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SEDIMENTARY PIGMENTS AND RECENT PRIMARY
PRODUCTIVITY IN NORTHERN ITALIAN LAKES

Abstract

Spectrophotometrically measured chlorophyll degradation products and carotenoids are reported from 90 cm long sediment cores from 4 northern Italian lakes, some of which have well documented histories. Sedimentation rates are very high in 3 of these lakes, and the cores represent sediments accumulated within the past century or less except probably in Lake Orta. Superficial sediments from two other lakes also were analyzed. The pigment data were analyzed in relation to sedimentary calcium carbonate, phosphorus and organic matter, general lake history, and contemporary primary productivity. A good correlation existed between 0-10 cm sediment depth pigment concentrations per unit organic matter and recent primary productivity.

INTRODUCTION.

Spectrophotometric analyses of plant pigments in sediment cores from lakes have been used to obtain ecological information in assessing lake history and past production (Vallentyne, 1955; Gorham, 1961; Fogg and Belcher, 1961; Belcher and Fogg, 1964; Czezuga, 1965; Wetzel, 1970; Sanger and Gorham, 1972a; Gorham and Sanger, 1976; Adams and Duthie, 1976). Gorham (1960) related concentrations of chlorophyll derivatives in profundal surface sediments to present-day trophic status of lakes in England, and Gorham, Lund, Sanger and Dean (1974) have correlated algal standing crops with concentrations of carotenoids and chlorophyll derivatives.

Wetzel (1970) used pigment concentrations to quantify recent and post-glacial production rates of Pretty Lake, a marl lake in northwestern Indiana. Changes in pigment products were related to the history of the lake's productivity and to environmental factors that

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would be expected to affect rates of deposition and preservation of pigments. Wetzel's data provided further evidence for the usefulness of the sedimentary pigment analyses in back-calculation of primary production through the post-glacial period from current production rates.

Sedimentary pigments also have been used in studies to partition autochthonous from allochthonous sources of organic matter in lake sediments (Gorham, 1960; Gorham and Sanger, 1967, 1975; Sanger and Gorham, 1970). Eutrophic lakes have sedimentary pigment concentrations much greater than the concentrations in terrestrial litter and humus (Gorham and Sanger, 1967), and the ratios of chlorophyll derivatives to carotenoids in sediments are lower where autochthonous production of organic matter is dominant over allochthonous sources (Gorham and Sanger, 1967; Sanger and Gorham, 1972a, 1972b). Further discussion of the use of sedimentary pigments to assess lake history, primary production and autochthonous vs. allochthonous production is reviewed by Sanger and Gorham (1972a).

Light, temperature, and oxygen probably are very important in affecting pigment compositional changes with time. The effects of environmental factors on pigment changes are reviewed extensively by Moss (1968) and Wetzel (1970).

Daley, Brown and McNeely (1977), and Brown, Daley and McNeely (1977) have questioned spectrophotometrically measured sedimentary chlorophyll degradation products (SCDP) as paleoecological indicators. Daley, Brown and McNeely (1977) discussed evidence that SCDP, earlier thought to be dominated by pheophytins, in some lakes consist of many pigment derivatives. These derivatives have different absorption maxima and extinction coefficients. At least 16 well characterized a and b phorbins were found in meromictic Little Round Lake, Ontario (Brown, Daley and McNeely, 1977). Such compounds were identified by chromatographic fractionation of the phorbin extract. Daley, Brown and McNeely (1977) tentatively concluded that the spectrophotometric SCDP procedure provides a variable overestimation of the phorbin content in Little Round Lake. They concluded that probable sources of error include variations in the composition of the \( a \) and \( b \) phorbins or interference by contaminants in the 90% acetone extracts that are commonly used in the analyses.

In this paper we report exclusively on data obtained by spectrophotometric SCDP analyses of sedimentary pigments. Somewhat different conclusions might be reached with the use of the slower, direct fractionation techniques, used by Brown, Daley and McNeely (1977) and Daley, Brown and McNeely (1977).

A number of Italian subalpine lakes cover a range of trophic states and relative size of drainage basins, and, thus, provide an opportunity to examine some aspects of the applications of spectrophotometric sedimentary pigment analyses to the study of ecological lake history and to the comparison of present day production rates among the
lakes. We selected six lakes within Lombardia and Piemonte, including two large lakes (Maggiore and Orta) and four smaller ones (Monate, Montorfano, Mergozzo and Varese).

