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Chemical Characterization of the Effluent from the Lake Utopia Paper Ltd. Pulp Mill, and Water and Sediment from the Upper Letang Estuary

V. Zitko

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Chemical characterization of the effluent from the Lake Utopia Paper Ltd. pulp mill, and water and sediment from the Upper Letang estuary

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ABSTRACT

Zitko, V. 1999. Chemical characterization of the effluent from the Lake Utopia Paper Ltd. pulp mill, and water and sediment from the Upper Letang estuary. Can. Manuscr. Rep. Fish. Aquat. Sci. 2498: iii +14 p.

The effluent from a small sulfite pulp mill, discharged to an impoundment and ultimately reaching Letang inlet, contains mainly lignosulfonates with molecular weight over 1000 daltons, and salts, primarily sulfates and nitrates. Before reaching the inlet, the effluent is diluted 5-15 times by freshwater runoff. The lignosulfonates are not precipitated in sea water and are not present in marine sediments in the upper Letang. The concentration of organic compounds in the sediments corresponds approximately to that of a background aquaculture site. Infrared, ultraviolet and visible spectra were used to characterize the effluent, water in the impoundment, and sediments.

RÉSUMÉ

Zitko, V. 1999. Chemical characterization of the effluent from the Lake Utopia Paper Ltd. pulp mill, and water and sediment from the Upper Letang estuary. Can. Manuscr. Rep. Fish. Aquat. Sci. 2498: iii +14 p.

Les effluents d'une petite usine de pâte à papier au sulfite, rejetés dans un réservoir de retenue et, en bout de ligne, dans la baie Letang, contiennent surtout des lignosulfonates, dont le poids moléculaire est supérieur à 100 daltons, et des sels, en grande partie des sulfates et des nitrates. Avant que les effluents atteignent la baie, les eaux de ruissellement les diluent de cinq à quinze fois. Les lignosulfonates, qui ne se précipitent pas en mer, sont absents des sédiments retrouvés dans le fond de la baie Letang. La teneur en composés organiques dans les sédiments correspond environ à celle d'un site aquacole de base. On a fait appel à des spectres infrarouge, ultraviolet et à la lumière visible pour établir les caractéristiques des effluents, de l'eau du réservoir de retenue et des sédiments.

INTRODUCTION

This work was undertaken in response to a request from the Co-operative Bacterial Monitoring Program (CBMP) of Eastern Charlotte Waterways Inc., St. George, NB, to chemically characterize compounds present in the water and sediment of the Upper Letang estuary.

A small, neutral, sulfite, semi-chemical pulp mill discharges 10,000 m^3/d of treated effluent into the Upper Letang estuary. The effluent is treated by Upflow Anaerobic Sludge Blanket (see, for example Rintala and Puhakka 1994), followed by activated sludge treatment and a secondary clarifier. The system was installed in the late 80's under an operating contract with Pacques Lavalin. Lake Utopia Paper Ltd. now operates the system and since 1992, all effluent from the mill has been treated in the anaerobic system. In 1994, one of the original aeration basins was converted to an activated sludge treatment system and a secondary clarifier was added. The complete system consists of a primary clarifier, an equalization basin, an anaerobic system, followed up with an aerobic system. The treated mill effluent is then combined with cooling water, steam condensates, and blowdown water and the combined effluent released to the Upper Letang (G. Lindsay 1999, personal communication).

The effluent's sublethal toxicity expressed as IC25 ('effluent concentration at which test organisms show a 25% inhibition of the characteristic tested') was, in 1995-98, 1.6 %, 26%, 77%, 1.9% , >66%, and 2.8%, in tests with *Ceriodaphnia dubia,* fathead minnow, *Lemna minor,* sea urchin, inland silverside, and *Champia parvula,* respectively (Zisserson and Parker 1999). Hydrographic and benthic conditions in the Letang estuary have been studied by Wildish (see, for example, Wildish et al. 1986). A model of nutrient loading and oxygen demand for the Letang inlet has been published (Strain et al. 1995).

MATERIALS

A water sample collected at the causeway at the Upper Letang estuary on December 8, 1997, was provided by Mr. Leblanc of CBMP, who also supplied on October 19, 1998 five sediment samples, collected between September 29, 1998 and October 5, 1998 by Washburn and Gillis Asociates Ltd. (Fig.1). The pulp mill provided a sample of effluent and the author took water samples at the causeway on February 11, 1998 and on July 19, 1999. In July, the causeway culvert was several feet above the water level, and only limited seepage through the west side of the causeway was visible.

METHODS

WATER

The ultraviolet (UV) spectra of the water samples were measured after dilution by freshwater as well as by sea water, and after adjusting pH to 2.0 and 12.0, with 10% hydrochloric acid and sodium hydroxide, respectively. An HP diode array spectrophotometer model 8452A was used.

For the determination of total solids, aliquots of the samples were evaporated to dryness on a rotary evaporator and the residue was kept overnight in vacuo in a desiccator with phosphorus pentoxide.

Other portions of the samples were concentrated by evaporation on a rotary evaporator and the concentrates were dialyzed against distilled water in Spectra/Por CE, flat width 16-mm membrane, with a molecular weight cutoff at 1000 daltons. The non-dialyzable fractions were freeze dried, and the first dialyzates were evaporated to dryness on a rotary evaporator. Infrared (IR) spectra of both fractions were determined in KBr disks, on a Perkin Elmer Model 700 spectrophotometer.

Other portions of the water samples were also percolated through a column (2.4 by 13 cm) of BioRad AG3-X4, 20-50 mesh anion exchange resin in free-base form, the column was washed with distilled water. Retained anions were eluted with 1N ammonium hydroxide and fractions following the brown-colored effluent were collected. Nitrate concentrations were calculated from the absorbance at 210 nm and expressed as sodium nitrate.

SEDIMENT

Sediment sub-samples (50 g) were vacuum-dried at 60 C and were extracted with 1 N sodium hydroxide (100+100+50 mL) at room temperature. The extracts were neutralized and yielded precipitates. These were removed by centrifugation, dialyzed together with a small amount of supernatant and dried first in the air at room temperature and then in a vacuum desiccator over phosphorus pentoxide. The supernatants were concentrated on a rotary evaporator, while the concentrates were dialyzed as above and freeze dried. IR spectra of the precipitates, of the dialyzates and of the non-dialyzable fractions, were determined in KBr disks.

Other sediment sub-samples were freeze-dried and 1-g amounts were extracted with dichloromethane and, subsequently, with methanol, as described (Burridge et al 1999).

