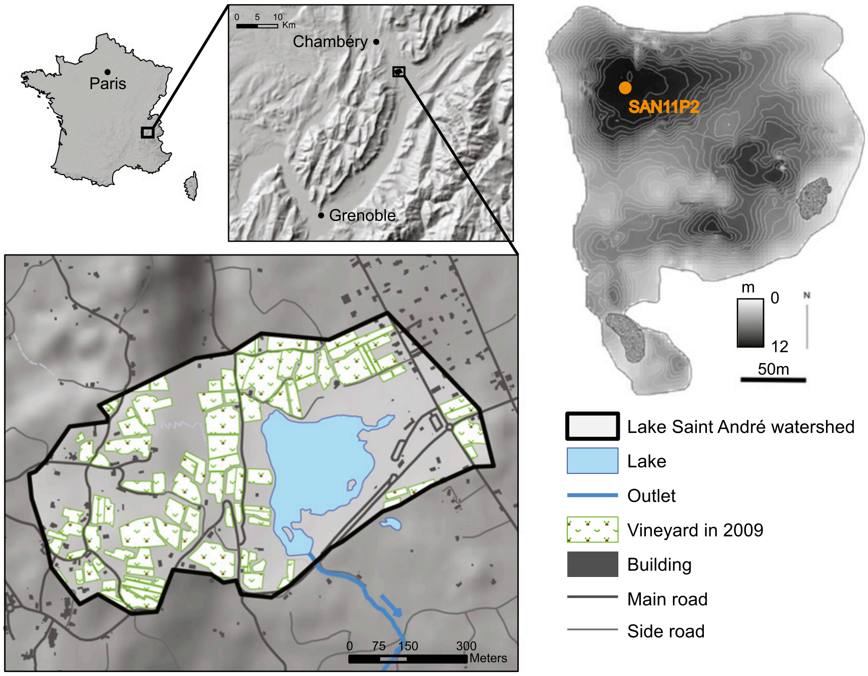

Fig. 1. The Lake Saint André watershed and the vineyards in 2009 (interpreted from aerial photographs), as well as the bathymetric map with the location of core SAN11P2 retrieved from the deeper part of the lake.

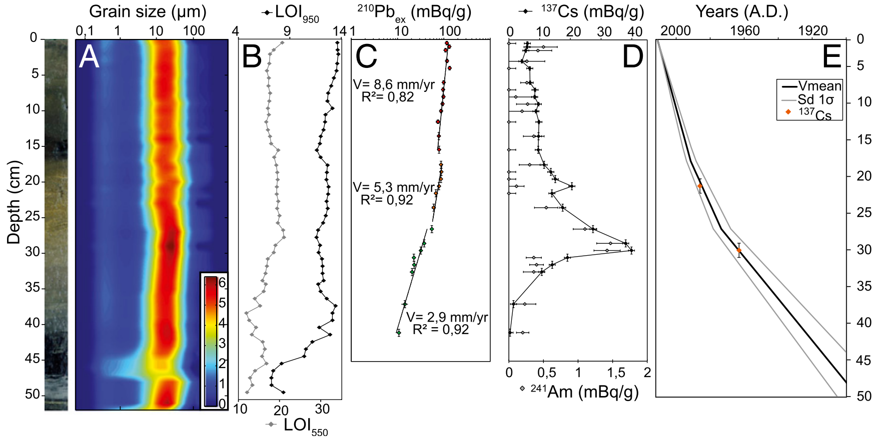

Fig. 2. Data from core SANP2. From left to right: (*A*) photograph and grain size contour plot with two primary populations centered at 0.3 and 14 µm, (*B*) LOI at 550 °C (organic matter) and 950 °C (carbonates), (*C*) ^{210}Pb$_{ex}$ activity, (*D*) ^{137}Cs activity, and (*E*) the age model.