Our study of the Italian lakes was designed with 3 purposes in mind:

1) To determine if a correlation exists between current levels of primary production in the lakes and concentration of plant pigments in the surface sediments.

2) To determine depth-correlated changes in sedimentary pigments products (SCDP and carotenoids) from short (0.8 to 1 m) cores from the profundal of several lakes which show differences in current levels of primary production and to examine the differences in relation to expected levels of production from the recent past.

3) To examine a possible relationship between phosphorus and pigment concentrations in the cores. Because phosphorus is commonly a factor limiting production of phytoplankton, we expected to see a correlation between phosphorus and pigment concentrations, both calculated on an organic weight basis.

In addition, from three other lakes (Alserio, Pusiano and Segri-no) short cores in the littoral zones (depth ca. 1 m) were analyzed for pigment concentration to be compared with pelagial primary production.

**STUDY SITES.**

The oligomictic Lake Maggiore is undergoing eutrophication, but the hypolimnion is always oxygenated to 50-60 per cent saturation (Bonomi, Calderoni and Mosello, 1978). Lake Mergozzo, since 1969-1970, has developed in the deeper water near of anoxic conditions (65-70 m) during 2 summer months (Zutshi, 1976; Calderoni, Mosello and Tartari, 1978). The benthic animals also indicated eutrophic conditions; no benthic animals were found at the deepest (70 m) point (Ruggiu and Saraceni, 1972). Later work (Ruggiu et al., paper in preparation) suggested that by 1975 the lake had become less eutrophic with respect to water chemistry and primary productivity than a few years earlier. By 1956, Lake Varese was considered eutrophic on the basis of apparent high primary production and the species of benthic animals present (Bonomi, 1962; Tonolli, 1965). Summer anoxia below 7 m has been demonstrated since 1963. In isothermal conditions of winter dissolved oxygen (D.O.) can be as low as 1.3% of saturation (Turati, 1970). Little information is available for Lake Monate. It appears that hypolimnetic D.O. is always present, although it can be low during summer (de Bernardi, Giussani and Mosello, research in progress). D.O. is always present in Lake Montorfano (De Paolis, Gaggino and Gerletti, 1977). Lake Orta has near zero D.O. from September to January below the 50 m depth (Bonacina, 1970).
These lakes differ considerably in primary production with Lake Varese being the most and Lake Montorfano the least productive of the six lakes. Although Lake Orta is now intermediate in productivity, it was once almost devoid of life due to severe copper and ammonia pollution beginning in 1927 (Monti, 1930; Baldi, 1949; Corbella, Tonolli and Tonolli, 1958; Bonacina, 1970). As of 1971 and 1972 the plankton consisted of one copepod (Cyclops strenus), a few species of Rotifera, two species of bluegreen algae, one green alga and a few species of diatoms. The pH of the hypolimnion is very acidic, usually about 4.5 (Bonacina, Bonomi and Ruggiu, 1975).

MATERIALS AND METHODS

One quick-frozen sample was collected from near the deepest part of each of four northern Italian lakes (cf. Table 1). The sampler, a crust freezer designed after Swain and Peterson (in press), was a 2 m-long aluminium tube 58 mm in diameter fitted with a pointed brass head on one end and a finned steel cap on the other. Lead weights were added, and the sampler filled with dry ice and ethanol. The steel cap had a small hole in it to release pressure. With a cable attached, the sampler was allowed to free-fall from a boat to the sediment, with penetration of 80-100 cm. After eight minutes the sampler was recovered, with a crust of sediment 1-3 cm thick. Every 10 cm section of crust was removed, washed and frozen until analysis. Hereafter, we refer to these frozen crust samples as cores. Due to equipment problems, the crust freezer was not used for Lake Maggiore; instead, a surface sediment sample was taken (at a depth of 344 m in front of Ghiffa) with a dredge. The core we took from Lake Mergozzo was potentially the most interesting, in that it was laminated very distinctively. However, we could not use data from the Mergozzo core in our analysis because it appeared we had not successfully frozen the sediment-water interface on the corer. We subsequently obtained a surface sediment sample from the profundal of Mergozzo