RESULTS AND DISCUSSION

UTOPIA MILL EFFLUENT AND WATER SAMPLES

The dark brown effluent contained a small amount of suspended solids, which were removed by centrifugation. The IR spectrum of the solids resembled that of a lignosulfonate (Fig.2). The UV spectrum of the supernatant showed increasing absorbance with decreasing wavelength, with a slight 'hump' at about 280 nm (see Fig.3 for several UV spectra at different concentrations of the effluent in distilled water). The absorbance at 250 nm (A_{250}) was related to the effluent concentration (%) in distilled water, by the equation

$$A_{250}(1cm) = -0.061 + 0.576\ c\ (\%) \quad [1]$$

UV spectra of water samples taken at the causeway are, at the first glance, similar to those of the effluent (Fig.4), and according to equation [1], correspond to the effluent diluted 5-6 times in December 1997 and in July 1999, and 15 times in February 1998. This is supported by the concentration of total solids, which was 5.25 g/L in the effluent, and 0.85, 1.16, and 0.4 g/L in causeway water collected in December, July, and February, respectively. An approximate material balance carried out on the February sample, yielded the following distribution of the solids: salts 0.44 g/L, non-dialyzable ('high-molecular weight') organics 0.25 g/L, dialyzable ('low-molecular-weight') organics 0.12 g/L, and non-polar (dichloromethane-extractable) organics 0.03 g/L.

Practically all of the UV absorbance is caused by the non-dialyzable (molecular weight >1000 daltons) fraction of the material (Fig.4).

Base minus acid difference spectra (Fig.5) have a maximum at 300 nm, and a shoulder at 240 nm and indicate the presence of phenolic groups of lignosulfonates (Zitko 1970).

The A_{250} values change linearly with dilution of the causeway water with seawater (Fig.6). This indicates that the UV-absorbing material is not precipitated by seawater and is dispersed only by dilution.

IR spectra of the dialyzable fractions of both the effluent and the causeway samples show a characteristic sharp nitrate absorption peak at 850 cm^{-1} (Fig. 7). The presence of nitrate was also confirmed by its reaction with brucine (Feigl 1958). The concentration of nitrate, estimated after the removal of the UV-absorbing organic compounds on the anion exchange resin, was 128 mg/L in the effluent and 0.6 mg/L in the impoundment water collected in July 1999. These values are only approximate and are probably on the low side. Measurement of nitrate was not the objective of this work and the method, UV absorbance after separation on an anion exchanger, was not validated. The method of choice is ion chromatography, which is not available at the moment. The important thing is to draw the attention of modelers (see, for example, Strain et al 1995) to the presence of nitrate in the effluent.

In terms of A_{250}, the fraction of absorbance, not retained on the anion exchange resin, was 83% for the effluent, and 88% for the causeway water. It is likely that the not retained fraction contains compounds of relatively higher molecular weight. Consequently, the increase in the proportion of the not retained fraction may indicate degradation of the lower-molecular weight fraction in the receiving waters.

IR spectra of the non-dialyzable fraction of effluent and causeway water are practically identical (Fig.8). They are similar to an IR spectrum of sodium lignosulfonates (Zitko 1970) and differ from the spectra of some commercial calcium lignosulfonates (Fig.9).

SEDIMENTS

Characteristics of the sediment samples are presented in Table 1.The precipitates formed on neutralization of sodium hydroxide extracts of sediments, are, with one exception, silicates (a broad strong maximum at 1050 cm^{-1}). The exception is the precipitate formed in the extract of sediment #2, whose IR spectrum resembles that of a calcium lignosulfonate (Fig.10). UV spectra of the neutralized supernatants, as their 4% solutions in distilled water, resemble somewhat those of the effluent and impoundment water (Fig.11). Interestingly, the extract of sediment #3 exhibited the highest absorbancies. The IR spectra of the supernatants (Fig.12) bear little resemblance to that of the effluent (Fig. 8) and indicate that the material is related more to humic substances and polysaccharides, again with the exception of sediment #2 (Fig.13).

Extraction of freeze-dried sediments with dichloromethane yielded strongly UV-absorbing extracts, particularly for sediment #2 (Fig. 14, see Fig.15 for the less well resolved spectra). Dichloromethane extracts of sediments are, at the moment, an ill-defined mixture of relatively non-polar organic compounds. In spite of this, their spectra are good indicators of organic enrichment of sediments (Burridge et al. 1999). The spectrum of an

Table 1. Description of sediment samples

Sample	1	2	3	4	5
Location	Impoundment	Below causeway	PBD narrows	Opposite Trainors Cove	North of Guthrie Pt
Collected	30.9.98	29.9.98	5.10.98	7.10.98	5.10.98
DO	5.5	4.9	8.5	9.1	8.9
Cond/Sal	827	1014	32.9	32.9	32.5
pH	7.0	7.1	7.0	7.9	7.9
Hydroxide extract,mg/kg	2060	7680	3000	2920	1870
A250, AU * L/g	38.9	19.3	107	31.9	12.6
Loss on ignition, %	2.5	7.9	8.9	7.5	19.4
DCM A250, AU*L/g	209	2414	563	266	405
M A400 AU*L/g	291	659	567	654	653
M A664, AU*L/g	122	123	158	165	197

* DCM = dichloromethane, AU = absorbance units in a 1-cm-cell, M = methanol; see text for details.

aquaculture reference sediment is included as a benchmark (see Fig.15). With the exception of sediment #2, the concentration of non-polar organic compounds in the Letang sediments is relatively low.

UV/visible spectra of methanol extracts of the sediments (Fig.16) characterize primarily the presence of the chlorophyll decomposition product, phaeophytin and may be a measure of primary production in the area. The phaeophytin absorption maxima at 414 and 666 nm are practically absent from the spectra of methanol extracts of sediments #1 and #2. Spectra of the remaining sediment extracts are roughly within the range observed at an aquaculture reference site.

CONCLUSIONS

The Utopia pulp mill effluent contains mainly water soluble, strongly light-absorbing compounds with molecular weights over 1000 daltons. Water in the impoundment is essentially the effluent, diluted 5-15 times, depending on the amount of freshwater runoff into the impoundment. Accordingly, water discharged from the impoundment into coastal seawater may still have sublethal toxicity; however, the overflow from the impoundment is rapidly diluted in the estuary. The dilution is 200:1 within 1.3 km of the control dam (W. R. Parker, 1999, personal commun.), and the potentially affected area is small. Major components of the effluent are sodium lignosulfonates. The compounds do not precipitate in seawater and dilution eliminates their light absorption (colour). A small, lower molecular weight (<1000 dalton) fraction of the Utopia 'lignosulfonates' is present both in the effluent and in the impoundment. Organic compounds with molecular weight above 1000 dalton are usually not toxic to aquatic fauna. However, herring avoid lignosulfonates and avoided in the past the effluent from this pulp mill (Wildish et al. 1977).