the Lake Saint André sediment (Fig. 3*A*): AMPA [a metabolite of glyphosate, a main ingredient in Roundup (Monsanto)], which is used as a nonselective postemergence herbicide; deisopropyl atrazine (a metabolite of triazine herbicides, such as atrazine and simazine); and diflufenican [a main ingredient in Buffalo (Bayer)], which is used as a preemergence herbicide. Monsanto introduced glyphosate into the market in the 1970s, but it has been used widely and increasingly more often only since the early 1990s. High levels of AMPA were found in the core representing deposition during the previous 20 y, with a primary increase since 1990. AMPA is also present in low but significant concentrations before this period, most likely because of contamination of the deeper part of the core by downward smearing of the very high concentrations found in the upper layers. The metabolite of atrazine, which was used at the end of the 1950s and was banned in 2003, was observed in a sample that dates to the period between 1960 and 1970. Diflufenican, which was introduced at the end of 1990s and is still allowed, was identified in the sediments deposited beginning in 2005.

Three fungicides were identified in the core and at various concentrations with depth (Fig. 3*B*). Higher fluxes of captan [e.g., Sigma (Arysta LifeScience)], which was introduced in the early 1950s, and dimethomorph [e.g., Acrobat and Forum (BASF Agro)], which was introduced in the early 1990s, were observed in the samples representing the periods between 1960 and 2005 and after 1990, respectively. Both of these fungicides were used to combat mildew in vineyards, and both are still allowed. Pyrimethanil (e.g., Scala and Toucan), which was introduced during the 1990s and is used to treat the Botrytis fungi ("pourriture grise") in grapes, was identified in the sediments dating to the period between 2000 and 2008. Metals are also currently used against fungi in vineyards: Cu in the Bordeaux mixture is used as an antimildew and powdery mildew treatment, and Zn in mancozeb [$(C_4H_6MnN_2S_4)x(Zn)y$] is primarily used against black rot (caused by *Guignardia bidwellii* fungi). Because Cu and Zn are metals, they may accumulate in vineyard soil, and long-term applications have led to elevated concentrations (1). Thus, we can use certain geochemical ratios (i.e., metals/terrigenous elements) to quantify the amounts of these fungicides. Rubidium was selected as a background metal tracer because it can be attributed to the terrigenous input from the watershed (Fig. S1), it is associated with the thinner sediment particles (clay minerals) with greater specific surface areas for metal adsorption, and it is readily measured using the XRF core scanner. We therefore used the Cu/Rb ratio as a proxy for the Bordeaux mixture and the Zn/Rb ratio as a proxy for mancozeb. The Cu/Rb ratio (Fig. S2) displays a constant increase dating from 1900 and a marked increase at the end of WWII. This trend is consistent with the historic use of the Bordeaux mixture beginning at the end of the 19th century and its widespread use after WWII. The Zn/Rb ratio increased after 1965, with 2 primary peaks in ~1980 and 2010 separated by low values in ~1995. Mancozeb was first marketed in the early 1960s.

Four insecticides were identified in the sediment: dicofol, bromopropylate (e.g., Néoron), bifenthrin (Fig. 3*C*), and DDT (dichlorodiphenyltrichloroethane) and its metabolites [DDD (dichlorodiphenyldichloroethane) and DDE (dichlorodiphenyldichloroethene)] (Fig. 3*D*). Insecticides used in vineyard treatments against tetranychid and eriophyid mites were present in the post-1940 sediments. The level of dicofol increased in 1970 and exhibited peaks in ~1970, 1992, and 2000. The level of bromopropylate increased in 1985 and exhibited a primary peak in ~1998, and the level of bifenthrin increased in 1994. These three insecticides were not detected or were present at very low levels in the youngest part of this core, and their earliest appearances in the sediment are consistent with their introductions into the environment. The ΣDDT profile displays a complex trend, with a first appearance between 1910 and 1920, a small peak in 1970, and a more prominent peak during the 1990s. DDT was first used in agriculture after WWII, and it was banned in 1972. Thus, the ΣDDT record does not correlate well with the known history of this insecticide. The apparent pre-WWII appearance of this compound may be explained by its possible diffusive behavior in the lake sediment: Others (28) have found, by computer simulation, that this compound diffuses at a rate of 10^{-8} $cm^2 \cdot s^{-1}$, which could fully explain this earlier appearance. The 1970 peak may be related to the timing of maximum use of this insecticide (29, 30). The decreasing trend of ΣDDT after this date reflects the banning of DDT. A later peak during the 1990s cannot be attributed to the agricultural application of DDT but, rather, is most likely a result of the reworking of old sources of contamination, which is supported by high concentrations of DDT metabolites (high DDE/DDT ratio; Fig. 3*D*) in this upper part of the sediment core. The ratio of DDD/DDE is an indicator of the degradation pathways of DDT because DDE and DDD are, respectively, the aerobic and anaerobic degradation products of DDT (31). Thus, the first peak in ΣDDT levels corresponds to a high DDD/DDE ratio, indicating that degradation under anaerobic conditions most likely occurred in situ in the lake sediment after its maximum use around 1970, whereas the low DDD/DDE ratio corresponding to the second peak indicates that degradation of the precursor DDT was prevalent under the aerobic conditions operating on this