Table 1 - Some morphometric characteristics for the six sampling stations.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Surface (Km²)</th>
<th>Volume (Km³)</th>
<th>Area of drainage basin (Km²)*</th>
<th>Depth where cored (m)</th>
<th>Max. depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Varese</td>
<td>14.9</td>
<td>0.162</td>
<td>111.0</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>Maggiore</td>
<td>212.2</td>
<td>37.100</td>
<td>6599</td>
<td>344</td>
<td>370</td>
</tr>
<tr>
<td>Montorfano</td>
<td>0.5</td>
<td>0.002</td>
<td>1.94</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Mergozzo</td>
<td>1.8</td>
<td>0.089</td>
<td>10.5</td>
<td>70</td>
<td>74</td>
</tr>
<tr>
<td>Monate</td>
<td>2.5</td>
<td>0.045</td>
<td>5.75</td>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td>Orta</td>
<td>18.1</td>
<td>1.3</td>
<td>116</td>
<td>100</td>
<td>143</td>
</tr>
</tbody>
</table>

* Included lake surface

(1) Dredge sample only from Maggiore
with a Jenkin corer, to use in the regression of contemporary lake primary productivity against surface sedimentary pigment concentrations.

Pigments were analyzed generally following Vallentyne (1955) as slightly modified by Wetzel (1970). We followed Wetzel’s procedure of acetone extraction except that we used a Beckman 25 spectrophotometer instead of a Beckman DK-2A and cell lengths of 10 mm and 40 mm instead of 10, 50, and 100 mm. Absorption data were expressed on the basis of a 10 mm pathlength. We defined sedimentary pigment degradation units in the same way as Wetzel, as a function of the optical density (O.D.) at the wavelength of maximum absorption in the red end of the spectrum (SPDU_{661}). A pigment index due to carotenoids and phaeopigments was calculated similarly from the adsorption peak at 411 nm (SPDU_{411}). The peak near 411 nm is probably not as useful as the 661 nm peak, when acetone extracts only are used. The peak near 410 or 411 nm may be due more to pheophtyins than to carotenoids, and other organics probably affect the 410-411 nm peak considerably in some uses (Gorham, personal communication).

In calculation of the absorption peak near 661 nm we determined absorption from a baseline, prepared with a French curve, between absorption at 550 nm and 750 nm (Orr and Grady, 1957). The baseline-corrected 661 nm absorption peak is generally used to represent an index of sedimentary chlorophyll degradation products (SCDP), although some investigators have used curves not corrected to a baseline. Wetzel (1970) corrected against absorption at 750 nm.

Dry weights, organic matter, and calcium carbonate (CaCO₃) were determined as by Wetzel (1970), except that we used samples of 0.1 mg instead of 0.03 mg. Repeatability of the measurements was good. For six replicates from a very wet Varese 0-10 cm sample (dry weight 7.75% of wet weight) where error could be relatively high, standard errors expressed as a percent of the mean were as follows: dry weight as % of wet, 0.26; organic weight as % of wet, 2.42; organic weight as % of dry, 1.90; CaCO₃ as % of dry, 0.47.

For six replicated samples from Mergozzo surface sediment sample (dry weight 6.33% of wet weight), standard errors as % of the mean for baseline corrected spectrophotometric analyses were O.D. at 661/g dry wt., ± 0.69%; O.D. at 661/g organic, ± 0.65%; O.D. at 411/g dry, ± 0.50%; O.D. at 411/g organic ± 0.52%.

Sediment phosphorus levels were determined after extracting phosphorus by the Mehta, Legg, Goring and Black (1954) method. Approximately 0.6 g dry weight equivalent of wet sediment were used for each sample. The extracts were treated by persulfate digestion and then analyzed for reactive phosphorus after Murphy and Riley (1962). The analysis of the Mehta extracts for total phosphorus gives results about 95% of those obtained from more rigorous sample treatment (Sommers, Harris, Williams, Armstrong and Syers, 1970).
RESULTS AND DISCUSSION.

Correlation of sedimentary surface pigment concentrations and contemporary primary productivity.

From the summarized data on primary productivity and surface sedimentary pigment concentrations (Table 2), a number of linear correlations were tested (Table 3). The data are for surface sediments which were obtained from near the deepest points of six lakes (Montorfano, Mergozzo, Varese, Orta, Maggiore and Monate) for which various primary productivity data were available from other sources.