Both the effluent and the impoundment water contain nitrate. Nitrate seems to be a by-product of the anaerobic treatment of the effluent. The nitrate may influence the nitrogen budget of the Letang inlet and, consequently, nitrate concentration should be monitored for some time, both in the effluent and in the impoundment.

With the exception of sediment #2, the sediments do not contain compounds that could be associated with present Utopia pulp mill effluent.

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I thank Drs. D.J. Wildish and W.R. Parker for comments, Ms. Marilynn Rudi for editing, and Ms. Brenda Best for formatting the report.

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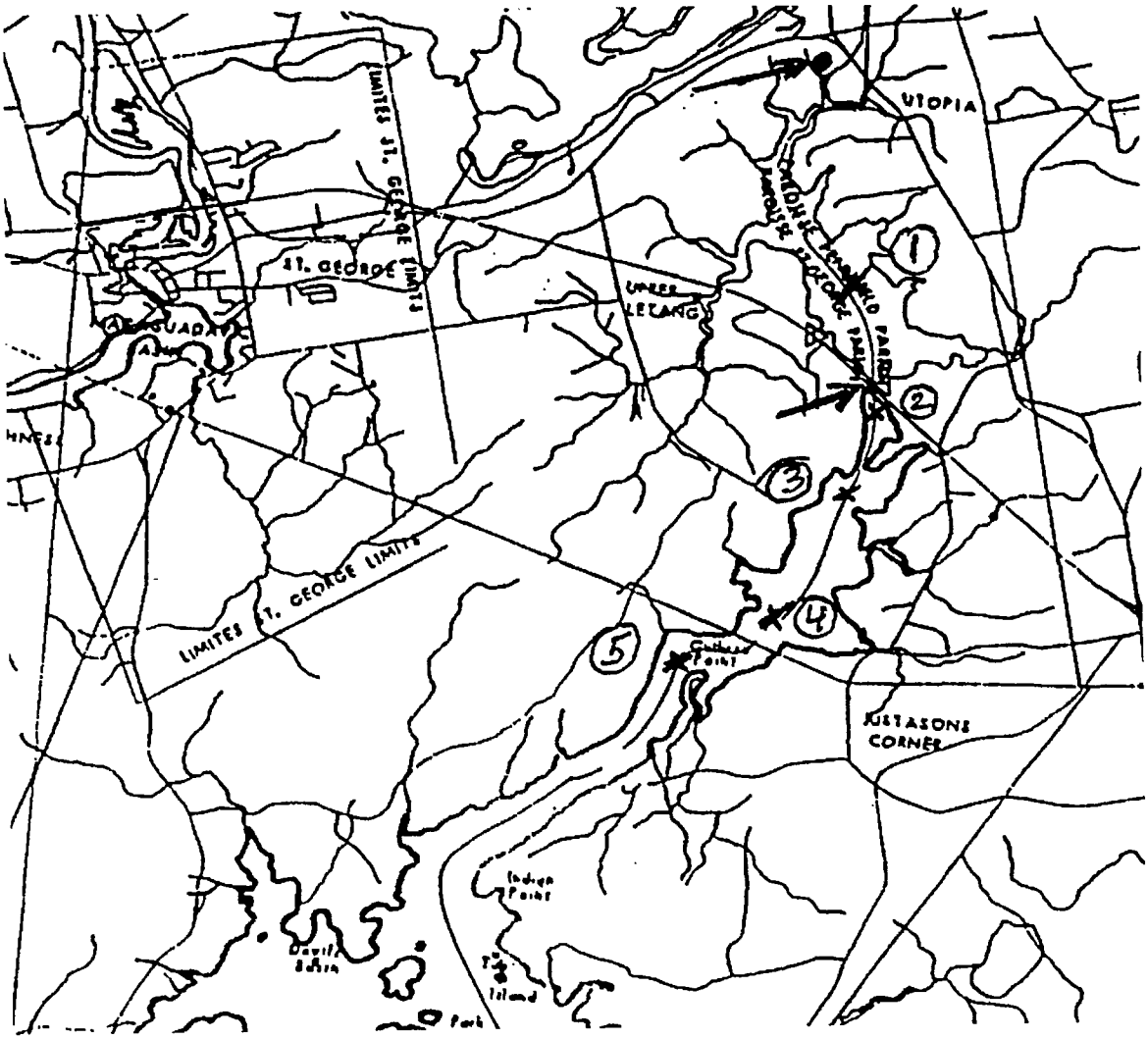


Fig.1. Map of upper Letang. Arrows indicate Utopia pulp mill and the causeway, numbers indicate sediment sampling stations.