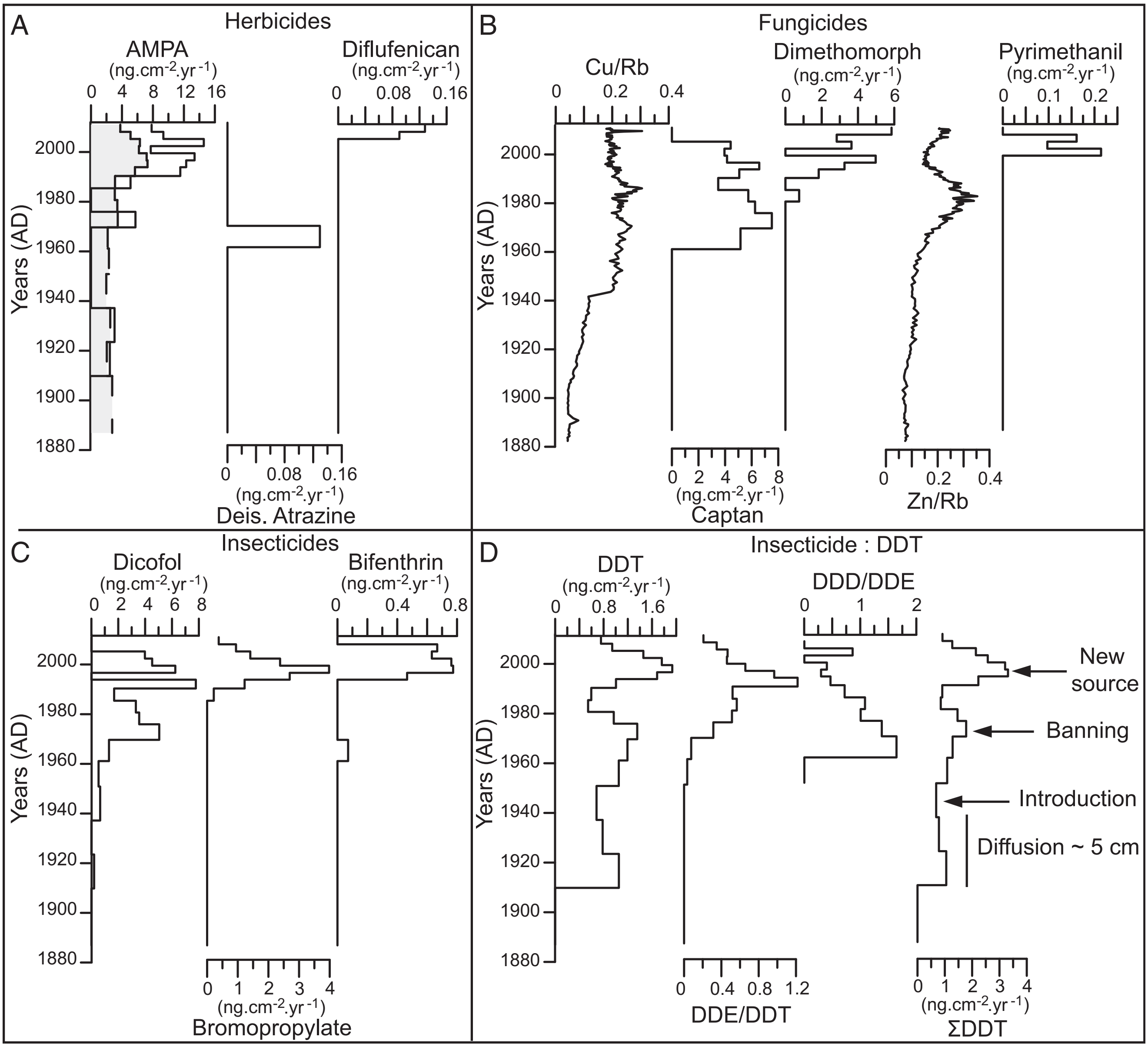

Fig. 3. Chronological variations in pesticide fluxes. (*A*) Herbicides: AMPA, deisopropyl atrazine, and diflufenican; (*B*) fungicides: Bordeaux mixture (Cu/Rb), captan, dimethomorph, mancozeb (Zn/Rb), and pyrimethanil; (*C*) insecticides: dicofol, bromopropylate, and bifenthrin; (*D*) DDT and metabolites: DDT, DDE/DDT, DDD/DDE, and ΣDDT. The gray area in the AMPA profile denotes the lower detection limit for this compound.

secondary source of DDT (e.g., in subaerial soil), and these compounds were then remobilized before their deposition on the lake bottom (32).

This chronology of pesticide (herbicides, fungicides, insecticides) use, which was reconstructed from high-resolution lake sediment analysis and validated by the historical introduction and application of these compounds in vineyards, makes it possible to apply a wide range of methods to the reconstruction and evaluation of the long-term effects of agricultural practices on the transport and fate of chemical contaminants in the environment.

Herbicides and Soil Erosion. We observed three changes in the sedimentation rate (Fig. 2) in this sediment sequence, which display a general increase in the terrigenous flux into the lake, going from ~0.9 $g{\cdot}cm^{-2}{\cdot}y^{-1}$ (1900–1972) to 1.7 $g{\cdot}cm^{-2}{\cdot}y^{-1}$ (1973–1993), and then to as much as 3.4 $g{\cdot}cm^{-2}{\cdot}y^{-1}$ (1994–2005). A drastic decrease was then observed during the following years (Fig. 4). These variations in the terrigenous sediment supply from the watershed may be directly attributed to soil erosion via vineyard practices. In the early 1970s, the local use of heavy farm machinery (12), which is known to contribute to soil erosion (11) and is associated with the first application of preemergence herbicides (Atrazine metabolite) to combat grass between the rows of vines, may have induced the first increase of terrigenous flux into the lake (Fig. 4). In 1990, we observed synchronous increases in AMPA, ΣDDT (with a low DDD/DDE ratio), and terrigenous soil fluxes into the lake (Fig. 4). In the early 1990s, applications of postemergence herbicides increased widely, including the use of Roundup, as indicated by the high flux of AMPA dating from this period (Fig. 4). It has been demonstrated that application of this chemical has a strong effect on soil erosion, as it acts on grass development and leads to permanently bare soil (12). Moreover, this high flux of sediment supply to the lake is synchronous with the reemergence of