Ratios of pelagial phytoplanktonic photosynthesis for use in regression against sedimentary pigment concentrations were taken from the literature, using data from Rodhe (1965) for Lake Varese, Ruggiu and Saraceni (1977) for Lake Maggiore, Zutshi (1976) and Ruggiu et al., (paper in preparation) for Lake Mergozzo, Chiaudani (1977) for Montorfano, and Gerletti and Melchiorri Santolini (1968) for Lake Monate. The value for Orta was calculated by Carlo Saraceni with the Gächter (1972) method applied to the data of Vollenweider (1963). The Gächter method of calculation requires 4 hour measurements primary production per day instead of the 6 hour mea-

<table>
<thead>
<tr>
<th>Lake</th>
<th>Primary productivity (mg C·m⁻²·d⁻¹)</th>
<th>% Amax</th>
<th>Surface SPDUₘᵣ/g org. wt.</th>
<th>Surface SPDUₘᵣ/g org. wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Varese</td>
<td>1660(1)</td>
<td>0.22</td>
<td>579</td>
<td>2083</td>
</tr>
<tr>
<td>Maggiore</td>
<td>320(2)</td>
<td>0.13</td>
<td>50</td>
<td>278</td>
</tr>
<tr>
<td></td>
<td>790(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>888(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>x=656</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montorfano</td>
<td>333(5)</td>
<td>0.32</td>
<td>105</td>
<td>346</td>
</tr>
<tr>
<td>Mergozzo</td>
<td>934(6)</td>
<td>0.11</td>
<td>233</td>
<td>916</td>
</tr>
<tr>
<td></td>
<td>503(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>x=718</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monate</td>
<td>518(8)</td>
<td>0.11</td>
<td>39</td>
<td>288</td>
</tr>
<tr>
<td>Orta</td>
<td>706(9)</td>
<td>0.14</td>
<td>210</td>
<td>845</td>
</tr>
</tbody>
</table>

(1) Rodhe (1965).
(2) Vollenweider (1960) as cited in Gerletti (1972) - based on 14 sampling periods from 1959-60.
(3) Goldman et al. (1968) as cited in Gerletti (1972) - based on 14 sampling periods in 1965.
(4) Ruggiu and Saraceni (1977) - based on 20 sampling periods from 1972-74.
(5) Chiaudani (1977) - based on 8 sampling periods from 1972-73.
(6) Zutshi (1976) - based on at least 26 sampling periods from 1969-70.
(7) Ruggiu et al. (in preparation) - based on 42 sampling periods from 1974-75.
(8) Gerletti and Melchiorri-Santolini (1968) - based on 4 sampling periods from 1966-67.
(9) Calculated from Vollenweider (1963).
Table 3 - Correlation of primary productivity, as mg C \cdot m^{-2} \cdot d^{-1}, or as $\%A_{max}/\Sigma A$, with sedimentary pigments.