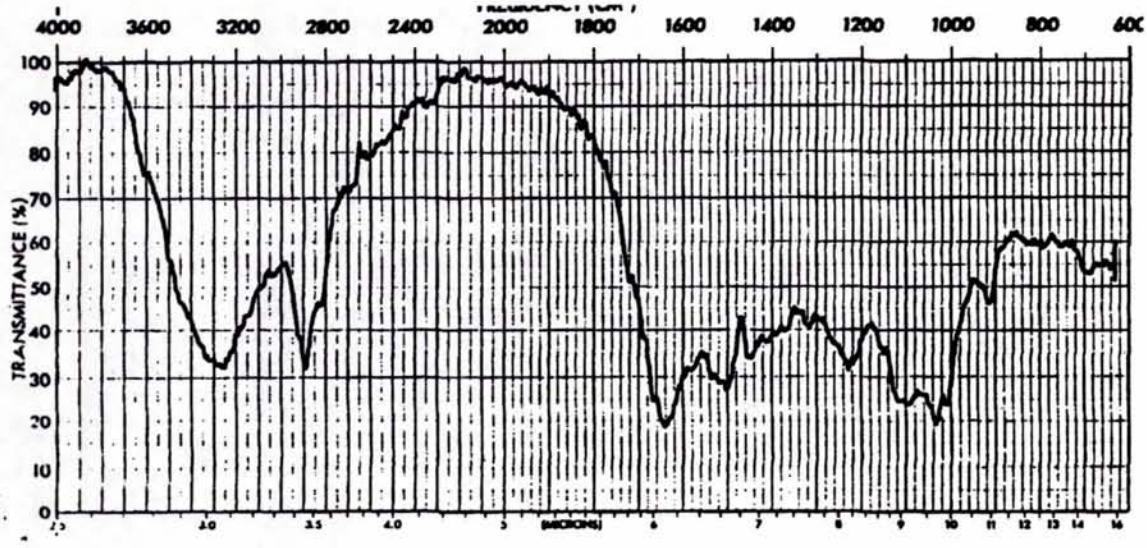


Fig. 2. Solids in Utopia pulp mill effluent

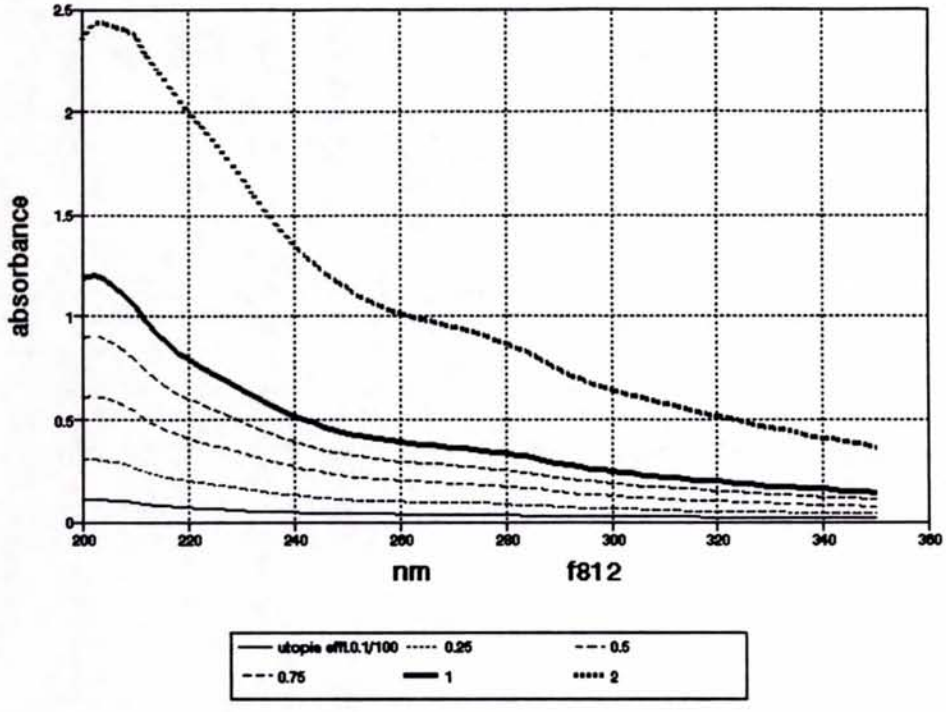


Fig.3. UV spectra of Utopia pulp mill effluent solution in distilled water

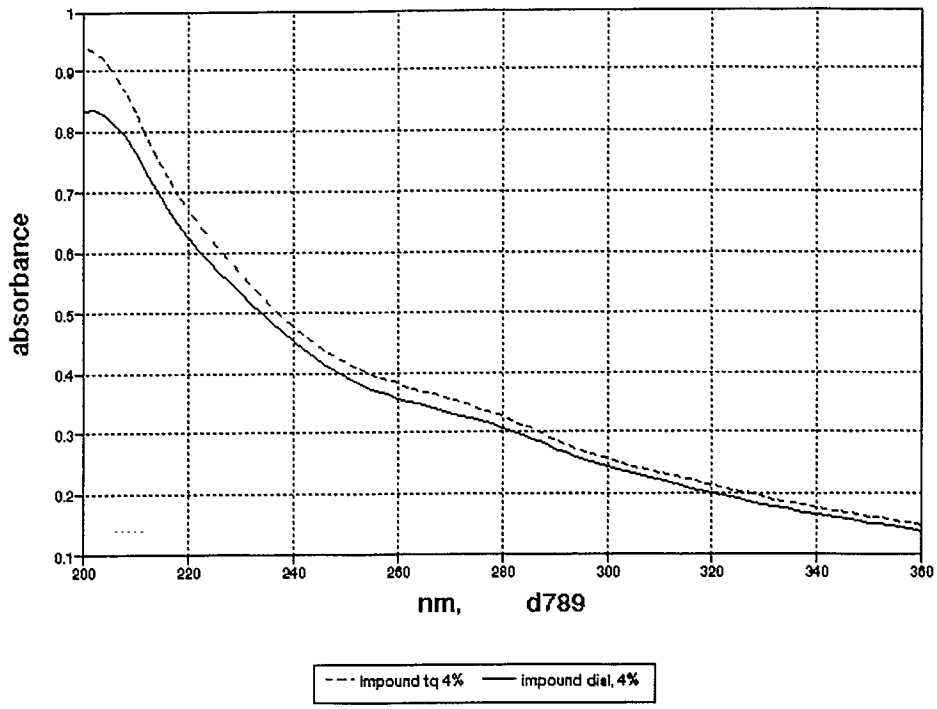


Fig. 4. UV spectra of 4% impoundment water in distilled water as such (-----) and after dialysis (solid line). The dialysis retains compounds with molecular weight above 1000 daltons.

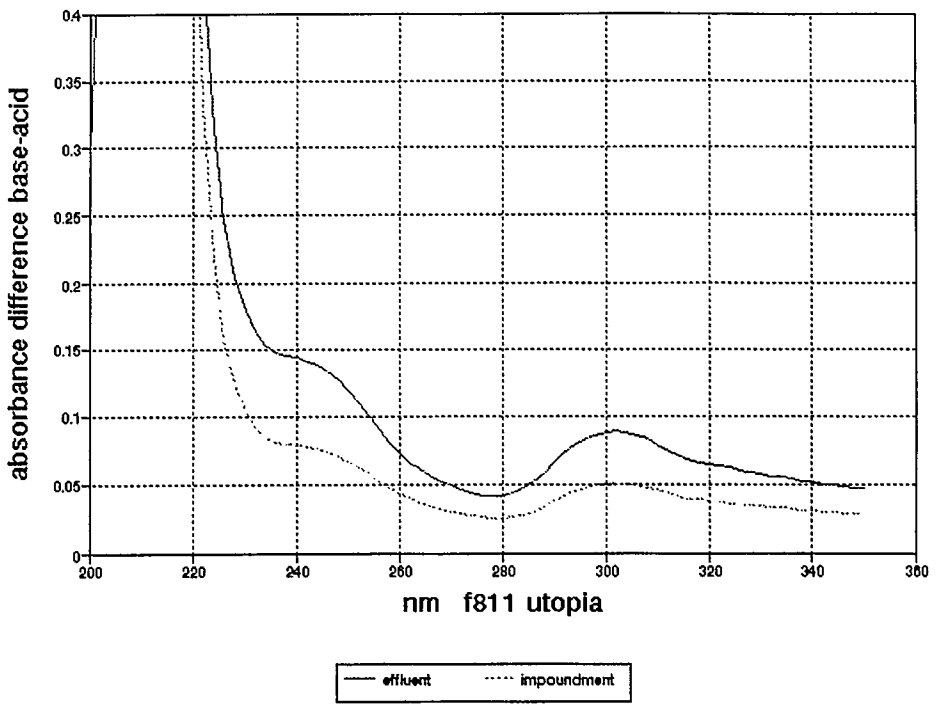


Fig.5. Difference base (pH 12) – acid (pH 2) spectra. Maxima indicate the presence of phenol groups