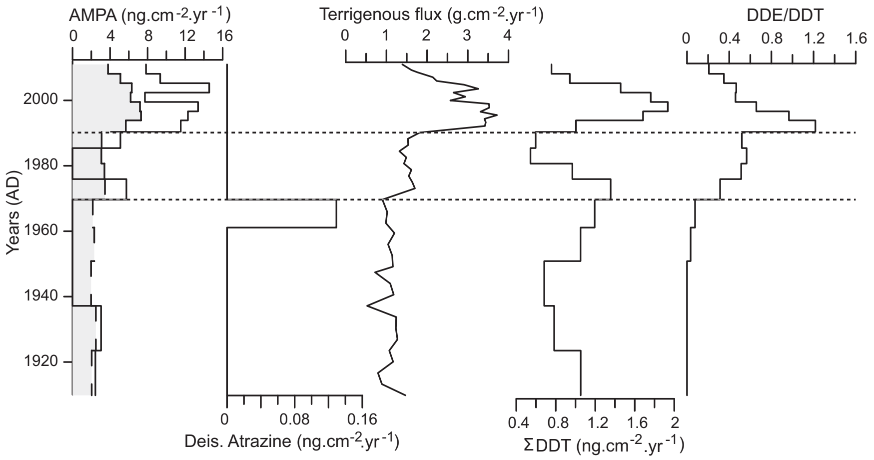

Fig. 4. Chronological variation in levels of AMPA, deisopropyl atrazine, subaerial flux, and sum of DDT and DDE/DDT. The horizontal dotted lines denote the two primary changes in the sedimentation rate.

banned pesticides, such as DDT and its aerobic metabolites (DDE), which were most likely stored in the vineyard and other agricultural soils in the watershed (33, 34) and subsequently remobilized by the herbicide-triggered rise in soil erosion. Several studies of similar environmental situations (proglacial lakes) also resulted in the identification of a second peak in the levels of DDT and its metabolites in lake sediments in the 1990s, which is more than 20 y after the chemical's prohibition. This delayed contamination was correlated with old pesticides stored in the ice cap and released by the recent retreat of glaciers (35, 36). In the context of agricultural watersheds, pollutants stored in soil have rarely been taken into consideration (37). In this study, we demonstrate for the first time to our knowledge that the recent widespread use of herbicides (glyphosate) induced an important release and reemergence of contaminants into the environment 20 y after their use was banned. The soils underwent a change in storage conditions, converting from sinks to sources of pesticides. The decrease in pesticide concentrations during the most recent years (Figs. 3 and 4) may be attributed to French and European regulations controlling the use of micropollutants in agriculture.

In summary, our study demonstrates the possibility of reconstructing the use of various pesticides (herbicides, fungicides, insecticides) in an agricultural watershed over the last century, using sedimentary archives. The dates of first use and prohibition of products used to control pests in vineyards and the changes in the soil erosion flux are recorded in the lake sediments. This work demonstrates that this high-resolution analysis of lake sediment allowed us both to reconstruct past agricultural practices in this watershed and to precisely determine the 100-y-long dynamics of chemicals (organic and inorganic) used in vineyards. In particular, this study highlights the effects of postemergence herbicides (glyphosate) on soil erosion and the remobilization of banned remnant pesticides (DDT) stored in vineyard soil. Thus, any study of the environmental fates of pesticides should take into account these potential pesticide–environment interactions.

In light of this study, it appears crucial that ecotoxicological risk assessment and the management of new agricultural practices take into account such mechanisms of pesticide mobility in the environment (38, 39).