<table>
<thead>
<tr>
<th>$X$ Variable</th>
<th>$Y$ Variable</th>
<th>n(number of lakes)</th>
<th>Correlation Coefficient ($r$)</th>
<th>$P$</th>
<th>Remarks $^{(1)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg C \cdot m^{-2} \cdot d^{-1}</td>
<td>661/g organic</td>
<td>6</td>
<td>.82</td>
<td>.05</td>
<td>Ruggiu et al. data for Mergozzo.</td>
</tr>
<tr>
<td>411/g</td>
<td>6</td>
<td>.83</td>
<td>.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>661/g</td>
<td>6</td>
<td>.88</td>
<td>.01</td>
<td>Zutshi data for Mergozzo.</td>
<td></td>
</tr>
<tr>
<td>411/g</td>
<td>6</td>
<td>.90</td>
<td>.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>661/g</td>
<td>5</td>
<td>.96</td>
<td>.01</td>
<td>Maggiore excluded; uses Zutshi data for Mergozzo.</td>
<td></td>
</tr>
<tr>
<td>411/g</td>
<td>5</td>
<td>.98</td>
<td>.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>661/g</td>
<td>6</td>
<td>.94</td>
<td>.01</td>
<td>Uses 1960 data for Maggiore; Ruggiu et al. data for Mergozzo.</td>
<td></td>
</tr>
<tr>
<td>411/g</td>
<td>6</td>
<td>.95</td>
<td>.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>661/g</td>
<td>6</td>
<td>.85</td>
<td>.02</td>
<td>Uses 1965 data for Maggiore; Ruggiu et al. data for Mergozzo.</td>
<td></td>
</tr>
<tr>
<td>411/g</td>
<td>6</td>
<td>.87</td>
<td>.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>661/g</td>
<td>6</td>
<td>.94</td>
<td>.01</td>
<td>Uses mean data for 1960, 1965, and 1973 (from Gerletti, 1972 and Ruggiu and Saraceni, 1977) for Maggiore and the mean value for Mergozzo from Ruggiu et al. and from Zutshi.</td>
<td></td>
</tr>
<tr>
<td>411/g</td>
<td>6</td>
<td>.95</td>
<td>.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$%A_{max}/\Sigma A$</td>
<td>661/g</td>
<td>6</td>
<td>no correl.</td>
<td>ns</td>
<td>Uses Ruggiu et al. data for Mergozzo.</td>
</tr>
<tr>
<td>411/g</td>
<td>6</td>
<td>no correl.</td>
<td>ns</td>
<td></td>
<td></td>
</tr>
<tr>
<td>661/g</td>
<td>5</td>
<td>.93</td>
<td>.01</td>
<td>Excludes Montorfano; uses Ruggiu et al. data for Mergozzo.</td>
<td></td>
</tr>
<tr>
<td>411/g</td>
<td>5</td>
<td>.92</td>
<td>.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{(1)}$ Ruggiu and Saraceni (1977) estimate used for Maggiore, unless otherwise specified.
surements which are in Vollenweider’s paper; the Orta data were first approximated to 4 hours by multiplying by 0.67.

In general, there appeared to be reasonably good correlations between primary productivity and pigments in the surface sediments, with several of the various correlations significant at the 0.01 level or less (Table 3). Pigment concentrations in the Maggiore deep-water surface sediments were lower than expected on the basis of current productivity and comparison with other lakes. For example, in the correlation in which Maggiore is excluded and the Zutshi data are used for Mergozzo, linear regression based on the five remaining lakes would predict that the Maggiore sediment index for SPDU_{561}/g organic matter would be 246 (based on 1975 primary productivity values), a value considerably higher than we found at the 344 m depth where we sampled the lake. For primary productivity levels of 790, 657, and 320 mg C.m^{-2}.d^{-1} for Maggiore (values from the literature and our calculated mean of 656, as before), SCDP concentrations (SPDU_{561}/g organic weight) would be predicted from linear regression as 218, 165, and 34, respectively. The measured value of approximately 50 (SPDU_{561}/g organic weight) is much lower than would be predicted (246) on the basis of contemporary productivity of 863 mg C.m^{-2}.d^{-1}. This Maggiore sediment sample from 344 m depth was also low in SPDU_{411} and organic matter. We consider it likely that the extreme water depth where we sampled was a factor in reducing the pigment concentrations, since the long water column would allow more opportunity for pigment oxidation, as well as loss of phytoplankton from zooplankton grazing and bacterial degradative activity.

We did not find a correlation of the primary productivity index of $% A_{\text{max}}/\Sigma A$ (the ratio of percent maximum photosynthesis to the depth integral of photosynthesis) with pigments in the sediments in the example shown, except when we excluded the data for Lake Montorfano (Table 2, 3). When Montorfano is excluded, the correlation of pigments and this index of primary productivity (considered usually to be a quite sensitive index of production) is good (Table 3). We believe this is due to Lake Montorfano being only 7 m deep; it is the only lake without a water layer of at least 20 m. Thus, the depth integral of phytoplankton photosynthesis is lower than otherwise expected and this may explain the unusually high index ratio of 0.32, ($% A_{\text{max}}/\Sigma A$), characteristic of very eutrophic lakes (see data in Rodhe, 1965).

Pigment concentrations from the three littoral zone sediment samples from lakes Alserio, Pusiano and Segrino (not shown in Tables 2 and 3) were not correlated with pelagial phytoplanktonic primary productivity.

The data from the various depth classes imply that caution should be used when attempting to correlate autochthonous primary productivity with sedimentary pigment decomposition products, since depth
of the water column may result in differences in pigment concentrations.

Estimated ages of the cores.