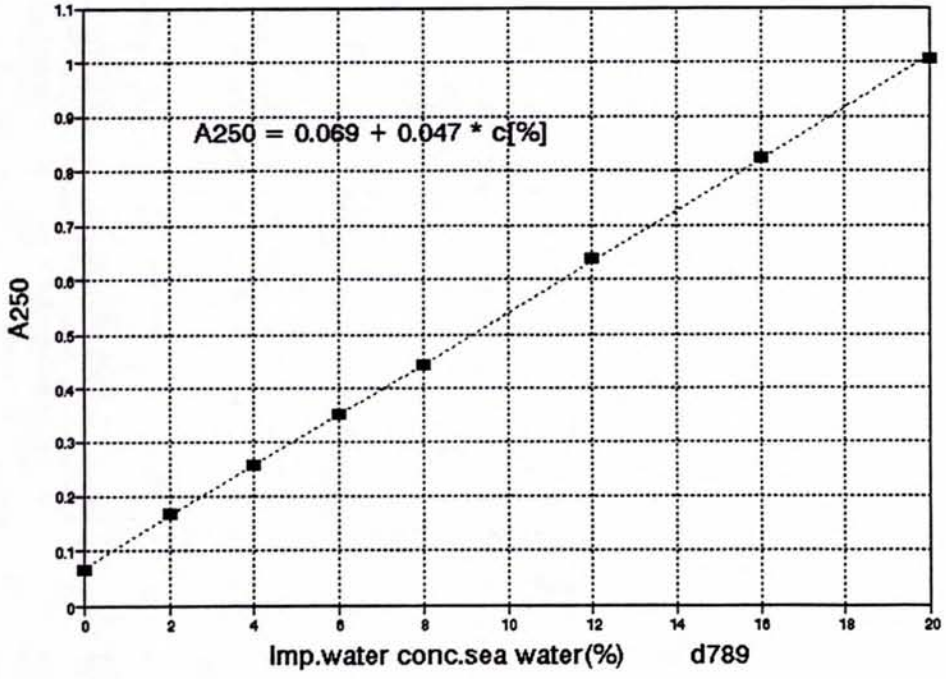


Fig.6. Absorbance at 250 nm of impoundment water in sea water. Straight line indicates no precipitation of UV-absorbing compounds in sea water.

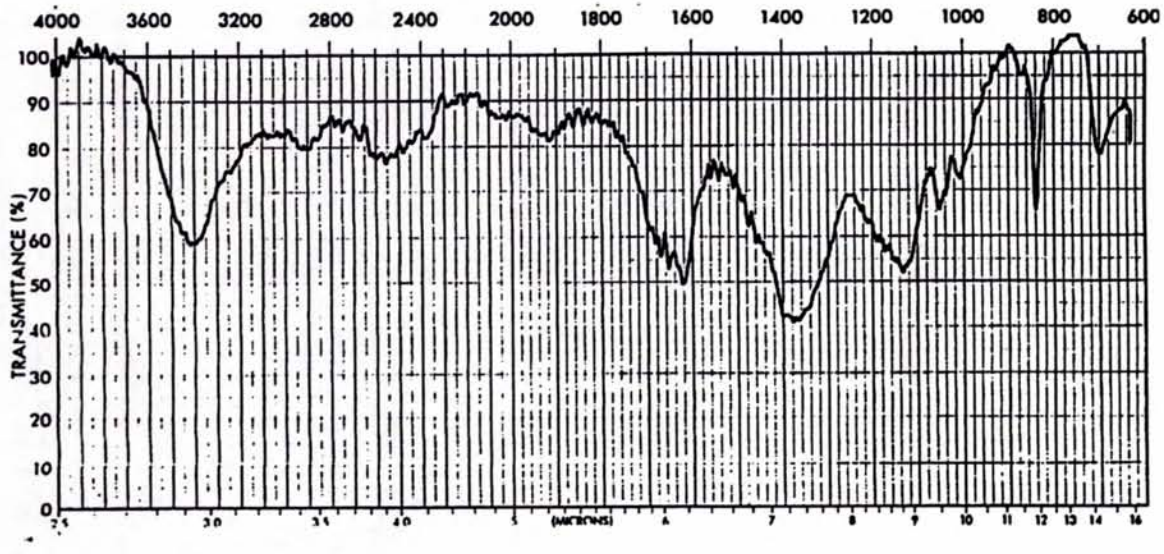


Fig. 7. IR spectrum of the dialyzable (molecular weight less than 1000 daltons) fraction of impoundment water. Main anions are nitrate (maxima at 1380 and 840 cm^{-1}) and sulfate (maximum at 1140 cm^{-1}).

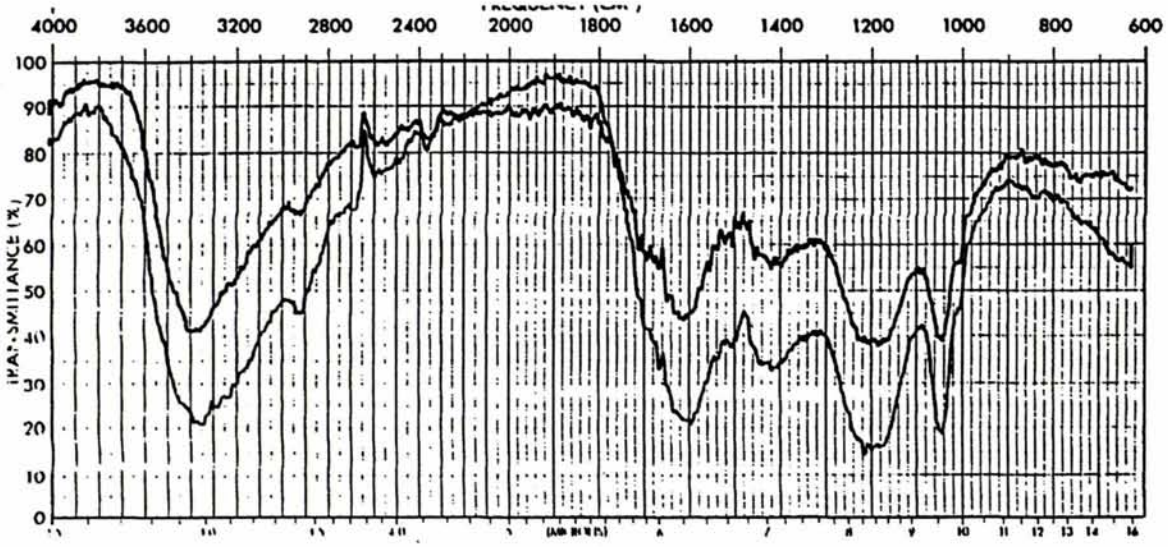


Fig. 8. IR spectra of non-dialyzable (molecular weight > 1000 daltons) fractions the Utopia pulp mill effluent (lower spectrum), and causeway water (upper spectrum)