Materials and Methods

Logging. Three 1-m-long cores [registered in the International Geo Sample Number (IGSN)/System for Earth Sample Registration Database (www.geosamples.org) as SAN11P1 (IGSN: EDYSAN004), SAN11P2 (IGSN: EDYSAN001), and SAN11P3 (IGSN: EDYSAN007)] were collected from Lake Saint André in December 2011 (Fig. 1), using an Uwitec gravity corer (Environnement, Dynamique et Territoires de Montagne). In the laboratory, the cores were split, photographed, and logged in detail, noting all physical sedimentary structures and the vertical succession of facies. The sediment colors were determined, with a spatial resolution of 5 mm, using a Minolta CM 2600d. The spectra span wavelengths between 400 and 700 nm (31 channels). The total reflectance (L*) parameter was used to confirm the visual lithological description. The grain size distributions of core SAN11P2 were determined using a Malvern Mastersizer S (Environnement, Dynamique et Territoires de Montagne) at a continuous interval of 1 cm. After inserting the bulk sediment into the fluid module of the granulometer, ultrasound was applied to minimize particle flocculation. Core SAN11P2 was also sampled at 1-cm steps and dried at 60 °C over the course of 4 d to obtain its dry bulk density, and then the LOI of each 1-cm interval was measured using the protocol of Heiri (40). The LOI at 550 °C and 950 °C corresponds to the organic and carbonate components of the sediment, respectively. The XRF analysis was performed on the surfaces of the split sediment SAN11P3 core at 2-mm intervals, using a nondestructive Avaatech core-scanner (Environnement, Dynamique et Territoires de Montagne, at the Université de Savoie) on the upper 50 cm. The split core surface was first covered with 4-μm-thick Ultralene to avoid contamination of the XRF measurement unit and desiccation of the sediment. The geochemical data were obtained at various tube settings: 10 kV at 1.5 mA for Al, Si, S, K, Ca, Ti, Mn, and Fe; 30 kV at 1 mA for Cu, Zn, Br, Sr, Rb, Zr, and Pb; and 50 kV at 2 mA for Ba (41). Each individual power spectrum was converted through a deconvolution process into relative components (intensities), expressed in counts per second. The PCA was performed using "R" software.

Dating. The ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{228}Th, ^{234}Th, ^{241}Am, ^{137}Cs, ^{7}Be, and ^{40}K activities of the samples were analyzed using well-type, germanium detectors placed at the Laboratoire Souterrain de Modane, which is located under 1,700 m of rock. The reduction of the crystal background was obtained by the selection of low-activity materials and the suppression of cosmic radiation and by placing the detectors in the Laboratoire Souterrain de Modane (42). At the same time, the detector sensitivity allows for the reduction of the sample mass required for a measurement. These improvements allowed for the measurement of both very low radioactivity levels (with background levels of less than 0.6 cpm in the 30–3,000 keV energy range) and small sample weights (1 g). The levels of ^{226}Ra activity were determined using its short-lived daughters ^{214}Pb (295- and 352-keV peaks) and ^{214}Bi (609-keV peak), assuming secular equilibrium with ^{226}Ra. The ^{238}U activities in the sample were determined by measuring its ^{234}Th daughter peak (63.2 keV). The ^{40}K level was measured by way of its gamma emissions at 1,460 keV, whereas the ^{228}Th and ^{228}Ra levels were measured using the gamma-rays emitted by their short-lived descendants: ^{212}Pb (238 keV) and ^{208}Tl (583 keV) for ^{228}Th and ^{228}Ac (338, 911, and 970 keV) for ^{228}Ra. ^{210}Pb (22.3 y), ^{241}Am (432.2 y), ^{7}Be (53.4 d), and ^{137}Cs (30.2 y) activity levels were directly measured by way of their gamma emissions at 46.5, 60, 477, and 662 keV, respectively. In general, counting times of 24–48 h were required to reach a statistical error of less than 10% for excess ^{210}Pb in the deepest samples and for the 1963 ^{137}Cs peaks. In each sample of core SAN11P2, the (^{210}Pb unsupported) excess activities were calculated by subtracting the (^{226}Ra-supported) activity from the total (^{210}Pb) activity.

Pesticide Analysis. Pesticides were analyzed on cores SAN11P1 and SAN11P2 by the CARSO-Laboratoire Santé Environement laboratory, Lyon, France (www.groupecarso.com), which is COFRAC (Comité français d'accréditation)-accredited (1-1531). Two hundred eighty-two compounds were searched, compounds were searched, using three runs: solid dried and sieved sample was extracted with dichloromethane by an accelerated solvent extractor (ASE) system and then concentrated and analyzed by GC/MS in accordance with AFNOR standard XP ×33-012 (205 pesticides searched); solid dried and sieved sample was extracted with dichloromethane by an ASE system and analyzed by high-performance liquid chromatography (HPLC) with diode-array detection in accordance with a certified inner standard method (75 pesticides search); and solid dried and sieved sample was extracted with water and evaporated and analyzed by HPLC, using postderivatization in accordance with a certified inner standard method for glyphosate and AMPA.

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