On the basis of data from Ravera (1974) and Ravera and Premazzi (1972) on sedimentation rates in Lake Monate and Varese, the 85-cm Monate core represents about 85 years, while the 90-cm Varese core is about 57 years old at the bottom. We could distinguish faint laminations throughout 50 cm of the 100 cm long Orta core and estimate the Orta core to have 56 laminations. However, the number of laminations in the Orta core may not correspond to annual sediment accretion. Corbella, Tonolli and Tonolli (1958) estimated sediment accretion in Orta to be about 2 mm per year, based on measurement of copper concentrations in the sediment. The dates of high copper input to Lake Orta are known from the historical record. In addition, we had a small number of sediment samples analyzed for Cs-137 by D.N. Edginton (Argonne National Laboratory, Argonne, Illinois). From the limited samples that were available to Dr. Edginton, he estimated the Orta sedimentation rate to be greater than or equal to 2 mm per year. More intensive sampling will be required to clarify the age of the Orta core. We could not distinguish laminations in the Montorfano core, and could find no other information regarding the sedimentation rate in that lake.

Organic weight of sediments.

Cores from Lakes Monate, Varese, Orta and Montorfano exhibited three trends (Figure 1). The Montorfano sediments showed a decrease in organic weight as percent of dry weight, from ca. 42% at the 80-90 cm depth to ca. 28% at the surface. The organic weight of the Monate sediments changed very little and ranged from 20% to 25% organic weight throughout its 85 cm length. Both Varese and Orta cores changed very little from the lower depths to the 10-20 cm zones, above which the concentration of organic matter nearly doubled.

From the organic matter data alone, it is not possible to know if the changes in organic matter as % of dry weight are due to changes in autochthonous production, differences in inorganic loading to the lake, variations in the percent of organic matter in the allochthonous loading to the lake, changes in sedimentation rates, or combinations of these and other factors.

Calcium carbonate in the sediments.

Orta, Montorfano, and Monate showed changes in CaCO₃ as % of dry weight (Figure 2), from ca. 6% in the lower part of the core to ca. 9-12% at the surface 10 cm. In contrast, Varese changed markedly, from 17% in the lower part of the core to ca. 43% at the surface. Such changes in CaCO₃ of lake sediments are of interest with regard to primary production of lakes; changes from below 10% CaCO₃ to
near 40% CaCO$_3$ in Pretty Lake, Indiana, were correlated with reductions in primary productivity on the basis of pigment concentrations of sediments (Wetzel, 1970) approximately 10,000-11,000 years old. With the possible exception of Varese, we would not expect the levels of CaCO$_3$ which we found to have been sufficiently great to have affected primary productivity during the periods of time indicated by our cores. In the case of Varese, it is also possible that the increase in sedimentary CaCO$_3$ in the upper sediment layers could be related to biogenic marl formation induced by increase in primary productivity, as in Little Round Lake, Ontario (Daley, Brown and McNeely, 1977).
Fig. 2 - Calcium carbonate as per cent of dry weight, in cores from Lakes Orta, Monate, Montorfano and Varese. Calcium carbonate weights are based on the difference in weight from 550° to 950°, using subsamples from 10-cm long homogenized sections.

Depth distribution of the SPDU_{661} peaks

SPDU_{661} per gram organic matter in surface sediments ranged from about 579 for Lake Varese, to a low of 39 for Lake Monate (Figure 3). Varese is the most eutrophic and Monate among the least productive of the lakes considered. These two lakes are representative of the extremes of trophic conditions to be found today in the subalpine Italian lakes.

Simple correlations of SPDU_{661} with depth in the cores are shown in Table 4. For Lakes Orta, Monate, Varese and Montorfano, the highest values for SPDU_{661}/g org. wt. were found in the surface se-
Fig. 3 - Sedimentary pigment degradations units (SPDU) per gram organic weight, based on absorbance at 661 nm wavelength and 10 mm pathlengths. Data for Lakes Orta, Monate, Montorfano and Varese.

Table 4 - Simple correlation of SPDU$_{661}$ (per gram organic weight) with depth in four cores. A = Statistics for 0-10 cm level of core excluded. B = Statistics with 0-10 cm level of core included.