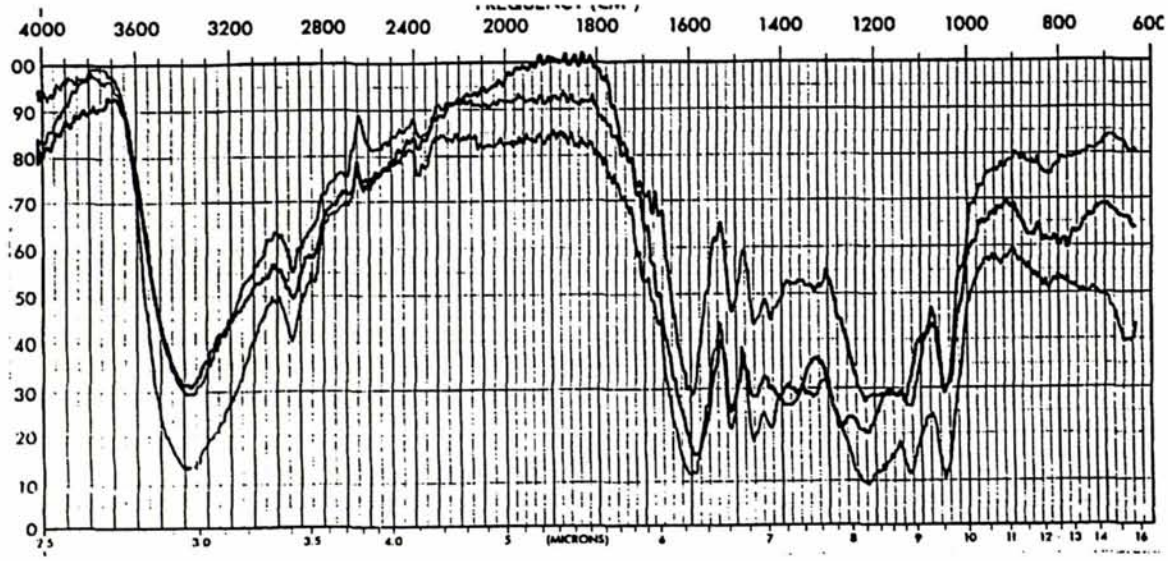


Fig.9. IR spectra of calcium lignosulfonates. From top to down at 800cm^{-1}: 14.3% and 5.4% SO_3Na and 12.2% $Ca(SO_3)_2$, respectively.

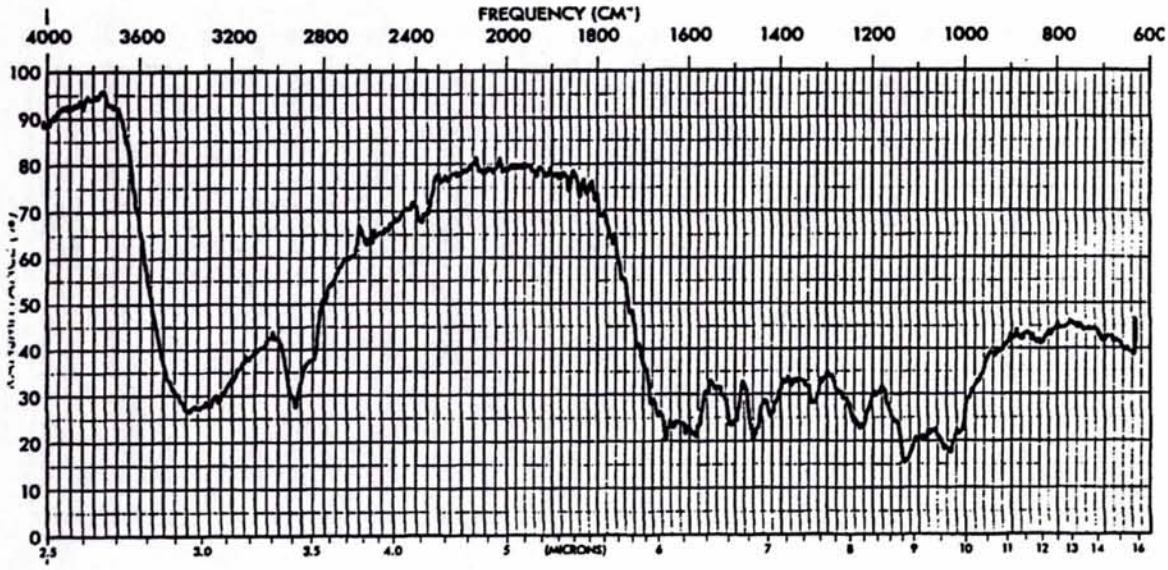


Fig.10. IR spectrum of precipitate formed on neutralization of sodium hydroxide extract of sediment #2.