<table>
<thead>
<tr>
<th>Lakes</th>
<th>n</th>
<th>r</th>
<th>Slope</th>
<th>Significance level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monate</td>
<td>8</td>
<td>0.900</td>
<td>−0.153</td>
<td>0.001</td>
</tr>
<tr>
<td>Montorfano</td>
<td>9</td>
<td>0.930</td>
<td>−0.743</td>
<td>0.001</td>
</tr>
<tr>
<td>A</td>
<td>9</td>
<td>0.557</td>
<td>−0.139</td>
<td>0.10</td>
</tr>
<tr>
<td>Orta</td>
<td>8</td>
<td>0.869</td>
<td>−0.831</td>
<td>0.01</td>
</tr>
<tr>
<td>Varese</td>
<td>8</td>
<td>0.892</td>
<td>−0.209</td>
<td>0.001</td>
</tr>
<tr>
<td>B</td>
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</tr>
<tr>
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<td>−1.166</td>
<td>0.10</td>
</tr>
<tr>
<td>Varese</td>
<td>9</td>
<td>0.636</td>
<td>−4.001</td>
<td>0.05</td>
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</tbody>
</table>

sediments, with the lowest values generally near or at the lower depths of the cores. In Lake Montorfano the decrease in SPDU$_{661}$/g org. wt. with depth fit an exponential curve ($r = 0.981$); for linear regression of SPDU$_{661}$/g org. wt. depth, $r = 0.93$. When we examined the upper 10 cm of the Orta core, at 2 cm intervals, SPDU$_{661}$/g org. wt. also declined exponentially ($r = 0.97$).
Below the 10-20 cm level, the lakes could be ranked for all depths with respect to increasing concentrations of chlorophyll degradation products, in the following order: Orta, Monate, Montorfano and Varese. During the last 50 years, at Lake Orta degradation of the pigments might be affected in the water column, due to the low pH resulting from industrial pollution. The low pH might inhibit microbial breakdown of pigments (E. Gorham, personal communication). Bonaccina (1970) observed pH values at 140 m depth to range from 4.2 to 6.0. After the pigments have been deposited in the sediment they are not subjected to such low pH. We observed pH to range from 6.2 to 6.7 in 16 samples from the 100 cm core we took from Orta, and these values were only slightly more acidic than 3 samples we measured from Varese core.

In general, the ranking of the core profiles approximates a trend that we would expect on the basis of estimates of historical levels of primary productivity over the period the core probably represent. Approximately the lower four-fifths of the Orta core represents a period of low trophic status of the lake, if the sedimentation rate in that lake is 2 mm/year. Before about 50-60 years ago Lake Orta was oligotrophic with valuable fish, low nutrient concentration and pH of 7.2 (Monti, 1930). The upper part of the Orta core (Figure 4) may represent the period of industrial pollution and its consequent effects on aquatic life. In this section of the core the largest changes occurred. Probably the large increase of sedimentary pigments is due to heavy mortality of the phytoplankton (Corbella, Tonolli and Tonolli, 1958), and during recent years to the increase in productivity with numerous blue-green algal blooms. The other cores are in the same sequence that current levels of production would indicate.

When SPDU$_{665}$/g org. wt. data from the 0-10 cm depth samples were compared to the 80-90 cm depth samples (the lowest depth examined which was common to all lakes), the ratios for Lakes Monate, Montorfano, Varese and Orta were 1.9, 4.9, 16.6, and 15.9, respectively. When the same comparison was made using the 10-20 cm depth and 80-90 cm depth, ratios of 1.5, 3.9, 3.0, and 2.5 were found for the same series of lakes. We suggest that the increase in SPDU$_{665}$/g org. matter toward the surface of the cores reflect recent increase in lake primary productivity, but suspect that the ratios obtained in comparing the different depths may not be directly convertible to productivity changes over time.

**Correction factors for calculation of chlorophyll derivatives.**

Acetone extracts of sediment contain, in addition to chlorophyll derivatives such as pheophytins and pheophorbides, a number of other compounds which have some absorbance in the red portion of the spectrum (Orr and Grady, 1957; Sanger and Gorham, 1972a). Approximate corrections for these impurities have been made by drawing a baseline absorbance curve free-hand or with a French curve from
520 to 550 nm to 750 or 800 nm (Sanger and Gorham, 1972a; Gorham, Lund, Sanger and Dean, 1974). We computed this correction factor for 52 samples from 4 lakes; the mean correction factor \( n = 54 \) was 19\% of initial optical density with a standard error of \( \pm 9\% \) of the mean; individual correction factors ranged from 2\% (24 cm section from the Orta core) to 52\% (70-80 cm section from the Orta core). We calculated correction factors for chlorophyll derivatives with the same procedure Gorham, Lund, Sanger and Dean (1974) used with some English lakes; they reported correction factors generally near 10\%, except for three unproductive lakes in which the correction exceeded 20\% (31\% for Wastwater). Thus, the correction factors we found for the Italian lakes are higher than those from some of the English lakes studied by others who used similar techniques.

**Depth distribution of SPDU_{441} peaks.**

The changes in SPDU_{441}/g organic weight (Figure 5; Table 5) from the deepest sections of the cores to the surface generally followed a similar trend to that of SPDU_{661}/g org. wt. Changes in concentrations of SPDU_{441}/g org. wt. from the lowest parts of the cores to the surface sediments were 2.4, 3.0, 8.4 and 6.7 times for Monate, Mon-torfano, Varese and Orta, respectively. In comparing 80-90 cm depths with 10-20 cm depths, the ratios were 1.6, 2.3, 2.2 and 2.6. As in the case of chlorophyllous products, there is a decrease in pigment products with depth in the core, and SPDU_{441} data suggest a trend in historical levels of primary productivity of the lakes.

**Phosphorus of the sediments.**

Twenty-two sediment samples were selected from various core
Fig. 5 - Sedimentary pigment degradation units (SPDU) per gram organic weight, based on absorbance at ca. 411 nm wavelength and 10 mm pathlengths. Data for Lakes Orta, Monate, Montorfano and Varese.

Table 5 - Simple correlation of SPDU\textsubscript{411} (per gram organic weight) with depth in four cores. \textit{A}=Statistics for 0-10 cm level of core excluded. \textit{B}=Statistics with 0-10 cm level of core included.

<table>
<thead>
<tr>
<th>Lakes</th>
<th>n</th>
<th>r</th>
<th>Slope</th>
<th>Significance level</th>
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</thead>
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<tr>
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<td>8</td>
<td>0.917</td>
<td>1.205</td>
<td>0.001</td>
</tr>
<tr>
<td>Montorfano</td>
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<td>0.951</td>
<td>2.002</td>
<td>0.001</td>
</tr>
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<td>0.684</td>
<td>1.614</td>
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<tr>
<td>Varese</td>
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<tr>
<td>Monate</td>
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<td>1.785</td>
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<td>0.668</td>
<td>13.943</td>
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</table>

depths among 5 lakes (Varese, Monate, Orta, Montorfano and Mergozzo) to provide a wide range of pigment concentrations (per gram organic weight). Total inorganic P per gram oven-dry sediment, total organic P per gram oven-dry sediment, and total organic P per gram
organic weight were measured in the samples and compared with pigment concentrations. No general relationship could be found between the various measures of phosphorus concentrations and pigment concentrations, except for Lake Montorfano, where total inorganic P from four depths (10-20 cm, 30-40 cm, 70-80 cm, 90-100 cm) decreased with depth in the sediment core. In this lake the changes in inorganic phosphorus were parallel to those of SPDU$_{66}$ (r = 0.977, P < 0.01) and SPDU$_{411}$ (r = 0.976, P < 0.01). The organic P levels in the Montorfano core samples ranged from 728 μg P g$^{-1}$ (oven-dry sediment) to 308 μg P g$^{-1}$ (oven-dry sediment). Available phosphorus might be a better index of P to compare with sedimentary pigments (Douglas, Murray, Halliday and Greene, 1978).

GENERAL CONCLUSIONS

The surface sediment samples and cores which we analyzed provide some limnological data on the basis of the sediments that have formed within approximately the last century (except for Lake Orta), in several Italian lakes. The 0-10 cm depth sedimentary pigment concentrations measured spectrophotometrically provide an approximate index of recent levels of primary production of the lakes. Since the phorbin composition of lacustrine sediments can be quite complex, further analyses using the direct fractionation, chromatographic technique should be applied to these lakes as well.

A problem we see in the use of sedimentary pigment analyses to index contemporary lake productivity is the probable effect of sampling site within the lakes. Depth of the water column above the sediment sampled may be an important factor, at least when samples from over 300 m water depth are compared with sediments under water less than 100 m deep.

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