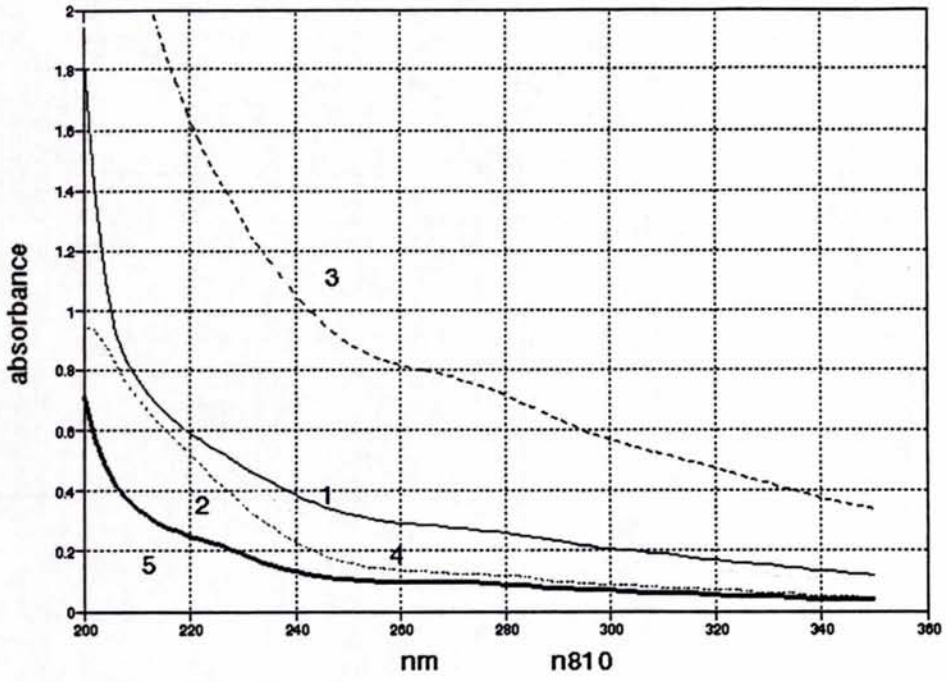


Fig.11. UV spectra of sediment extracts (1 N sodium hydroxide, and neutralized with hydrochloric acid), 4% solutions in distilled water. Numbers are sediment stations.

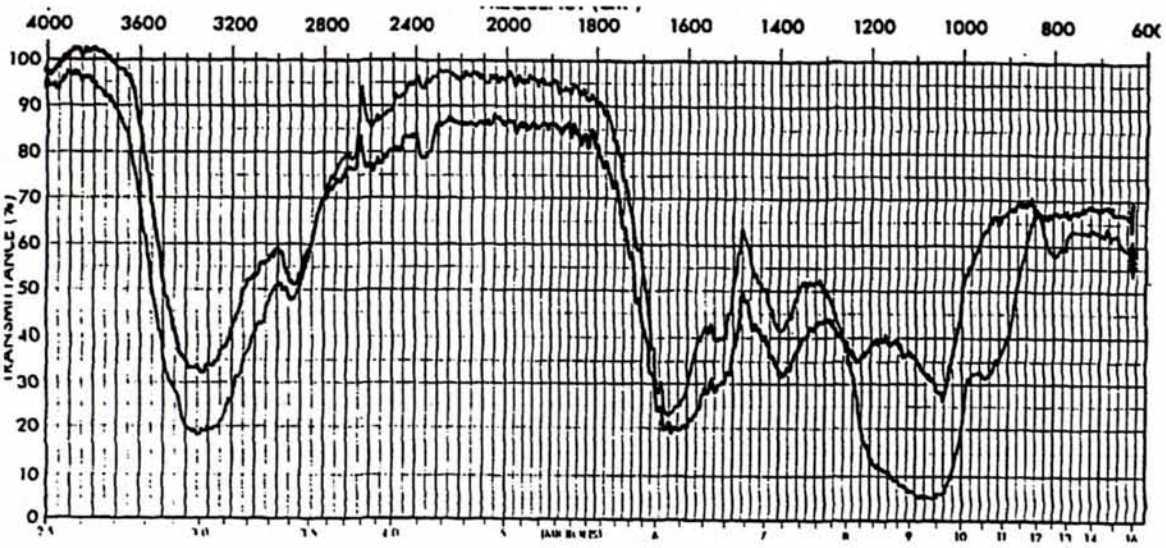


Fig. 12. IR spectra soluble fractions of sediment extracts. Upper spectrum (3300 cm^{-1}) sediment #3, lower spectrum sediment #4.

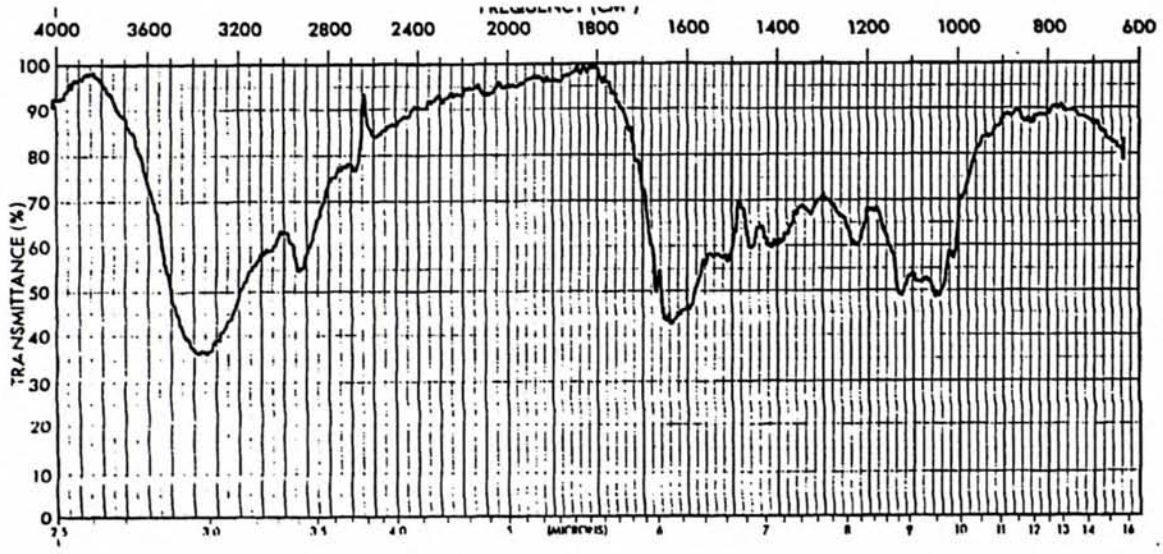


Fig. 13. IR spectrum of soluble fraction of sediment #2 extract.

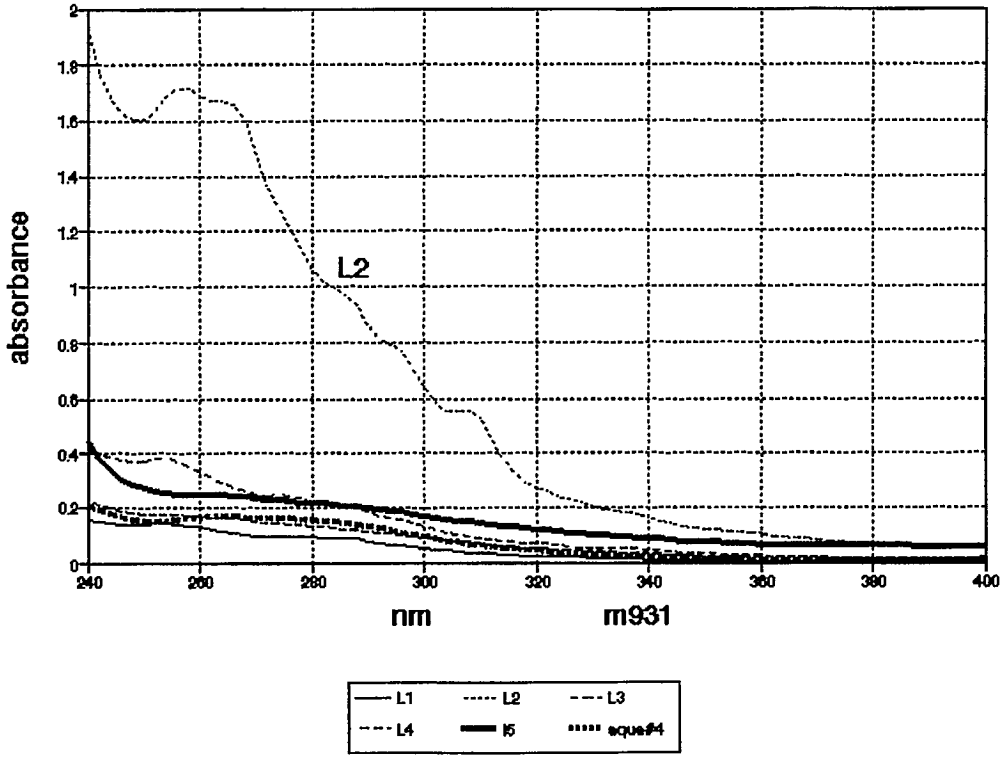


Fig.14. UV spectra of dichloromethane extracts of sediments. Spectrum of dichloromethane extract of a sediment sample from an aquaculture reference site (aqua #4) is included for comparison. For a better resolution of the lower spectra see Fig.15.

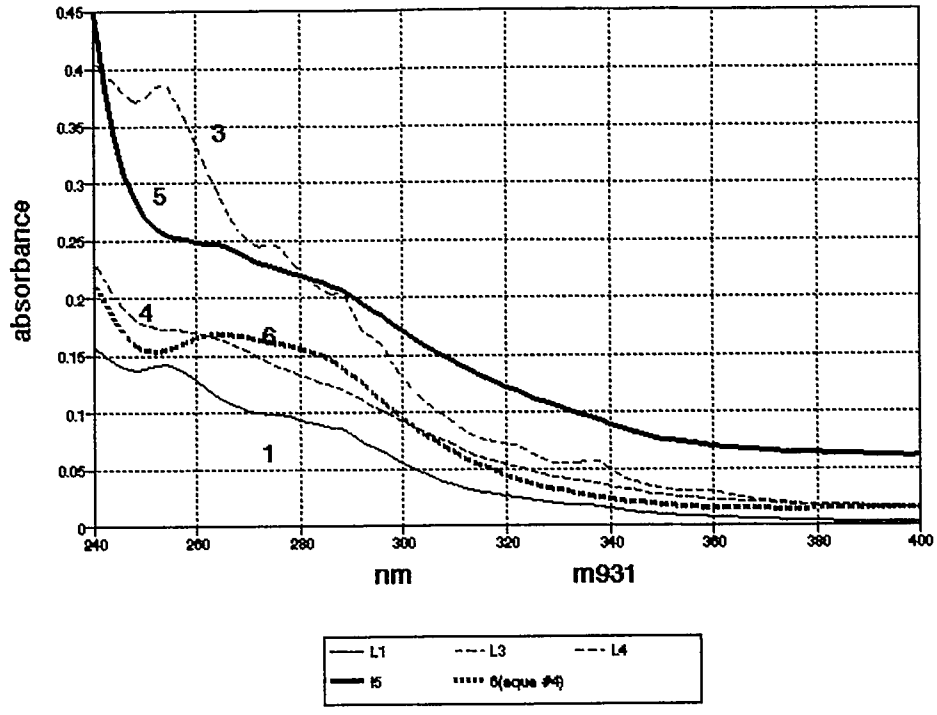


Fig. 15.. UV spectra of dichloromethane extracts of sediments. Spectrum of dichloromethane extract of a sediment sample from an aquaculture reference site (aqua #4) is included for comparison. For spectrum of sediment #2 see Fig.14.

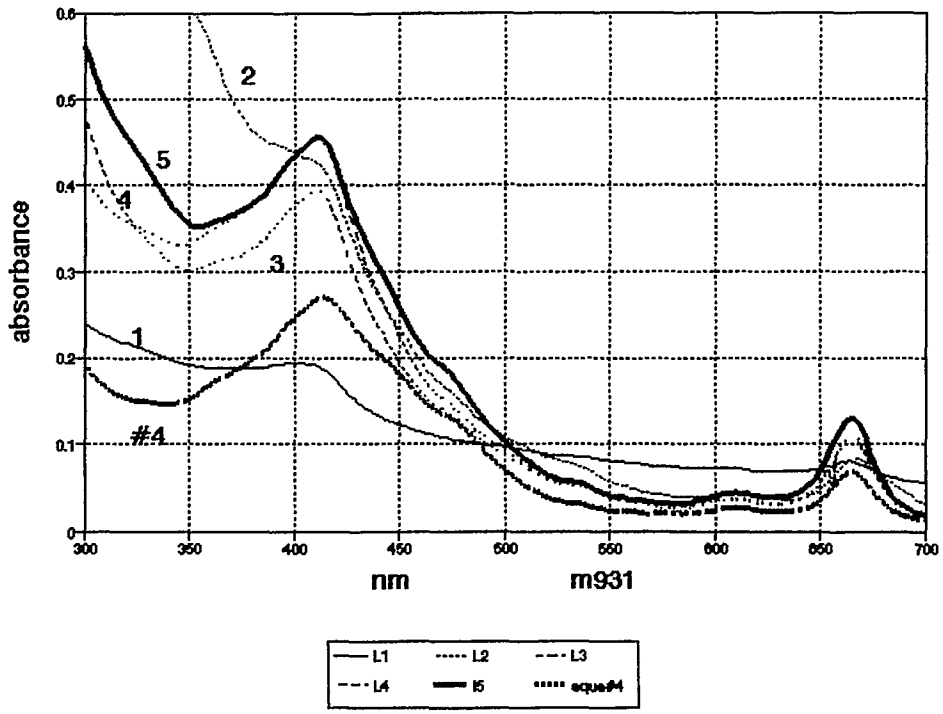


Fig. 16. UV /visible spectra of methanol extracts of the sediments. Spectrum of the methanol extract from a reference aquaculture site (#4) is included for comparison.

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